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Estimadas/os congresistas,

Nos sentimos honrados de dar nuestra más cordial bienvenida a la XXXV Reunión Bienal de la Real Sociedad Española de Química. Muchas gracias por su esfuerzo para acudir a este Congreso y por compartir su investigación a través de sus comunicaciones, que es, en el fondo, lo que ha hecho posible que este evento pueda tener lugar. Les animamos a tener una participación activa en el Congreso y esperamos que encuentren en él un foro apropiado para intercambiar, ampliar puntos de vista científicos y establecer futuras colaboraciones.

Nos disponemos a celebrar la XXXV edición de este Congreso, tras una larga serie de exitosas Bienales previas, que se remontan a 1928. Hemos concebido esta edición como parte de los eventos para conmemorar el 25 aniversario de la institución anfitriona, la Universidad de A Coruña. Durante esta Bienal tendremos oportunidad de aprender, intercambiar conocimientos y contactar con investigadores y profesionales de una amplia representación de Universidades, organismos de investigación e industrias, que resaltarán y discutirán los avances más recientes en Química, así como los desafíos de cara al futuro en sus respectivas áreas, de entre los distintos temas a tratar. Por resumir, los más de 850 congresistas tendremos la oportunidad de asistir a 17 simposios diferentes, 5 conferencias plenarias, 78 conferencias invitadas, 163 comunicaciones orales, 108 comunicaciones flash, y de leer y discutir en torno a 370 pósteres.

Estamos enormemente agradecidos a todos los patrocinadores y colaboradores del congreso, así como a la Universidad de A Coruña y a la Real Sociedad Española de Química por colaborar en la organización de este Congreso. Damos las gracias, especialmente a los miembros del comité científico y del comité organizador local, cuyo trabajo ha sido fundamental para hacer realidad este evento.

En nombre de los comités organizadores, les animo a disfrutar de la hospitalidad y de todas las oportunidades de ocio que ofrece A Coruña, y les expreso nuestro deseo de que esta XXXV Bienal cumpla las expectativas de todos sus participantes.

¡Bienvenidos a la XXXV Reunión Bienal de la Real Sociedad Española de Quimica!

Moisés Canle López
Presidente del Comité Organizador, en nombre de los comités científico y local.

Prof. Dr. Moisés Canle López

Dear participant,

We are honoured to give all of you our warmest welcome to the XXXV Biennial Meeting of the Royal Spanish Chemical Society. We thank you for your efforts to join this Congress and for sharing your research through your communications, which make it possible for this meeting to take place. We look forward to your active participation and hope you find here an appropriate forum to exchange and expand scientific views and collaborations.

We face now the XXXV edition of this congress, following a long series of successful previous Biennial Meetings, dating back to 1928. We have conceived this edition as part of the events to commemorate the 25th anniversary of the host institution, the University of A Coruña. During this event, we will have an opportunity for learning, exchanging knowledge and contacting researchers and professionals from a wide representation of Universities, research institutions and industries, who will highlight and discuss the most recent advances in current Chemistry, as well as the challenges and perspectives for the future of their respective areas, from among the different topics developed here. To summarize, we will have the opportunity to attend 17 symposia, with 5 plenary lectures, 78 invited oral lectures, 163 oral communications, 108 flash communications, and to read and discuss 370 poster communications.

We deeply acknowledge all our sponsors and collaborators, and the University of A Coruña and the Royal Spanish Chemical Society for supporting this Congress. Special thanks are due to the members of the Scientific and Local Organizing Committees, whose work has been fundamental to make this event a reality.

On behalf of the organizing committees, I encourage you to enjoy the hospitality and all the leisure opportunities offered by A Coruña, and I express our wishes that the event fulfils the expectations of us all.

Welcome to the XXXV Biennial Meeting of the Royal Spanish Chemical Society!

Moisés Canle López

Conference Chair, on behalf of the Scientific and Local Organizing Committees.

Prof. Dr. Moisés Canle López

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Organización Temporal de Simposios

	Domingo 19 [a]	Lunes 20	Martes 21	Miercoles 22 [b]	Jueves 23 [c]
Conferencias Plenarias	Richard R. Schrock	Tomás Torres Cebada	Samuel I. Stupp	Luis M. Liz-Marzán	Avelino Corma Canós
Sala Arao		S2. Nanociencia y Materiales Moleculares (Día completo)	S10. Química en la Frontera con la Biología (Día completo)	S7. Metodología Sintética y Síntesis Total (Día completo)	S7. Metodología Sintética y Síntesis Total (Mañana)
Sala 1		S3. Catálisis Organometálica como Solución a Retos Sintéticos (Día completo)	S8. Química Sostenible (Día completo)	S10. Química en la Frontera con la Biología. (Mañana) --- S15. Ingeniería Química y Medioambiente (Tarde)	S15. Ingeniería Química y Medioambiente (Mañana)
Sala 2		S1. Sistemas Luminiscentes: Caracterización y Aplicaciones (Día completo)	S9. Síntesis, Caracterización y Propiedades de Materiales Emergentes (Día completo)	S5. Derivados de Metales Representativos (Mañana) --- S16. Química y Cristalografía: Materia y Vida con Precisión Atómica (Tarde)	S16. Química y Cristalografía: Materia y Vida con Precisión Atómica (Mañana)
Sala 3		S13. Productos Naturales en la Señalización Química en Sistemas Biológicos (Día completo)	S11. Polímeros para Aplicaciones Avanzadas (Día completo)	S12. Más Allá del Grafeno y sus Aplicaciones (Día completo)	S14. Aplicaciones Científico-Tecnológicas del Análisis Térmico (Mañana)
Sala 4		S4. Enseñanza, Historia y Divulgación de la Química (Día completo)	S6. Avances en Organocatálisis Asimétrica (Día completo)	Escuela de Verano de Líquidos Iónicos (ReGaLIs) (Día completo)	Escuela de Verano de Líquidos Iónicos (ReGaLIs) (Mañana)

[a] Sólo **Sesión de Tarde**. Incluye: Registro y Entrega de Documentación, Ceremonia de Apertura y Cóctel de Bienvenida.

[b] El miércoles 22 tendrá lugar la Cena del Congreso a las 21:00 h.

[c] Sólo **Sesión de Mañana**. Incluye: Ceremonia de Clausura.

Symposium Topics Schedule

	Sunday 19th [a]	Monday 20th	Tuesday 21st	Wednesday 22nd [b]	Thursday 23rd [c]
Plenary Lectures	**Richard R. Schrock**	**Tomás Torres Cebada**	**Samuel I. Stupp**	**Luis M. Liz-Marzán**	**Avelino Corma Canós**
Room "Arao"		**S2. Nanoscience and Molecular Materials** (Full Day)	**S10. Chemistry Bordering Biology** (Full Day)	**S7. Synthetic Methodology and Total Synthesis** (Full Day)	**S7. Synthetic Methodology and Total Synthesis** (Morning)
Room 1		**S3. Organometallic Catalysis as a Solution for Synthetic Challenges** (Full Day)	**S8. Green Chemistry** (Full Day)	**S10. Chemistry Bordering Biology** (Morning) --- **S15. Chemical Engineering and Environment** (Afternoon)	**S15. Chemical Engineering and Environment** (Morning)
Room 2		**S1. Luminescent Systems: Characterization and Applications** (Full Day)	**S9. Synthesis, Characterization and Properties of Emergent Materials** (Full Day)	**S5. Derivatives of Representative Metals** (Morning) --- **S16. Chemistry and Crystallography: Matter and Life with Atomic Precision** (Afternoon)	**S16. Chemistry and Crystallography: Matter and Life with Atomic Precision** (Morning)
Room 3		**S13. Chemical Signaling Mediated by Natural Products in Biologycal Systems** (Full Day)	**S11. Polymers for Advanced Applications** (Full Day)	**S12. Beyond Graphene Chemistry and Applications** (Full Day)	**S14. Scientific and Technological Applications of Thermal Analysis** (Morning)
Room 4		**S4. Teaching, History and Popularization of Chemistry** (Full Day)	**S6. Advances in Asymmetric Organocatalysis** (Full Day)	**Workshop on Ionic Liquids (ReGaLIs)** (Full Day)	**Workshop on Ionic Liquids (ReGaLIs)** (Morning)

[a] Only **Afternoon Session**. Including: Registration, Opening Ceremony and Welcome Reception.

[b] Wednesday 22nd : Conference Dinner at 21:00 h.

[c] Only **Morning Session**. Including: Closing Ceremony.

Conferencias Plenarias (PL)

Domingo 19 de Julio 2015

Chairman: Pedro Pérez

19:00 – 20:00	**PL-1**	(Común a todos los simposios) **Richard R. Schrock** *"Recent Advances in Olefin Metathesis by Molybdenum and Tungsten Catalysts"*

Lunes 20 de Julio 2015

Chairman: José Manuel Pingarrón

08:40 – 09:40	**PL-2**	(Común a todos los simposios) **Tomás Torres Cebada** *"Phtalocyanines: Old Dyes, New Molecular Materials"*

Martes 21 de Julio 2015

Chairman: José Luís Mascareñas

08:40 – 09:40	**PL-3**	(Común a todos los simposios) **Samuel I. Stupp** *"Supramolecular Materials Chemistry"*

Miércoles 22 de Julio 2015

Chairman: Agustí Lledós

08:40 – 09:40	**PL-4**	(Común a todos los simposios) **Luis Liz-Marzán** *"Chemical Growth of Metal Nanoparticles: Why and How?"*

Jueves 23 de Julio 2015

Chairman: Jesús Jiménez

08:40 – 09:40	**PL-5**	(Común a todos los simposios) **Avelino Corma Canós** *"Intentos para Establecer Puentes entre la Catálisis Homogénea y Heterogénea"*

RECENT ADVANCES IN OLEFIN METATHESIS BY MOLYBDENUM AND TUNGSTEN CATALYSTS

Richard R. Schrock

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Keywords: *Olefin metathesis, molybdenum, tungsten*

One of the most important developments in the last five years in olefin metathesis chemistry employing Mo or W catalysts has been the synthesis and application of M(NR)(CHCMe$_2$R')(OR)(Pyrrolide) (MonoAlkoxidePyrrolide or MAP) complexes, especially those in which OR is a sterically demanding terphenoxide such as 2,6-dimesitylphenoxide (OHMT). MAP species under the right circumstances have proven to be *Z*-selective in a variety of olefin metathesis reactions, among them enantioselective ring-opening/cross-metatheses, ROMP to give highly stereoregular polymers, ethenolysis of internal olefins such as oleates, coupling of terminal olefins, cross coupling of terminal olefins, and synthesis of macrocyclic natural products. An important second recent development has been the synthesis of a variety of tungsten oxo alkylidene complexes. Oxo complexes can be "activated" by binding B(C_6F_5)$_3$ to the oxo ligand and are likely to be analogs of metathesis catalysts found in classical metathesis catalyst systems. Recent applications of metathesis includes stereoregular ring-opening metathesis polymerization to give *cis,isotactic* or *cis,syndiotactic* polymers as well as alternating AB copolymers. These and other subjects will be explored as time allows.

References

For a discussion of the synthesis of stereoregular polymers through ring-opening metathesis polymerization see Schrock, R. R. *Acc. Chem. Res.* **2014**, *47*, 2457-2466.

PHTHALOCYANINES: OLD DYES, NEW MOLECULAR MATERIALS

T. Torres

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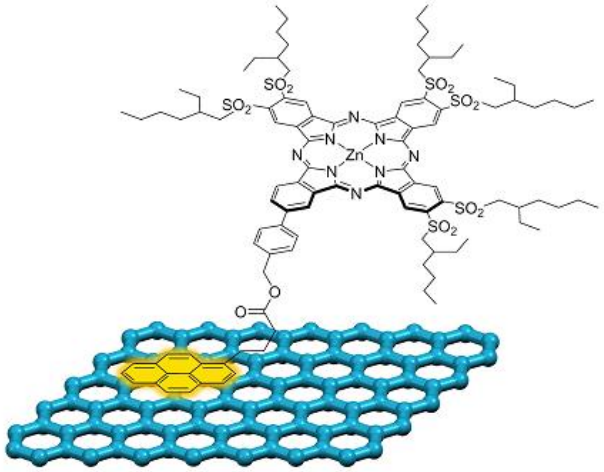
Keywords: *phthalocyanines, light harvesting antennas, carbon nanostructures, photovoltaic and artificial photosynthetic devices*

Porphyrinoids are employed as components of photovoltaic and artificial photosynthetic devices. However, synthetic porphyrin analogues such as phthalocyanines [1] have the advantage, as photon harvesters, of exhibiting very high extinction coefficients in a wavelength range that extends to around 700 nm, where the maximum of the solar photon flux occurs. Consequently, Pcs have emerged as excellent light harvesting antennas for incorporation into donor-acceptor systems, in connection with carbon nanostructures as acceptor or donor moieties. During this talk an overview of the results obtained by our group in Madrid during the last few years will be given [2].



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SUPRAMOLECULAR MATERIALS CHEMISTRY

Samuel I. Stupp
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Keywords: Supramolecular soft materials

Supramolecular soft materials have the potential to mimic the structures and dynamics of biological systems through the design of strong, complex, and externally responsive intermolecular interactions. The interesting features of soft materials designed through non-covalent interactions include nanoscale control of dynamics, highly responsive behavior to external stimuli, capacity to self-heal defects, noncovalent co-localization of functional domains, and the use of self-assembling systems to optimize functions, among many others. This lecture will describe supramolecular soft materials that mimic the photosynthetic machinery of plants by integrating the necessary functions to generate solar fuels, and others in which electron donor and acceptor molecules are organized for photovoltaic or ferroelectric response. The lecture will also discuss highly dynamic bioactive supramolecular materials with filamentous architectures, designed to interact with cells in order to trigger signaling pathways relevant to regenerative medicine.

CHEMICAL GROWTH OF METAL NANOPARTICLES: WHY AND HOW?

Luis M. Liz-Marzán

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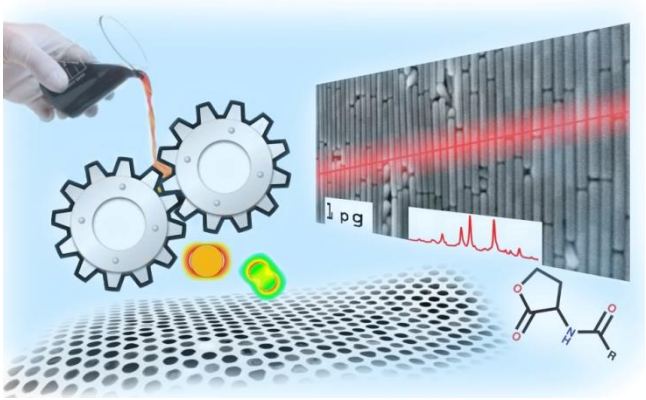
Keywords: *Metal Nanoparticles, Nanoplasmonics, Self-assembly, Sensing*

Nanoplasmonics can be defined as the science studying the manipulation of light using materials of size much smaller than the radiation wavelength. This is typically achieved using nanostructured metals, since they can very efficiently absorb and scatter light because of their ability to support coherent oscillations of free (conduction) electrons. Although the remarkable optical response of “finely divided” metals is well known since more than 150 years ago, the recent development of sophisticated characterization techniques and modeling methods has dramatically reactivated the field. Another extremely important pillar on which the development of nanoplasmonics has been based was the great advance in fabrication methods, which provide us with an exquisite control over the composition and morphology of nanostructured metals. Both lithography and solution chemistry have seen a tremendous increase in the control that can be achieved, to a degree that seemed impossible only a decade ago. In particular, Colloid Chemistry has the advantage of simplicity and larger scale production, while offering a number of parameters that can be used as a handle to direct not only nanoparticle morphology but also surface properties, assembly and subsequent processing. This talk will focus on recent advances in “colloidal nanoplasmonics”, highlighting promising directions in the various aspects involved, from synthesis to applications.



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INTENTOS PARA ESTABLECER PUENTES ENTRE LA CATÁLISIS HOMOGÉNEA Y HETEROGÉNEA

Avelino Corma

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La síntesis de catalizadores sólidos con centros activos bien definidos viene limitada por la dificultad en determinar, en muchos casos, la naturaleza de los centros activos, especialmente en condiciones dinámicas. En nuestro caso presentamos la síntesis de catalizadores sólidos mediante técnicas “bottom up” en la que los futuros centros activos están ya predeterminados en la etapa de síntesis. En este sentido se describirán catalizadores micro y mesoporosos inorgánicos e híbridos orgánicos-inorgánicos preparados por auto ensamblaje, mostrando sus propiedades de adsorción y reactividad química. Finalmente, describiremos la preparación de catalizadores formados por nanopartículas metálicas mediante una aproximación, tanto “bottom up” como “top down”. Se mostrará como dependiendo del tipo de reacciones a catalizar, nanopartículas metálicas con tamaños ≥ 1nm o clústeres metálicos con ≤ 15 átomos pueden representar una opción catalítica que introduce puentes entre la catálisis homogénea y heterogénea.

SIMPOSIOS / SYMPOSIA

S1. **(LSCA)** *Sistemas Luminiscentes: Caracterización y Aplicaciones / Luminescent Systems: Characterization and Applications*

S2. **(NMM)** *Nanociencia y Materiales Moleculares / Nanoscience and Molecular Materials*

S3. **(CO)** *Catálisis Organometálica como Solución a Retos Sintéticos / Organometallic Catalysis as a Solution for Synthetic Challenges*

S4. **(EHDQ)** *Enseñanza, Historia y Divulgación de la Química / Teaching, History and Popularization of Chemistry*

S5. **(DMR)** *Derivados de Metales Representativos: Estructura, Reactividad y Propiedades Únicas / Derivatives of Representative Metals: Structure, Reactivity and Singular Properties*

S6. **(AOA)** *Avances en Organocatálisis Asimétrica / Advances in Asymmetric Organocatalysis*

S7. **(MSST)** *Metodología Sintética y Síntesis Total / Synthetic Methodology and Total Synthesis*

S8. **(QS)** *Química Sostenible / Green Chemistry*

S9. **(SCPM)** *Síntesis, Caracterización y Propiedades de Materiales Emergentes / Synthesis, Chracterization and Properties of Emergent Materials*

S10. **(QFB)** *Química en la Frontera con la Biología / Chemistry Bordering Biology*

S11. **(PAA)** *Polímeros para Aplicaciones Avanzadas / Polymers for Advanced Applications*

S12. **(BGCA)** *Más Allá de la Química del Grafeno y sus Aplicaciones / Beyond Graphene Chemistry and Applications*

S13. **(PNSQ)** *Productos Naturales en la Señalización Química en Sistemas Biológicos / Chemical Signaling Mediated by Natural Products in Biological Systems*

S14. **(ATT)** *Aplicaciones Científico-Tecnológicas del Análisis Térmico / Scientific and Technological Applications of Thermal Analysis*

S15. **(QMA)** *Ingeniería Química y Medioambiente / Chemical Engineering and Environment*

S16. **(CRIS)** *Química y Cristalografía: Materia y Vida con Precisión Atómica / Chemistry and Crystallography: Matter and Life with Atomic Precision*

S17. **(OAQ)** *Otros Ámbitos de la Química / Other topics in Chemistry*

S1. Sistemas Luminiscentes: Caracterización y Aplicaciones (LSCA) / Luminescent Systems: Characterization and Applications

Este simposio pretende ser una muestra de las diferentes áreas de investigación en las que se involucran los sistemas lumninscentes (compuestos moleculares, nanopartículas, quantum dots, materiales luminiscentes...), así como sus numerosas aplicaciones (biológicas, fotocatálisis, materiales, sensores...). Es ideal para compartir e intercambiar intereses científicos comunes y establecer y/o fortalecer colaboraciones.

This symposim pretends to be a sample of the different research fields where luminescent systems are involved (molecular compounds, nanoparticles, quantum dots, luminescent materials...) and also of their different applications (biological, photocatalysis, materials, sensors...). It is an ideal environment to share common scientific interests and to establish and/or strengthening scientific collaborations.

Organizadores:

Laura Rodríguez (UB)

Uwe Pischel (UHU)

José M. López de Luzuriaga (ULR)

Francisco Galindo (UJI)

e-mail de contacto: laura.rodriguez@qi.ub.es

Simposio patrocinado por: linlab rioja, ChemSocRev, Grupos Especializados de Química Orgánica y de Fotoquímica, Facultat de Química – UB, UV-Consulting Peschl España y EULABOR

Lunes 20 de Julio 2015

08:40 – 09:40	**PL-2**	***Conferencia Plenaria*** (Común a todos los simposios) **Tomás Torres Cebada** *"Phtalocyanines: Old Dyes, New Molecular Materials"*

Chairwoman: Laura Rodríguez

10:00 – 10:30	**S1-IL-01**	**Antonio Laguna** *"Syntesis of Luminescent Gold Compounds"*
10:30 – 10:45	**S1-OC-01**	**Concepción Gimeno** *"Bimetallic Complexes as Cooperative Partners in Call Imaging and Cancer Therapy"*
10:45 – 11:00	**S1-OC-02**	**Mª Teresa Moreno** *"Compuestos Fosforescentes Ciclometalados Homo y Heterometálicos de Ir(III) con Ligandos Alquilino Puente"*
11:00 – 11:30		Pausa Café

Chairman: José Mª López de Luzuriaga

11:30 – 12:00	**S1-IL-02**	**João Carlos Lima** "*Aurophilic Gels*"
12:00 – 12:30	**S1-IL-03**	**Werner Nau** "*Spatiotemporally Resolved Fluorescent Chemosensing Ensembles*"
12:30 – 12:45	**S1-OC-03**	**Silverio Coco** "*Mesomorphic Triphenylene Platinum Complexes: Luminescent Columnar Mesophases*"
12:45 – 13:00	**S1-OC-04**	**Enrique García-España** "*Detection of Biological and Environmental Targets with Fluorescent Polyamines*"
13:00 – 13:15	**S1-OC-05**	**Julia Pérez-Prieto** "*Highly Luminescent and Photo(stable) $CH_3NH_3PbBr_3$ Nanomaterials*"
13:15 – 13:30	**S1-OC-06**	**Francesca Peccati** "*Disaggregation-Induced Fluorescence Enhancement of Niad-4 for the Optical Imaging of Amyloid-B-Fibrils*"
13:30 – 15:30		Comida

Lunes 20 de Julio 2015

Chairman: Uwe Pischel

15:30 – 16:00	**S1-IL-04**	**Ezequiel Pérez-Inestrosa** ***"Assembling Dendrimers and One/Two-Photon Excitation Fluorofores. Biomedical Applications"***
16:00 – 16:15	**S1-OC-07**	**Ismael López-Duarte** *"Bodipy-based Molecular Rotors for Mapping Viscosity in Plasma Membranes of Live Cells"*
16:15 – 16:30	**S1-OC-08**	**Mª Consuelo Jiménez** *"Photoactive Probes and their Interaction with Proteins"*
16:30 – 17:00		Pausa Café

Chairman: Francisco Galindo

17:00 – 17:15	**S1-OC-09**	**Rosario Núñez** *"Fluorescent Carborane-based Systems"*
17:15 – 17:30	**S1-OC-10**	**Boiko Cohen** *"Ultrafast Time-Resolved Emission Studies of Nile Red Embedded in Metal Doped Mesaporous Materials "*
17:30 – 17:35	**S1-FC-01**	**Raquel Echeverría** *"Experimental and Theoretical Study of the First Unsupported Interaction between Au(I)-Pb(II) Centers"*
17:35 – 17:40	**S1-FC-02**	**Vania F. Pais** *"Strongly Fluorescent Organoboron N,C-Chelates and their Application in Bioimaging"*
17:40 – 17:45	**S1-FC-03**	**Raquel Gavara** *"Formation of Gold(I)-Silver(I) Bimetalic Complexes: Study of their Luminescence and Aggregation Processes"*
17:45 – 17:50	**S1-FC-04**	**Alberto Juárez** *"Nuevo Sistema Cromo-Fluorogénico para Detección de NO_2 mediante el Uso de Bodipys Modificados"*
17:50 – 17:55	**S1-FC-05**	**Arturo Gamonal** *"New Family of Luminescent Antenna Ligands for Bioassays"*
17:55 – 18:00	**S1-FC-06**	**J. A. Murillo** *"Determinación de Ácido 3,5,6-Tricloro-2-piridiloxidiacético en Muestras Vegetales mediante Fluorescencia Inducida Fotoquímicamente"*
18:00 – 18:30	**S1-IL-05**	**A. Prasanna da Silva** *"Fluorescent Sensing and Logic Systems"*
18:30		***Sesión de Pósteres***

Comunicaciones Invitadas (IL)

S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

SYNTESIS OF LUMINESCENT GOLD COMPOUNDS

A. Laguna[1], M.C. Gimeno[1], J.M. López de Luzuriaga[2]

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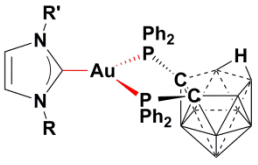
[2] Universidad de La Rioja. Departamento de Química. Madre de Dios 51. E-26006 Logroño, Spain

Keywords: *Luminescence, gold, thallium, silver*

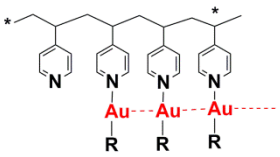
Recent interest in luminescent metal complexes has been driven by possible applications in OLED display technology as dopant emitters, in solar photoconversion chemistry as chromophores, and in sensor development for luminescence detection. Potentially attractive in this regard are gold(I) complexes that, in many cases, possess intense, long-lived luminescence in the solid state or in solution with emission energies spanning the visible spectrum. Part of the fascination of gold(I) chemistry is due to the frequent formation of inter- and intra-molecular gold-gold interactions (aurophilicity) and the tendency to adopt linear coordination.

Two common strategies in the synthesis of gold(I) compounds consist in the use of a) reactions between gold complexes with the gold center as acid and some basic ligands, or b) reactions in which the gold center can be the base and can interact with acid complexes.

The required conditions for a gold complex to show luminescence depend of the nature of the ligands, the geometry around the gold center or the presence of gold-gold interactions in the complexes. Nevertheless, the conjunction of more than one of these conditions makes the assignment more complicated. In addition, the presence of new metal centers can modify the relative energy of the frontier orbitals of gold and create new orbitals, as a consequence of the gold–metal interaction. We will see some examples of three-coordinate complexes (**1**), with gold-gold (**2**) or gold-thallium interactions, with charge-transfer (**3**) or intraligand transitions (**4**).



1



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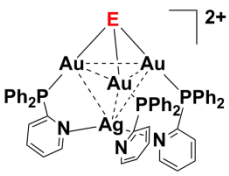

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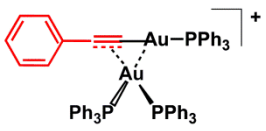

4

S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

AUROPHILIC GELS

Artur Moro [1], Elisabet Aguiló [2], Raquel Gavara [2], Laura Rodríguez [2], João Carlos Lima [1].

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Keywords: *aurophilicity; hydrogels; luminescence*

Metallogels are a subject of study in the last few years.[1] The reason for the growth of interest stems from the availability and the diversity of metal-ligand coordination that could readily induce or control the self-assembly process of the gel formation and thereby influence the gel properties, as a difference with what occurs in organic gels. Organometallic Au(I) complexes present the additional advantage to use both classical supramolecular interactions (*e.g.* π-π stacking or hydrogen bonding) together with the establishment of Au(I)···Au(I) bonds (aurophilic interactions), which are particularly strong. Furthermore, these complexes exhibit interesting emissive properties that usually are modulated by the presence of the aurophilic interactions.

We have reported on the formation of luminescent Au(I) hydrogels based on water soluble organometallic alkynyl complexes where aurophilic intermolecular interactions are involved on the gelation process.[2-5] Slight modifications on the chemical structure can induce significant changes on the supramolecular assemblies leading to hydrogels, rods or vesicles.

A detailed analysis of the thermodynamic and photophysical parameters that modulate and are modulated, respectively, by the gel formation has been performed and the results are supported by theoretical data.

The mononuclear[2,3] and polynucleal gold(I) supramolecular assemblies that are formed in water can be reorganized by the presence of particular molecules. In particular the assemblies containing charged residues or coordinating moyeties are sensitive to the presence of anions and cations and the changes in morphology impact the spectroscopic features opening an unexplored potential of these assemblies for sensing.

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

SPATIOTEMPORALLY RESOLVED FLUORESCENT CHEMOSENSING ENSEMBLES

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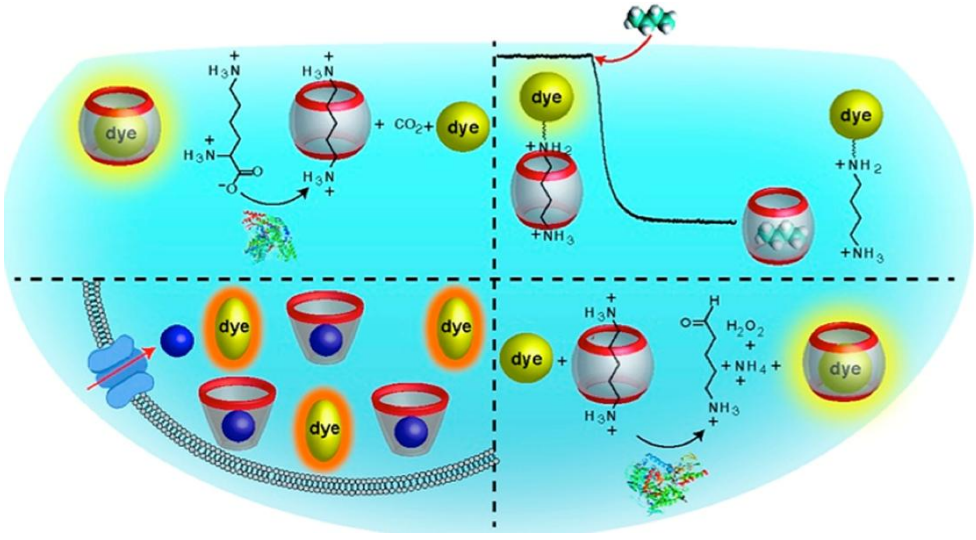
Keywords: *fluorescence, supramolecular, macrocycles, enzymes, membranes, sensors*

We have developed a label-free, fluorescence-based assay method (supramolecular tandem assays, see Scheme). The most recent developments include the transfer of the method to monitoring the translocation of analytes through membranes by fluorescent probes [1,2] and for chirality sensing by circular dichroism probes [3]. Well established is the method for monitoring a large range of enzymatic reactions [4,5]. Our assays rely on the pronounced changes to the photophysical properties upon analyte binding to host-guest complexes between a chromophoric guests and a water-soluble macrocycle as an artificial receptor, typically a cyclodextrin, calixarene, or cucurbituril. The binding of the analyte causes either a displacement of the dye (indicator) or the association to a ternary complex with distinct properties. We exploit, in particular, the fast kinetic response of host-guest exchange or association phenomena in order to achieve a spatiotemperal control of analyte sensing, that is, we follow chemical/enzymatic reactions in real time, or we monitor how an analyte moves from one compartment in a microheterogeneous system to another.



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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

ASSEMBLING DENDRIMERS AND ONE/TWO-PHOTON EXCITATION FLUOROFORES. BIOMEDICAL APPLICATIONS.

E. Perez-Inestrosa[1,2], F. Najera[1,2], D. Collado,[1,2] Y. Vida,[1,2] P. Mesa-Antunez,[1,2] N. Barbero,[1,2]

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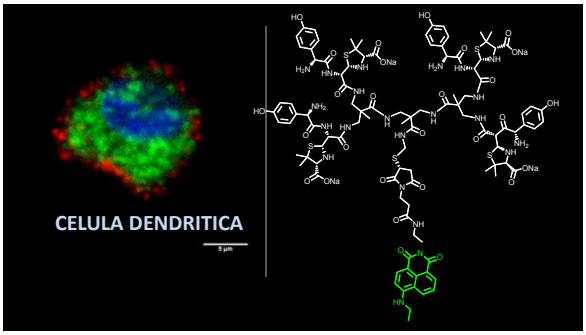
Keywords: *One-/Two- Photon Excitation; Fluorescent Labeling, Dendrimers.*

Fluorescence imaging has become an indispensable tool for modern biomedical research and pre-clinical studies. For many biomedical applications, optimal excitation and emission wavelengths extend from far-red to near infra-red (650–900 nm), which allow greater tissue penetration, lower biotoxicity, and reduced autofluorescence compared to shorter wavelengths. For this purpose two strategies can be established: 1) The design of fluorofores that can absorb one-photon (OPE) in the red wavelengths region, [1] or 2) The design of fluorofores that, although absorbing in the visible wavelengths region, could be excited by a two-photon absorption (TPE) process. [2]

We explain here our contributions to develop one- and two-photon fluorescent chromophores that can be useful for biomedical applications, their rational design, spectroscopic studies and photophysical characterization. The implementation of these fluorescent labels by assembling to molecules of biological interest, their assay in human samples and their validation in cell image is also reported.

In this way, their inclusion on dendrimeric structures[3] generates new tools that represents an excellent basis for new NIR probes able to cross biological barriers, with good fluorescence properties, low-toxicity and high photostability.



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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

FLUORESCENT SENSING AND LOGIC SYSTEMS

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Key words: Molecular logic, Molecular computation

Fluorescent sensors based on PET (photoinduced electron transfer) [1] are serving in hospitals [2], and working in tiny spaces forbidden to silicon-based electronic devices. Our introduction of molecular logic [1] enables sensor systems which process data from several sensory channels to give a single 'go/no-go' decision. Even human-scale computations, e.g. edge detection of objects [3], are achieved by molecular logic systems. A short video is available at www.youtube.com/watch?v=sLGnZDP5Ecg

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Comunicaciones Orales (OC)

S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

BIMETALLIC COMPLEXES AS COOPERATIVE PARTNERS IN CELL IMAGING AND CANCER THERAPY

M. C. Gimeno[1], V. Fernández-Moreira[1], I. Marzo[2]

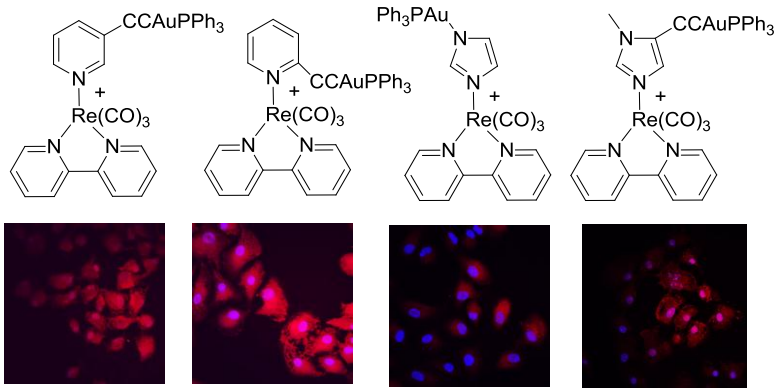
[1] Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain. E-mail: gimeno@unizar.es

[2] Departamento de Bioquímica y Biología Celular, Universidad de Zaragoza, E-50009 Zaragoza, Spain.

Keywords: *metallodrugs, cell imaging, gold, rhenium, luminescence*

Fluorescence microscopy has become one of the more powerful tools in cell biology and related areas of bioscience. Their high sensitive detection that allows to visualize single molecules together with the possibility of monitoring rapidly changing events make this technique as the ideal tool to reveal key information about the mechanism of action of multiple metallodrugs. The idea of using fluorescence microscopy for visualizing biomaterial relays in the availability of having molecules with the suitable photophysical properties that can be used as light-bulbs inside the cells. Unfortunately, gold(I) and gold(III) metallodrugs lack sometimes of such capacity. Therefore, it is imperative to be able to design new species that bear together anticancer activity and emissive properties. A reasonable approach would be the development of bioactive luminescent heterometallic derivatives, being each metallic fragment the responsible of bringing together those features.

Then a series of luminescent hometallic *fac*-$[Re(bipy)(CO)_3(L)]^+$ and heterometallic *fac*-$[Re(bipy)(CO)_3(L\text{-}AuPPh_3)]^+$ complexes, where L is a functionalised ligand, have been synthesised for the purpose of finding a synergic effect between the excellent photophysical properties of rhenium complexes and the good antiproliferative effects of gold compounds. Re(I)/Au(I) derivatives presented values of IC_{50} more than 10 times lower than their analogous Re(I) complexes. In addition, fluorescent cell microscopy pointed out the different biodistribution behaviour of the homometallic and heterometallic families.



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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

COMPUESTOS FOSFORESCENTES CICLOMETALADOS HOMO Y HETEROMETÁLICOS DE Ir(III) CON LIGANDOS ALQUINILO PUENTE

M. T. Moreno, J. Fernández, N. Giménez, E. Lalinde, P. Montaño, S. Sánchez

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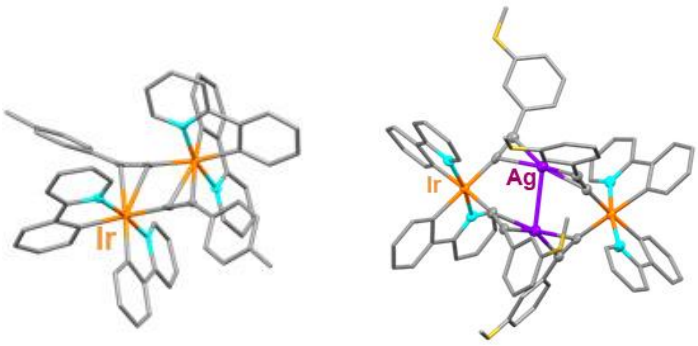
Palabras Clave: *alquinilo, ciclometalado, iridio, luminiscencia*

Nuestro grupo de investigación tiene una dilatada experiencia en la síntesis y estudio de las propiedades fotofísicas de alquinil derivados homo y heteropolinucleares de platino,[1] incluyendo en ocasiones ligandos cromóforos ciclometalados.[2] Por otro lado, aunque los compuestos fosforescentes ciclometalados de Ir(III) han despertado un creciente interés, resulta sorprendente el escaso número de ejemplos descritos en la bibliografía de compuestos de Ir(III) que combinan ligandos alquinilo y ciclometalados, a pesar de las interesantes propiedades fotoluminiscentes que se esperan de estos sistemas. De hecho, sólo se han descrito recientemente los compuestos mononucleares del tipo $[Ir(C^{\wedge}N)_2(C{\equiv}CR)L]$.[3]

En este contexto, creemos que el diseño de sistemas homo y heteropolinucleares ciclometalados de Ir(III) con ligandos alquinilo puente es de gran interés. En esta comunicación se presenta la síntesis de los primeros derivados homodinucleares de Ir(III), $[Ir(ppy)_2(\mu\text{-}C{\equiv}CR)]_2$ (Hppy = fenilpiridina; R = Tol, C_6H_4OMe-4, 1-Np, $SiMe_3$, ^tBu), estabilizados mediante un sistema de doble puentes alquinilo $\sigma{:}\eta^2$. Asimismo, se presenta una serie de clusters tetranucleares heterometálicos $[\{Ir(ppy)_2(C{\equiv}CR)_2\}_2M_2]$ (M = Ag, Cu ; R = Tol, C_6H_4OMe-3, ^tBu), estabilizados por interacciones $M{\cdots}\eta^2$-alquinilo y $M{\cdots}M$. Para evaluar la influencia del sustituyente del grupo alquinilo y la naturaleza del heterometal en la luminiscencia, se han estudiado en detalle las estructuras, propiedades ópticas y electroquímicas de estos compuestos, con apoyo de cálculos teóricos.



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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

MESOMORPHIC TRIPHENYLENE PLATINUM COMPLEXES: LUMINESCENT COLUMNAR MESOPHASES

Emiliano Tritto, Rubén Chico, Silverio Coco, and Pablo Espinet

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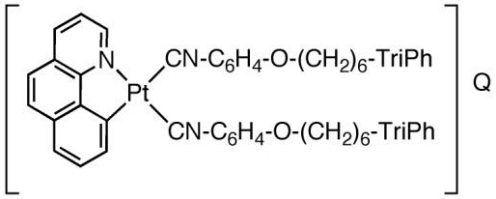
Keywords: *Liquid crystals, triphenylene, isocyanide, platinum, luminescence*

The study of columnar liquid crystals constitutes an active branch in liquid crystals research, aimed at obtaining materials with unique electronic and optoelectronic properties.[1] Although the type and intensity of intermolecular interactions responsible for molecular stacking determine the properties of the system, little is known about the influence of self-assembly metallophilic interactions in discotic liquid crystals. In this context, we have recently reported a family of liquid crystalline mono and dinuclear orthometallated palladium complexes derived from triphenylene with an original mesophase structure, where there is an accumulation of Pd-containing columnar zones supported by fully organic columns, although not associated through metal–metal interactions.[2]

On these grounds we decided to extend the study of triphenylene metal complexes, hoping that the use of metallic fragments prone to generate metal-metal interactions, might get mesophases supported by metallophilic interactions and generate mesomorphic systems with interesting properties along the columnar stacking. We report here cationic benzoquinolinate (bzq) platinum complexes with 2-(6-(4-isocyanophenoxy)hexyloxy)-3,6,7,10,11-pentakis(dodecyloxy)triphenylene (CN-C_6H_4-O-$(CH_2)_6$-TriPh], which display luminescent columnar mesophases supported through Pt---Pt and π–π interactions. Their structure consists of a central column formed by stacking of benzoquinoline-platinum groups, surrounded by six columns formed by the stacking of the triphenylene groups in hexagonal disposition.



[Q = NO_3^-, BF_4^-, PF_6^-]

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Acknowledgments. This work was sponsored by the Ministerio de Ciencia e Innovación (Project CTQ2014-52796-P) and the Junta de Castilla y León (Project VA302U13).

S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

DETECTION OF BIOLOGICAL AND ENVIRONMENTAL TARGETS WITH FLUORESCENT POLYAMINES

Enrique García-España,[1] Estefanía Delgado-Pinar,[1] Paloma Lizondo,[1] Elena Salvador,[1] Mario Inclán,[1] M. Paz Clares,[1] Javier Alarcón,[2] Antoni Costa.[3]

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Keywords: *Luminescence, Sensor, Switches, Nanoparticles, Polyamines, Biological Substrates*

Polyamines are one of the most versatile types of receptors. Depending on pH and thereby, on its protonation degree, polyamines can interact with targets as different as metal ions, anions or neutral molecules. Moreover, polyamines are generally water soluble which is an important property for many applications. If polyamines are appended with signaling units, as they can be organic chromophores, then recognition can bring about detection. In this talk we present examples about the use of either simple or more elaborated fluorescent polyamines for the detection of analytes of environmental or biomedical interest. Furthermore, we discus about the use of functionalized boehmite nanoparticles for achieving multivalency in the recognition and detection events.

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

HIGHLY LUMINESCENT AND PHOTO(STABLE) CH_3NH_3PbBr3 NANOMATERIALS

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Keywords: *perovskite, colloidal, luminescence, lifetime, photostability*

Organolead halide perovskites of general $APbX_3$ (A= organic ammonium cation, X = halide anion) formula combine useful properties of both organic and inorganic materials, such as plastic mechanical properties (organic material) and good electronic mobility (inorganic material).[1],[2]

We report here an easy and simple preparation of colloidal $CH_3NH_3PbBr_3$ by following the general strategy described for the synthesis of other materials confined in the three dimensions, i.e., a good organic capping. [3] The synthetic method is based on the reaction of methylammonium halide and a long chain ammonium bromide with $PbBr_2$.[4] The nanomaterial is highly dispersible in organic solvents, and exhibit an extraordinarily high photoluminescence quantum yield (ca. 80%) and average recombination lifetime (> 420 ns), as well as high stability and photostability (<18% emission loss after 8.5 h).[5] The long chain ammonium salt plays a key role as the capping agent that stabilizes small sized $CH_3NH_3PbBr_3$ crystalline nanomaterial. The completion of the coordination sphere of the ions at the nanomaterial surface may be the origin for the low non-radiative recombination rate constant of these nanomaterials. These perovskites preserve their emissive properties in the solid state, which makes them promising for use in light emitting devices. The non-template strategy herein reported can be useful for the preparation of perovskite nanomaterials with other stoichiometry.

Figure 1. Image of toluene dispersion of $CH_3NH_3PbBr_3$ perovskite under lab light (left) and UV-laser pointer (centre) excitation, as well as HRTEM image of the nanoparticles, scale bar of 5 nm (right).

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

DISAGGREGATION-INDUCED FLUORESCENCE ENHANCEMENT OF NIAD-4 FOR THE OPTICAL IMAGING OF AMYLOID-β FIBRILS

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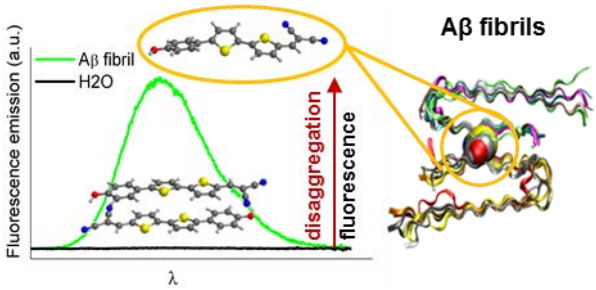
Keywords: *amyloid-beta, TD-DFT, aggregation, intersystem crossing, docking*



Aβ-induced disaggregation is responsible for the increased fluorescence of NIAD-4 observed upon interaction with amyloid-β

Alzheimer's disease, a progressive disorder of the central nervous system, shows several pathological hallmarks, including plaques caused by aggregation of the peptide amyloid-β (Aβ) into fibrils.[1] An early diagnosis of the disease requires the fast and accurate detection of such aggregates in vivo. The fluorescent marker NIAD-4, synthetized by Nesterov *et al.*,[2] is a promising Aβ marker due to its emission at high wavelength (> 600) nm and its ability to rapidly cross the blood-brain barrier and target Aβ deposits. Furthermore, it shows different photophysical properties in aqueous solution and when bound to amyloid fibrils, which is essential for attaining a good imaging contrast.

The present work analyzes the photophysics of NIAD-4, using a pool of computational (TD-DFT, post Hartree-Fock calculations, ab-initio MD and fit induced docking) and UV-Vis spectroscopic techniques with the goal of understanding the origin of the fluorescence enhancement observed upon binding to Aβ fibrils. Results show that neither variation in polarity nor in hydrogen bond donor/acceptor capabilities of the surrounding medium is responsible for such a difference. Concentration-dependent absorption spectra and fluorescence excitation spectra in aqueous solution, on the other hand, indicate that NIAD-4 aggregates in aqueous solution already at very low concentrations, accounting for the lack of fluorescence emission observed in this medium. Furthermore, the computational exploration of NIAD-4 binding to models of Aβ fibers shows that the dye is preferentially accommodated at the hydrophobic core of the fibril (see Figure). These sites are accessible by the monomeric form of the marker only, thus suggesting that disaggregation and diffusion into the hydrophobic amyloid voids is the main reason for the strong fluorescence enhancement of NIAD-4 upon binding to Aβ deposits.

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

BODIPY-BASED MOLECULAR ROTORS FOR MAPPING VISCOSITY IN PLASMA MEMBRANES OF LIVE CELLS

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Keywords: *Fluorescence Molecular Rotors, Viscosity, BODIPY, Fluorescence Life Time Imaging, Live Cells.*

Mapping viscosity in biological systems is of paramount importance for the understanding of biophysical processes governing both the normal cell function and the cell demise. In recent years, fluorescence imaging using molecular rotors has been at the forefront of major developments in measuring viscosity in heterogeneous and dynamic systems such as cells. The term molecular rotor refers to synthetic fluorophores in which fluorescence emission displays an extremely strong dependence on the viscosity of the surrounding environment.[1]

A wide range of molecular rotors are available for imaging of viscosity of internal cellular organelles.[2] However, in spite of the great importance of membrane viscosity in cellular processes, a probe to exclusively target the cellular plasma membrane has remained elusive. Here we report the synthesis, spectroscopic characterization and live cell imaging of a new family of BODIPY-based molecular rotors (Fig. 1A) which are effectively prevented from endocytosis by the double positive charge located on their hydrocarbon tail. To the best of our knowledge, this is the first example of viscosity sensitive molecular rotors which selectively stain the plasma membrane of live cells.[3]

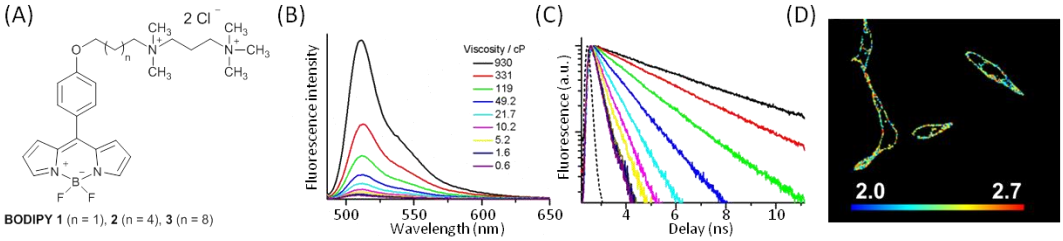

Fig 1. (A) Molecular structure of **BODIPY 1**, **2** and **3**; (B) fluorescence spectra and (C) time resolved fluorescence decays in methanol-glycerol mixtures of varied viscosity of **BODIPY 2**; (D) Fluorescence Lifetime Imaging (FLIM) of **BODIPY 2** in SK-OV-3 cells lifetime range from 2.0 to 2.7 ns.

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

PHOTOACTIVE PROBES AND THEIR INTERACTION WITH PROTEINS

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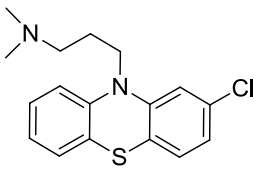
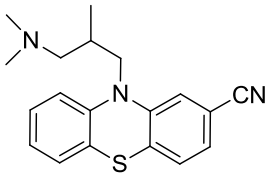
Keywords: *singlet excited state, triplet excited state, fluorescence, laser flash photolysis, drug, transport protein*

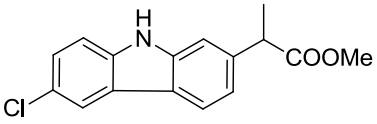
Chlorpromazine (CPZ), cyamemazine (CMZ), and carprofen methyl ester (CPM) are drug derivatives whose absorption spectra reach the UVB-UVA region; for that reason, they are potential photosensitizing agents. After irradiation, the singlet and triplet excited states of CMZ, CPZ and CPM are formed, together with other reactive species such as carbon-centered free radicals, reactive oxygen species, etc). In this context, a characterization of the photophysical and photochemical behavior of CPZ, CMZ and CPM within transport proteins (serum albumins and α-acid glycoproteins) has been performed, to investigate if the photogenerated intermediates can be responsible for biological damage.



CPZ



CMZ



CPM

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

FLUORESCENT CARBORANE-BASED SYSTEMS

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Keywords: *boron clusters, carboranes, fluorescence, luminescence*

The search for luminescent materials is continuously expanding due to their applications as light emitting diodes (LEDs), semiconductor lasers, probes or fluorescence sensors, among others. Icosahedral carborane clusters are versatile synthetic building blocks that possess three dimensional delocalization of electrons, σ-aromaticity and interact with π-conjugated systems. During the last few years, the interest in the development of new materials bearing polyhedral boron clusters that exhibit photoluminescence properties has increased notably.[1] For this reason, different fluorescent molecular systems, in which the carborane is linked to fluorescent π-conjugated organic systems, to different type of polymers, to fluorophores, among others, have been recently described, and the influence of the cluster on the emission properties studied. In addition, the carborane clusters are thermally very stable, and the incorporation of these systems into π-conjugated structures results in materials with extremely high thermal stability.

Our group has made significant progress in the synthesis and photophysical studies of small[2,3] and large fluorescent molecules based on carborane clusters[4,5] (see, Figure 1). We have conducted the study of their photoluminescent properties and demonstrated how relevant is the substituent attached to the adjacent cluster carbon atom in the case of o-carborane systems, as well as the nature of the cluster (ortho-, meta- or nido-carborane) on the fluorescence intensity. After that, a question arises: can the fluorescence be tuned or even predicted in these systems? The answer to this question will be given in this talk.

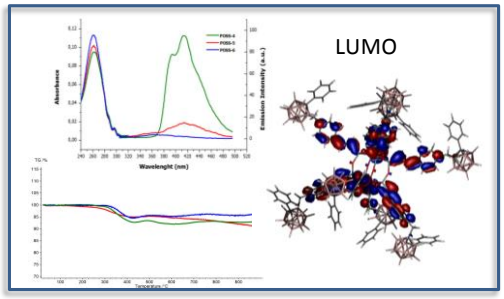

Figure 1

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

ULTRAFAST TIME-RESOLVED EMISSION STUDIES OF NILE RED EMBEDDED IN METAL DOPED MESOPOROUS MATERIALS

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Keywords: *MCM41, nile red, ultrafast dynamics, metal doping effect.*

The development of ordered porous silica materials, like zeolites, emerged as one of the most attractive alternatives to amorphous silica material, due to their unique physical and chemical properties [1,2]. Here, we present steady-state and femto- to nanosecond time-resolved study for a charge-transfer chromophore (Nile Red, NR) interacting with MCM41 mesoporous materials doped with Al, Ga, Zr and Ti in dichloromethane (DCM) suspensions. The presence of the silica materials leads to the formation of different populations of NR, including monomers, J- and H-aggregates. The large bathochromic shift of the absorption and the emission bands for NR interacting with the host frameworks are explained in terms of Brønsted (H-bonds formation) and Lewis interactions. The femtosecond results for R-MCM41, Al-MCM41 and Ga-MCM41 indicate that the excitation of NR leads to the generation of locally excited (LE) state followed by the internal charge transfer (ICT) giving rise to charge separated (CS) state within 340 – 420 fs. For the NR/Ti-MCM41 and NR/Zr-MCM41 samples, the ICT occurs in a time shorter than 200 fs. The presence of transition metals results in additional process of the electron injection (EI) from the CS state of NR to trap states formed by the d-orbitals of the dopants in the host framework (~250 fs).

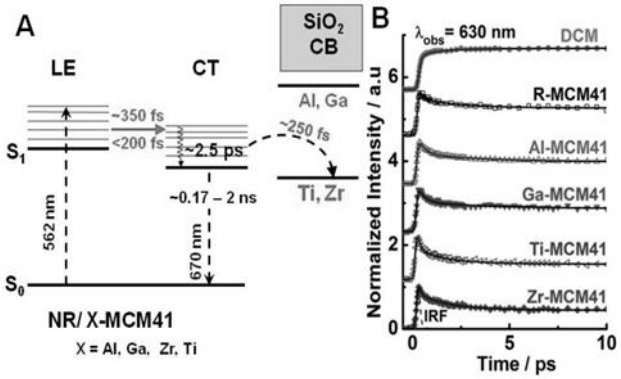

Figure 1. (A) Schematic presentation of energy levels S_0 and S_1 states of NR interacting with Ti-MCM41 and Zr-MCM41 in a DCM suspension. The scheme gives the values of time constants related to the processes occurring in these systems. (B) Femtosecond-emission transients of Nile Red in a DCM solution and interacting with MCM41 materials in DCM suspensions excited at 562 nm and observed at 630 nm.

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Comunicaciones Flash (FC)

S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

EXPERIMENTAL AND THEORETICAL STUDY OF THE FIRST UNSUPPORTED INTERACTION BETWEEN Au(I) – Pb(II) CENTERS

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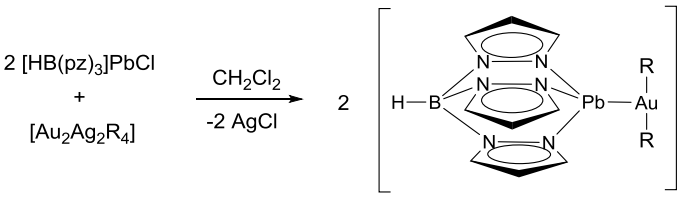
Keywords: *Luminescence, Lead, Gold.*

The synthesis of gold–heterometal complexes has gained increased attention during the last years due to their potential applications in solid-state chemistry, catalysis, electronics and imaging industry. The study of interactions between Au(I) and other closed shell metals is a research area in continuous growth due, especially, to the photophysical properties associated with these non bonding interactions.[1] In this context, the study of the closed shell interactions between Au(I) and metals of groups 14 and 15 is almost unexplored. In fact, as far as we are aware there are no examples of compounds displaying unsupported interactions between Au(I) and Pb(II) centers. The only complex displaying a Au(I)···Pb(II) interaction that has been structurally characterized is $[Au_2Pb(CH_2P(S)Ph_2)_4]$.[2] In this case, the Au(I)···Pb(II) interaction is supported by a bidentate ligand.

In this communication, we describe the synthesis of compounds of the type $[HB(pz)_3Pb][AuR_2]$[3] (pz = pyrazolate; R = $C_6F_5^-$ **(1)**, $C_6Cl_2F_3^-$ **(2)**, $C_6Cl_5^-$ **(3)** *p*-$C_6BrF_4^-$ **(4)**) in which unsupported Au(I)/Pb(II) interactions are characterized, in the solid state, through X-ray diffraction studies, for the first time.



R = $C_6F_5^-$ **(1)**, $C_6Cl_2F_3^-$ **(2)**, $C_6Cl_5^-$ **(3)**, *p*-$C_6BrF_4^-$ **(4)**

In addition, these compounds show interesting photoluminescent properties, that can be tuned according to the perhalophenyl ligands bonded to the gold(I) centers.

We have also performed theoretical calculations to study the nature of the Au(I)···Pb(II) interactions and the origin of the luminescence of such derivatives.

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

STRONGLY FLUORESCENT ORGANOBORON N,C-CHELATES AND THEIR APPLICATION IN BIOIMAGING

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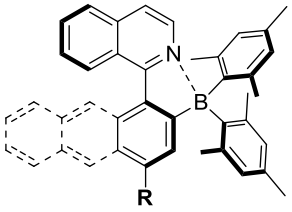
Keywords: *boron, fluorescence, ICT, photostability, bioimaging*

Boron-containing architectures with tunable and strong fluorescence have defined a landmark in the intersection area of organic chemistry, photophysics, and bioimaging applications.[1,2] Herein the design of six strongly fluorescent four-coordinate organoboron N,C-chelates (see general structure in Scheme 1), their photophysical characterization, and bioimaging applications will be presented. The highly fluorescent N,C-chelates (Scheme 1, photograph) can be easily prepared, using an iridium-catalyzed nitrogen-directed orthoborylation of arylisoquinoline precursors as a key step.[3] In addition, they contain electron-donating substituents promoting intramolecular charge-transfer processes (ICT).[4] Of particular interest is the observation of high quantum yields in solution and large Stokes shifts as well as high photostability, that qualify these compounds for bioimaging applications.



R: OCH_3, $N(CH_3)_2$ ....

Scheme 1

The financial support by the Spanish MINECO (CTQ2014-54729-C2-1-P, CTQ2013-48164-C2-1P and CTQ2013-48164-C2-2-P, CTQ2013-41339-P, Ramón y Cajal contract RYC-2013-12585), the European Union (FEDER), and the Junta de Andalucía (2012/FQM-2140 for U.P., 2009/FQM-4537 and 2012/FQM-1078, postdoctoral contract for V.F.P.) is gratefully acknowledged.

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

FORMATION OF GOLD(I)-SILVER(I) BIMETALLIC COMPLEXES: STUDY OF THEIR LUMINESCENCE AND AGGREGATION PROCESSES

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Keywords: *metallophilic and aurophilic interactions, aggregation, luminescence*

Aurophilic interactions are common in gold(I) compounds and are responsible for the formation of dimers, oligomers and supramolecular polymers [1]. They are a class of "metallophilic" bonds involving heavy metals with closed-shell configuration, having their maximum expression on Au(I) and can be defined as van der Waals forces enhanced by relativistic effects [2]. Together with aurophilicity (Au^{I}-Au^{I}), heterometallic Au^{I}-Ag^{I} interactions have attracted recent attentions due to the tunable luminescence of their clusters [3]. In this work we report on the synthesis and characterization of new gold(I)-silver(I) bimetallic complexes. They contain a water-soluble phosphine (Figure 1) which allows studies in aqueous solutions. In concrete, the dependence on the establishment of Au^{I}-Au^{I} and Au^{I}-Ag^{I} interactions regarding the luminescence properties both in solution and the solid state is investigated. Also, the formation of supramolecular assemblies of oligomeric or polymeric nature is explored.

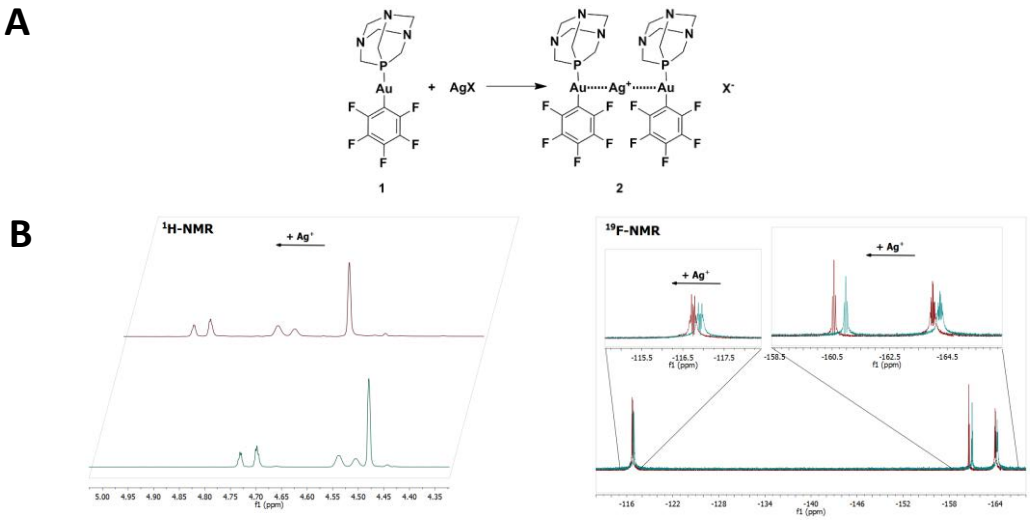

Figure 1. A) Formation of gold(I)-silver(I) bimetallic complexes. B) ^{1}H-NMR and ^{19}F-NMR spectra corresponding to **1** (green line) and **2** (X^{-} = PF_6^{-}, red line).

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

NUEVO SISTEMA CROMO-FLUOROGENICO PARA DETECCIÓN DE NO_2 (g) MEDIANTE EL USO DE BODIPYS MODIFICADOS.

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Palabras Clave: *NO_2, detección, fase gas, BODIPY, ppb, nanopartículas.*

El dióxido de Nitrógeno (NO_2) causa un gran número de efectos nocivos sobre la salud, especialmente problemas respiratorios[1]. En los últimos años se han desarrollado diferentes sistemas para su detección teniendo bastantes limitaciones para su uso. En el presente trabajo se propone para la detección de NO_2 (g) la utilización de un sistema cromo-fluorogenico basado en el uso de derivados de borodipirrometano (BODIPY) cuyas propiedades ópticas así como su estabilidad son ampliamente conocidas[2]. La base para la detección de NO_2 es su conocida capacidad para regenerar un aldehído desde su hidrazona aromática[3].

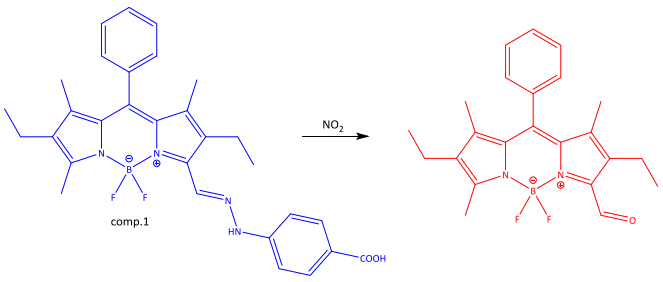

Figura 1: Mecanismo de detección.

Aprovechando las diferentes propiedades ópticas de la hidrazona y del aldehído del BODIPY se han realizado estudios exponiendo el compuesto 1 a diferentes concentraciones de NO_2 gas, obteniéndose límites de detección de 6,56 ppb en UV y de 5,48 ppb en fluorescencia. No se ha observado interacción con los interferentes más comunes. Con el objetivo de desarrollar un sistema de más fácil manejo y simplificar el método de detección se unió el compuesto 1 a nanopartículas de sílice y se obtuvo un sólido en el que se observa un cambio de color a simple vista con un límite de detección visual de 0,05 ppm en presencia de NO_2 (g). Hay que destacar que los límites de detección determinados están por debajo de los recomendados por la ASHRAE y la US EPA[4].

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

NEW FAMILY OF LUMINESCENT ANTENNA LIGANDS FOR BIO-ASSAYS

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Key words: *Luminescence, Lanthanide, polyheterocycle, genetic-bioassays*

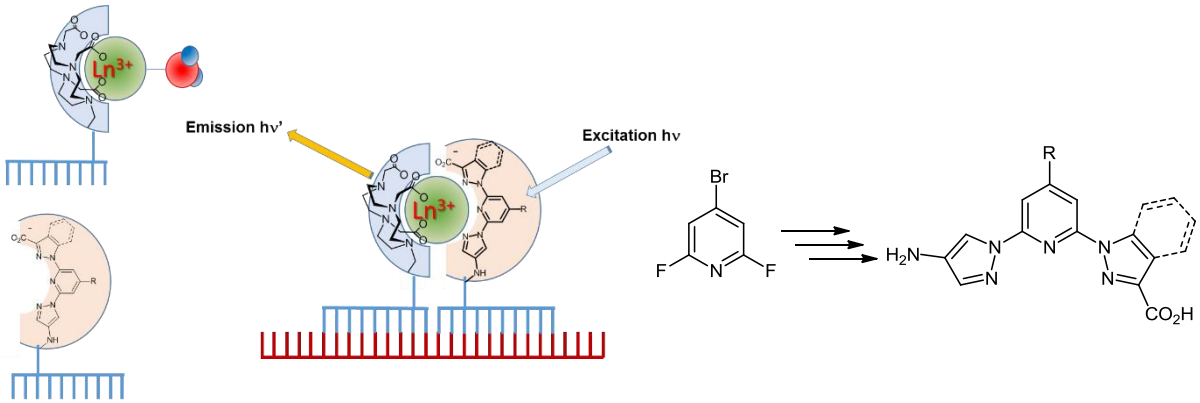
In this communication the synthesis of two new families of polyheterocyclic ligands, derived from 1-bispyrazolylpyridine (1-bpp) and 1-indazolylpyrazolilpyridine (1-ipp), and their applications as luminescent bacteria sensors are described [1].

Such compounds can be used as molecular switches due to their good properties for forming luminescent lanthanide ion complex.

Our research group has developed a synthetic method for obtaining derivatives of 2-indazolyl-6-pyrazolylpyridines and 2,6-bispyrazolylpyridines using as starting material 4-bromo-2,6-difluorobromopyridine. Thus polyheretocyclices derivatives were obtained with different substituents in position 4 of the pyridine (phenyl, thiophenyl, phenylethynyl ...), which were introduced via palladium coupling reactions [2].

A study of the photophysical properties of these ligands has been carried out when they form ternary complexes luminescent, using crown ethers as lanthanide ions carriers.

The communication also describe the application of some of these compounds in the labeling of oligonucleotides and their use as luminescent probes in determining bacterial DNA.



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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

DETERMINACIÓN DE ÁCIDO 3,5,6-TRICLORO-2-PIRIDILOXIACÉTICO EN MUESTRAS VEGETALES MEDIANTE FLUORESCENCIA INDUCIDA FOTOQUÍMICAMENTE

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Palabras Clave: *Fluorescencia inducida fotoquímicamente, 3,5,6-tricloro-2-piridiloxiacético, frutas, tomate.*

El ácido 3,5,6-tricloro-2-piridiloxiacético (triclopyr o TCP) es un herbicida hormonal con actividad reguladora del crecimiento, derivado del ácido picolínico. El TCP puede tener actividad herbicida cuando se utiliza el éster butoxietílico. El concentrado emulsionable del 48%, éster butoxietílico, puede ser utilizado en el desyerbe de caminos, cortafuegos, recintos industriales, redes de servicios, terrenos forestales y vías férreas. Con actividad como fitorregulador se usa el ácido, el cual se emplea en plantaciones de albaricoquero, nectarino, cítricos y de hortalizas como el tomate. Su vía de degradación principal en los sistemas terrestres es la microbiológica. Su tiempo de vida media puede variar entre los 8 y los 1300 días por lo que se hace necesario un control estricto tanto de su uso como en su determinación.

El TCP presenta en su molécula varios átomos de cloro unidos al anillo aromático, los cuales hacen que este analito no presente una fluorescencia natural. La reacción de fotolisis de los átomos de halógeno al aplicar radiación UV conducirá a la formación de un producto fluorescente, permitiendo la determinación fluorimétrica cuantitativa de este compuesto. Las condiciones óptimas de irradiación UV y de las variables químicas que afectan a la señal de fluorescencia seleccionada fueron: 3.3 min de irradiación, 5% de etanol, un 50 % de metanol y 0.04 mol L^{-1} de disolución reguladora de pH 5.

Se realizaron tres rectas de calibrado midiendo las intensidades de los espectros de emisión a λ_{em} = 435 nm (λ_{ex}=380 nm) en el intervalo 10-30 ng mL^{-1}. Se llevó a cabo un análisis de varianza y se comprobó la homocedasticidad en la calibración. Se evaluó la precisión del método obteniéndose una desviación estándar relativa inferior al 1 % y el límite de detección, obtenido según el criterio de Clayton, fue de 6.3 ng mL^{-1}. El método propuesto se aplicó a la determinación del TCP en muestras de ciruela, tomate, mandarina, madroño y el producto fitosanitario *Trident*. El producto fitosanitario fue analizado por dilución directa del mismo, mientras que para poder analizar el TCP en las frutas y hortalizas fue necesario un proceso de extracción en etanol. Las matrices etanólicas de las muestras que presentaban fluorescencia nativa (ciruela y tomate), tras ser sometidas al proceso de irradiación dejaban de presentarla mientras que las matrices que apenas la mostraban, tampoco eran fluorescentes después de ser irradiadas. Los porcentajes de recuperación del TCP tras su adición a las muestras indicadas fueron próximos 100%, lo que confirma la validez del método.

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J. Torres

S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

DIRECT OBSERVATION OF PROTON-TRANSFER FOR HYDRATED MCM-41 MATERIALS

N. Alarcos, B. Cohen and A. Douhal*

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Keywords: *Spectroscopy, photodynamics, confinement, nanohost, silica materials.*

Nanocaging of organic molecules may lead to large and significant changes in the spectroscopy and photodynamic of the molecular system. [1-5] The formed inclusion complexes have important applications in nanocatalysis, nanophotonics and nanomedicine. Recently, we reported on the photodynamics of trisodium 8-hydroxypyrene-1,3,6-trisulfonate (pyranine, HPTS), a strong photoacid, interacting with the human serum albumin protein and γ-CD in water solutions [5]. The results were interpreted in terms of ultrafast direct intermolecular-proton transfer (ESPT) between HPTS and the amino acid residues, as well as slow dynamics of the water molecules around the protein residues.

Here, we report on steady-state, pico- and femtosecond time-resolved emission studies of HPTS in dichloromethane solution (microcrystal formation) and interacting with dry and hydrated MCM-41 materials. The results exhibit that HPTS forms aggregates in both the DCM solution and interacting with dry MCM-41. However, when HPTS is interacting with hydrated MCM-41, an ESPT reaction takes place between the dye and water molecules. The observed time constant for the ESPT reaction is 200 ps, slower than the one reported for HPTS in pure water (90 ps) [5]. The data provide new insights on the nature of these complexes, and thus can help in the design of new nanophotonic devices (nanosensors, nanolasers) based on this kind of materials.

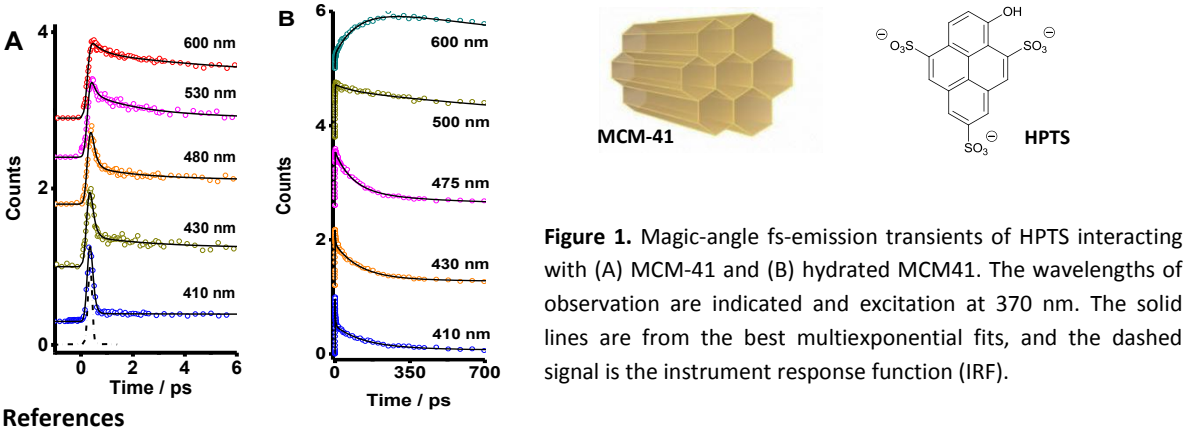

Figure 1. Magic-angle fs-emission transients of HPTS interacting with (A) MCM-41 and (B) hydrated MCM41. The wavelengths of observation are indicated and excitation at 370 nm. The solid lines are from the best multiexponential fits, and the dashed signal is the instrument response function (IRF).

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

WATER SOLUBLE LUMINESCENT SUPRAMOLECULAR STRUCTURES BASED ON *BIPY* AND *TERPY* LIGANDS AND Au(I)···Au(I) INTERACTIONS

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Keywords: *Gold(I), Aurophilic Interactions, Luminescence, Hydrogels, Supramolecular.*

Self-assembly of small molecules has received tremendous attention in materials science in the last decade, not only because of their fascinating and innumerable supramolecular morphologies[1] but also due to their potential applications in this field, and also mimic biological systems or functions[2] or in molecular devices.[3]
We recently reported on the formation of luminescent Au(I) hydrogels with organometallic alkynyl complexes where aurophilic intermolecular interactions should be involved on the gelation process (Fig. 1).[4,5] Herein, we present new Au(I) organometallic systems containing terpyridine and bipyridine units (Fig. 2) that are observed to give also rise to the formation of large supramolecular structures with interesting aggregation induced absorption (AIA) and emission (AIE). Fluorescence optical and electronic microscopies together with luminescence lifetime and quantum yields have been used for the characterization of the supramolecular assemblies of these complexes. Also, we have used ^{1}H-, ^{31}P- NMR (at different temperatures, concentrations and solvents) techniques to evaluate the effect of these aggregation processes. On the other hand, changes on AIA and AIE are used in molecular recognition processes, giving rise to the formation of heterometallic structures.

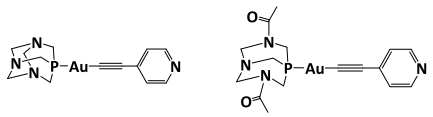

Fig. 1. General structures of phosphine PTA (left), DAPTA (right)-gold-alkynyl.

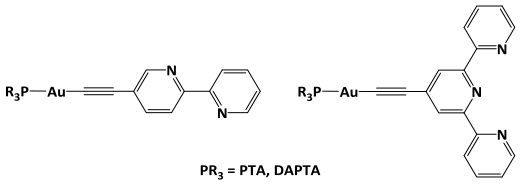

Fig. 2. General structures of phosphine-gold-pyridines derivatives.

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

HACIA LA DETECCIÓN FLUOROGÉNICA DE EXPLOSIVOS PEROXÍDICOS

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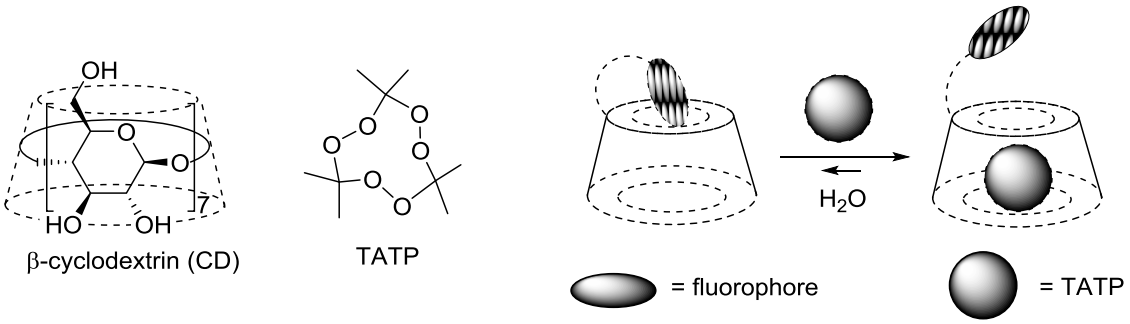
Palabras Clave: *Explosivos peroxídicos, TATP, ciclodextrinas, sensores*

La preocupación internacional por la posibilidad de nuevos ataques terroristas ha provocado en los últimos años un aumento del interés en la obtención de sistemas para la detección de explosivos peroxídicos. El presente trabajo se centra en la obtención de un sensor sensible al TATP (triperóxido de triacetona). Este explosivo presenta problemas para su detección directa ya que no posee ninguna banda característica en su espectro de UV-vis o fluorescencia. En la escasa bibliografía existente relativa a la detección del TATP se detecta el peróxido de hidrógeno que se genera en su descomposición ácida. [1] Por ello se pretende desarrollar una estrategia para la caracterización directa del TATP.

Teniendo en cuenta el carácter lipofílico de la molécula de TATP se plantea el empleo de una molécula con una cavidad lipofílica capaz de albergar en su interior esta molécula. La β-ciclodextrina es un polisacárido cíclico soluble en agua y con una cavidad lipofílica capaz de albergar moléculas de distintos tamaños. La funcionalización de la β-ciclodextrina con un fluoróforo como la dansilamida permite su uso como sensor químico. [2] Así pues se pretende llevar a cabo la detección fluorogénica de TATP mediante un mecanismo de desplazamiento, donde la unidad indicadora (el grupo dansilamida) en medio acuoso presentará propiedades fotofísicas (fluorescencia) diferentes en presencia o en ausencia de TATP. El mecanismo de acción se puede esquematizar como sigue:



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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

NEW FLUORESCENCE SENSOR FOR BIOTHIOL AND PHOSPHATE IMAGING

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Keywords: *FluorescenceSensors. FLIM. Intracellular Imaging.*

Fluorescent probes of low toxicity for multiplex sensing are remarkable tools for the analysis of biological systems. We have focused our attention in biothiols and phosphate anions, two naturally occurring compounds widely present in living organisms whose deregulation is related with cellular dysfunction.

Recently, a new methodology based in the dependence of the fluorescence decay time of xanthene-based dyes on the phosphate buffer concentration at near physiological pH was developed in our laboratories [1]. The highest sensitivity was obtained with a tailor-made compound with a fine-tuned pKa value of 7.3 denominated as Granada Green (**GG**) [2]. In this communication, we present the synthesis of the 2,4-dinitrobenzenesulfinate (**DNBS**) derivative of **GG**, **DNBS-GG**, a new sulphinate-based biothiol sensitive probe which, in addition, shows a good sensitivity for phosphate anions at near-neutral pH, both in vitro and extracellular medium.

The innovative dual probe for thiols and phosphate ions has been tested in solution by steady-state, and time-resolved fluorescence, and intracellularly by fluorescence lifetime imaging microscopy (FLIM). For this last purpose, **DNSB-GG** was added to the extracellular medium of HeLa cell cultures, and FLIM images were collected at different times, and different phosphate concentrations. Figure 1 shows the fluorescence intensity changes displayed with time due to reaction with the own biological thiols of the cells. In Figure 2 the changes in the fluorescence lifetime due to the different intracellular phosphate concentrations are shown.

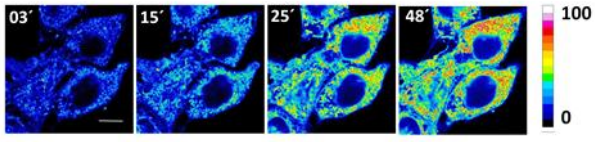

Figure 1

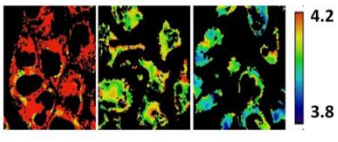

Figure 2

References

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

LUMINISCENCIA EN COMPUESTOS DE ORO(III): DESDE EL ROJO HASTA EL AZUL

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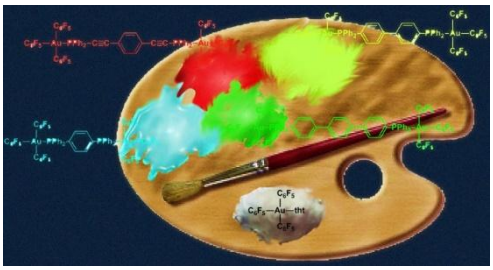
Palabras Clave: *oro, luminiscencia, difosfinas.*

Si bien en los últimos años ha crecido de manera exponencial la preparación de derivados de oro luminiscentes, siguen siendo muy mayoritarios los ejemplos en los que el metal se encuentra en estado de oxidación (I). En este trabajo, presentamos la síntesis y algunas propiedades ópticas de compuestos de oro(III) luminiscentes, obtenidos por coordinación de diferentes difosfinas al centro metálico. Para evitar la desactivación de la luminiscencia se emplearon ligandos pentafluorofenilo, que ayudan a la estabilidad de los centros de oro(III) y fosfinas bidentadas con diferente número de grupos espaciadores: fenilenos y/o alquinilos. Por reacción del precursor $[Au(C_6F_5)_3(tht)]$ con los ligandos difosfina correspondientes se obtuvieron el conjunto de complejos protagonistas de este trabajo.



El estudio posterior de su comportamiento óptico revela una amplia gama en las emisiones de energía, abarcando desde el azul hasta el rojo, pudiendo modularse dichas emisiones con el diferente número de grupos espaciadores en la difosfina.

S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

ESTUDIOS DE INTERACCIÓN ENTRE FÁRMACOS Y MACROMOLÉCULAS MEDIANTE ESPECTROSCOPÍA DE FLUORESCENCIA

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Palabras Clave: *Fármacos, Antioxidantes, Guanidinas, Fluorescencia, DNA*

Estudios de interacción de antioxidantes con BSA.

Actualmente existe un gran interés en el estudio de diversos antioxidantes fenólicos, como el ácido gentísico (GA), por su capacidad de capturar radicales libres y por las diversas aplicaciones médicas que presentan [1]. La interacción de GA con albúmina de suero bovina (BSA) ha sido estudiada en nuestro laboratorio mediante espectroscopía de fluorescencia de estado estacionario (SSFS) y resuelta en el tiempo (TRFS) gracias a la fluorescencia nativa de BSA. De los estudios de interacción proteína-ligando mediante SSFS y TRFS se obtuvieron las correspondientes constantes de Stern-Volmer (K_{SV}) y de unión (K_a), así como el porcentaje de *quenching* estático frente a dinámico. Variando la temperatura de trabajo pudieron además determinarse distintos parámetros termodinámicos de la unión como *ΔH, ΔS y ΔG,* que permitieron además dilucidar el mecanismo de interacción entre GA y BSA. El cambio en la estructura secundaria de la proteína debida a la interacción con GA fue finalmente analizada mediante espectroscopía de absorción UV-Vis e infrarroja por transformada Fourier (FTIR).

Propiedades ópticas y estudios de interacción con DNA de diversos agentes antitumorales

El cisplatino es uno de los principales fármacos empleados en quimioterapia para el tratamiento de varios tipos de tumores ya que reaccionan *in vivo* uniéndose covalentemente al DNA induciendo apoptosis [2]. La interacción de algunos derivados no comerciales del cisplatino con DNA ha sido estudiada en nuestro laboratorio mediante SSFS y espectroscopía de absorción UV-Vis. Se obtuvieron las constantes de interacción con DNA y se compararon con las del cisplatino comercial, relacionándolo con su actividad antitumoral.

Algunos derivados de guanidina también presentan una importante actividad antitumoral ya que pueden interaccionar tanto con proteínas como inhibidores, como con el DNA frenando su replicación [3]. Las propiedades ópticas de dos derivados de guanidina fluorescentes fueron estudiadas empleando SSFS, TRFS y UV-Vis. Se estudió su afinidad por el DNA así como el mecanismo de interacción, obteniéndose los distintos parámetros de dicha interacción.

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

SYNTHESIS OF LUMINESCENT CYCLOMETALATED Ir(III) COMPLEXES WITH ARYLAZOLES LIGANDS WITH POTENTIAL ANTICANCER AND SENSOR PROPERTIES

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Keywords: *Iridium, cyclometalated, arylazoles ligands, fluorescence, luminescence.*

Cyclometalated iridium (III) complexes are subjects of considerable attention because of their unique photophysical properties. In particular, their high-luminescence quantum yields offer high sensitivity, whereas their relatively long lifetimes (μs) allow suppressing the short-lived autofluorescence from biological samples. These properties have led to applications such as molecular probes, LEDs, potential anticancer agents in photodynamic therapy and photocatalysis.[1]

In this work, we present the synthesis and characterization of a family of cyclometalated Ir(III) complexes with arylazoles as the N^N ancillary ligands and different arylpyridines as the cyclometalated C^N ligands (Figure 1). New methodologies based on microwave reactions have been used to obtain some of the dimeric starting materials with improved reaction times, yields, and purity degrees. Moreover, the comprehensive study of the photophysical properties of the new derivatives has given rise to interesting structure-property relationships. Finally, we intend to show preliminary results regarding to the potential applications as therapeutics and fluorogenic sensors of the above-mentioned derivatives.

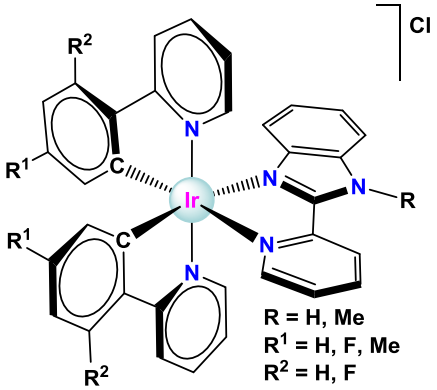

Figure 1. Model structure of the synthesized complexes.

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

DISEÑO Y SÍNTESIS DE SENSOR FLUORESCENTE PARA NO (g) BASADO EN EMISIÓN INDUCIDA POR AGREGACIÓN (AIE)

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Palabras Clave: *NO, detección, AIE, click chemistry, TPE*

El óxido de nitrógeno es un gas tóxico que suele estar como contaminante en el aire, provocando efectos adversos en los seres humanos y en el medio ambiente. Por otra parte, se ha observado que también actúa como regulador de varios procesos biológicos, por todo ello, resulta de gran importancia desarrollar métodos de detección fiables y fáciles de manejar [1]. Para ello, hemos utilizado un fenómeno de reciente interés conocido como Aggregation Induced Emission (AIE), consistente en un incremento de la fluorescencia de algunas sustancias al formar agregados o al adsorberse en superficies respecto a la que tienen en disolución [2].

Es conocido que el NO reduce el Cu(II) a Cu(I) [3], por lo que se ha utilizado el Cu(I) generado in situ en la reacción de la figura 1 para formar especies derivadas del tetrafeniletileno (TPE) que se agreguen con mayor facilidad con el objetivo de potenciar el efecto AIE. De esta forma, el incremento en la emisión fluorescente nos indica la presencia de NO.

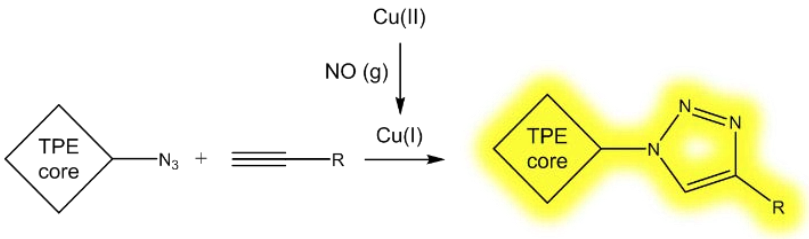

Figura 1: Cicloadición de azidas y alquinos de Huisgen. R: Alquilo

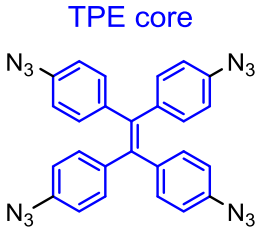

Figura 2: Núcleo de TPE

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

ESTUDIO DE LAS PROPIEDADES ÓPTICAS DE ARIL DERIVADOS DE ORO Y PLATA CON LIGANDOS HETEROCÍCLICOS

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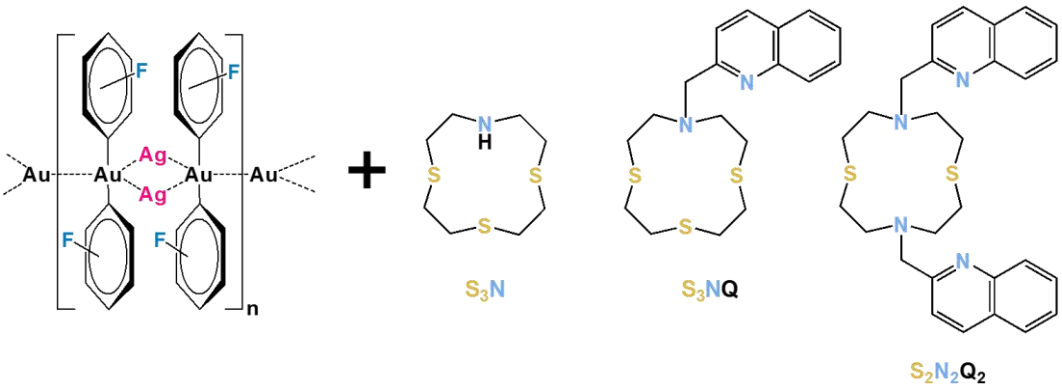
Palabras Clave: *luminiscencia, oro, plata, ligandos heterocíclicos.*

Durante los últimos años ha existido un gran interés en el estudio de sistemas polinucleares formados mediante interacciones metalofílicas, debido en gran medida a las interesantes propiedades ópticas que presentan y sus potenciales aplicaciones [1]. Por otro lado, uno de los objetivos de especial interés en el área de la química de los polímeros de coordinación es el control del proceso de auto-ensamblaje en la formación de dichos polímeros [2].

En este contexto, estudiamos la reactividad del compuesto polimérico $[\{Au(C_6F_5)_2\}_2Ag_2]_n$, formado a través de interacciones metalofílicas Au···Au, Au···Ag y Ag···Ag, frente a tres ligandos heterocíclicos con diferente capacidad coordinativa. De este modo, observamos la formación de compuestos con diferente estructura e interacciones en función del ligando y la estequiometría empleados en la reacción, lo que nos permitirá evaluar cómo afectan los diferentes parámetros estrucutrales en las propiedades ópticas.



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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

FLUORESCENCE TUNING BY STIMULI RESPONSIVE TWO-COMPONENT SMART GELS

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Keywords: *Supramolecular gels, photo-responsive materials, energy transfer*

Self-assembly and auto-organization is an astounding phenomena well known in the biochemical level and also has been recently harnessed to create new functional materials.[1] Supramolecular gels are reversible soft materials formed by low molecular weight components assembled by non-covalent forces. These weak interactions lead to the formation of fibres that entrap the solvent within it. Leading to stimuli responsive, photonic, and catalytic materials among others.[2,3]

In the present work we introduce a smart two-component photonic molecular gel, formed by acridine and naphthalimide derivatives that form co-aggregated networks in CH_3CN. Given the nature of the chromophores and their optical properties, fluorescence resonance energy transfer was detected in gel phase reaching efficiency levels up to 74% in equimolar co-aggregates and up to 98% in the xerogel. The composition of the fibrillar network can be modulated by external pH stimuli and therefore, control the energy transfer efficiency and fluorescence features for possible photo-electronic applications.

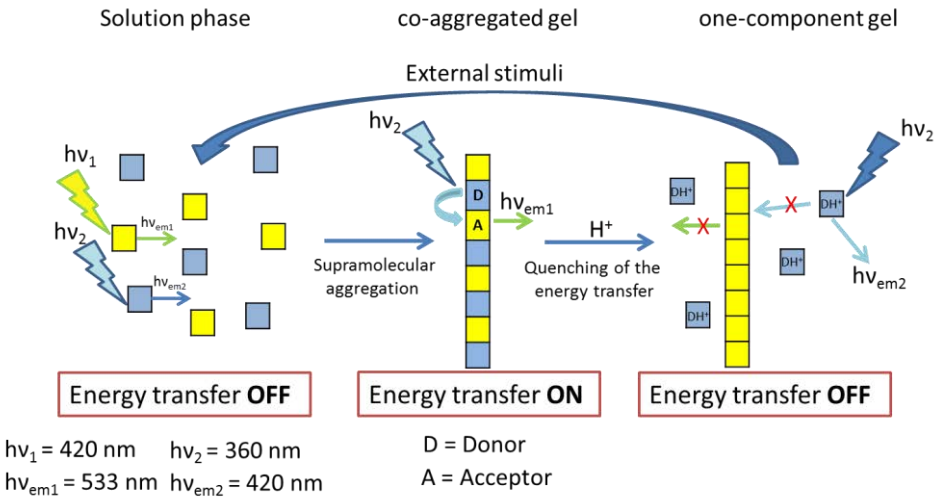

Fig.1 Scheme of the FRET mechanism on stimuli-responsive coaggregated fibrillar networks.

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

PRODUCCIÓN FOTOQUÍMICA DE HIDRÓGENO A PARTIR DE AGUA Y CLÚSTERES DE MOLIBDENO (II) OCTAÉDRICOS CON HALÓGENOS

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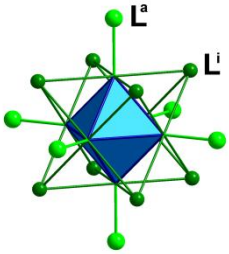
Palabras Clave: *molibdeno, clúster, fotocatálisis, generación de hidrógeno, materiales híbridos, grafeno, óxido de titanio.*

Desde el descubrimiento de las características fotoluminiscentes del compuesto clúster $[Mo_6Cl_{14}]^{2-}$ en 1981, se ha promovido el desarrollo de compuestos moleculares topológicamente análogos, de fórmula general $[Mo_6X^i_8Y^a_6]^{2-}$, con propiedades fotofísicas y redox intrínsecas.[1] Estos compuestos están constituidos por una unidad clúster hexametálica de geometría octaédrica, coordinada a ocho ligandos halógeno apuntados (X^i = Cl, Br o I) y a seis ligandos en posiciones apicales (Y^a), tal como se muestra en el siguiente esquema:



La respuesta fotoquímica de estas moléculas nanométricas es muy dependiente de la naturaleza de los ligandos. Los clústeres $[Mo_6X^i_8Y^a_6]^{2-}$ absorben luz desde el ultravioleta hasta el visible y muestran emisiones desde 600 a 900 nm, por lo que han resultado ser eficaces como sensores luminiscentes y en la activación de oxígeno para la generación de oxígeno singulete. Recientemente, se ha descrito que los clústeres $[Mo_6Br_{14}]^{2-}$ son activos catalíticamente en la reducción de CO_2 para proporcionar metanol con radiación visible.[2]
En la presente comunicación se presentará la actividad catalítica de los clústeres $[Mo_6X^i_8Y^a_6]^{2-}$ (X^i = Cl, Br, I; Y^a = halógeno, carboxilato) en la reducción de agua, promovida por radiación ultravioleta y visible. Se describirá la inmovilización de estos clústeres moleculares en superficies de materiales semiconductores, tales como óxido de titanio y grafeno, la caracterización de los materiales híbridos resultantes mediante técnicas espectroscópicas, y los resultados de su actividad catalítica en la activación del agua por vía fotoquímica.

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

MODULACIÓN DE LA FLUORESCENCIA EN ESTADO SÓLIDO EN 7-ARIL-4-FENIL-1,8-NAFTIRIDINAS

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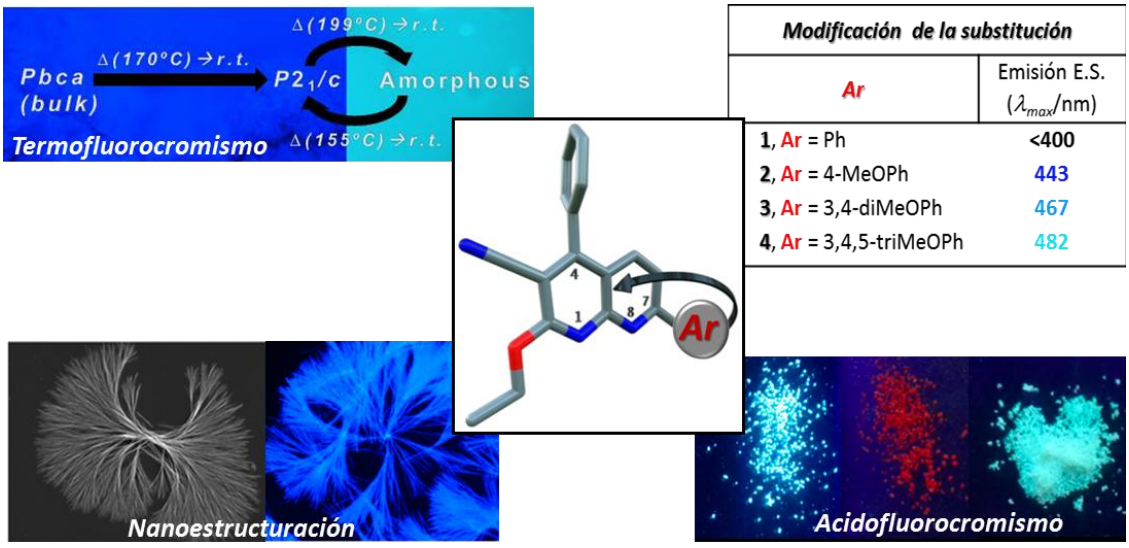
Palabras Clave: *fluoróforos, 1,8-naftiridinas, sólidos orgánicos, nanoestructuración.*

Debido a su inmensa aplicabilidad en el campo de la optoelectrónica, el diseño y síntesis de fluoróforos orgánicos cuya emisión sea fácilmente modulable se ha convertido en una meta muy deseable.[1] En particular, resulta especialmente atractivo el diseño de materiales cuya fluorescencia sea capaz de responder a estímulos externos (luz, calor, presión, etc.), debido a su potencial implementación en dispositivos tales como OLEDS, OLEFTs, sensores, láseres orgánicos, etc.[2]

En este contexto, en la presente comunicación se mostrará cómo la fluorescencia en estado sólido de derivados de 7-aril-4-fenil-1,8-naftiridina puede ser modulada de una forma versátil. Por un lado, la modificación de λ_{max} de emisión puede ser ajustada variando la naturaleza del sustituyente aromático en posición 7 del heterociclo. Por otra parte, los materiales resultantes muestran una emisión modulable dependiente de factores tales como la temperatura, exposición a vapores ácidos o básicos, grado de cristalinidad, nanoestructuración, etc.[3]



Modificación de la substitución	
Ar	Emisión E.S. (λ_{max}/nm)
1, Ar = Ph	<400
2, Ar = 4-MeOPh	443
3, Ar = 3,4-diMeOPh	467
4, Ar = 3,4,5-triMeOPh	482

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

PHOTOCATALYTIC AND COOL PIGMENTS FOR SUSTAINABILITY

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Keywords: *ceramic pigment, cool pigment, photocatalyst, NIR reflectance.*

Cool pigments are pigments which show high reflectivity in the NIR range (780-2100 nm) allowing air-conditioning energy saving by reducing the temperature of the buildings. Rutile (TiO_2) is well known as white pigment with a high NIR solar reflectance of about 87.0% used for roofing and wall materials. However, the owners of homes with pitched roofs visible from ground level often prefer non-white roofing products for aesthetic reasons (1). It can be used non-white pigments but the color introduces certain additional absorption in the visible range which should be compensated by an increase in the NIR reflectivity. Some cool inorganic pigments have been presented in the literature such as green pigments based on eskolaite Cr_2O_3 (NIR reflectance 50-57%) (2), brown pigments based on composites of hematite with other high NIR reflectivity oxides such as Sb_2O_3, SiO_2, Al_2O_3 and TiO_2 (NIR reflectance 46.7%) (3) or yellow cool pigments for cement, based on Si^{4+} doped yttrium molibdate (Y_6MoO_{12}) or Mo(VI) doped yttrium cerate ($Y_2Ce_2O_7$) (4). On the other hand the combined effect of the moisture and the solar rays produce the development of colonies of fungi and bacteria that dirty the building surfaces and reduces its reflectivity. The photocalytic capacity of pigments in ceramic matrix avoids the colonies development on the surfaces and preserves the color quality and the high NIR reflectivity of the surfaces (5). In this communication two traditional CMY families of ceramic pigments based on zircon $ZrSiO_4$ (vanadium blue turkish, iron pink koral and yellow of praseodymium) and on rutile TiO_2 (blue of V-W doped rutile, yellow of Ni-Sb doped rutile and pink of Cr-Sb doped rutile), and a new CMY family based on ilmenite $MgTiO_3$ structure (blue of cobalt-ilmenite, pink of iron-ilmenite and yellow of nickel-ilmenite), have been studied as photocatalyst (using Orange II test) and cool pigments (total NIR reflectivity by UV-Vis-NIR diffuse reflectance). The best photocalyst and cool pigments, enameled in conventional ZnO-SiO_2-CaO glazes, are the CMY palette based on blue of cobalt-ilmenite, pink of iron-ilmenite or iron-zircon and yellow of Ni-rutile or Pr-zircon respectively.

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

SÍNTESIS DE COMPLEJOS PENTAFLUOROFENIL-CICLOPLATINADOS. PROPIEDADES ÓPTICAS Y EVALUACIÓN DE SU ACTIVIDAD BIOLÓGICA

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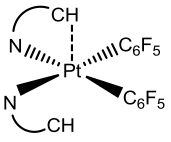
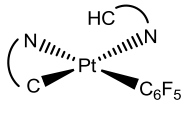
Palabras Clave: *Ciclometalados, platino, luminiscencia, citotoxicidad, biomarcadores*

En los últimos años los complejos ciclometalados de Pt(II) han atraído un notable interés debido a sus interesantes propiedades luminiscentes, con potenciales aplicaciones en la preparación de diodos emisores de luz, sensores químicos, fotocatálisis y en dispositivos para la conversión de energía solar[1]. Un campo fascinante de aplicación para estas especies en biología combina su uso como marcadores en luminiscencia celular y bioimágenes[2] con su posible citotoxicidad[3], lo que potencia su interés en el diseño racional de drogas anticancerígenas.

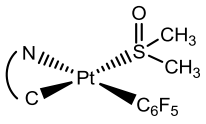
En esta comunicación presentamos la preparación de nuevos derivados neutros cicloplatinados [Pt(C^N-*k*CN)(HC^N-*k*CN)C_6F_5] (**2a-c**), obtenidos por activación C-H de los derivados [Pt$(C_6F_5)_2$(HC^N-*k*N)$_2$] (**1a-c**) y los correspondientes solvatos [Pt(C^N)(C_6F_5)(DMSO)] (**3a, 3b**). Todos los derivados son intensamente fotoluminiscentes y las emisiones se han asignado con el apoyo de cálculos teóricos (DFT y TD-DFT). Se ha investigado la citotoxicidad *in vitro* de los derivados [Pt(C^N)(C_6F_5)(DMSO)] (**3a**, **3b**, **4**) en dos líneas celulares de pulmón humano diferentes, una tumoral (A-549) y otra no tumoral (NL20), revelando buena actividad citotóxica. Además, la microscopía de fluorescencia ha mostrado su localización en el citoplasma perinuclear, aunque con sutiles diferencias entre los compuestos estudiados y entre las líneas celulares.



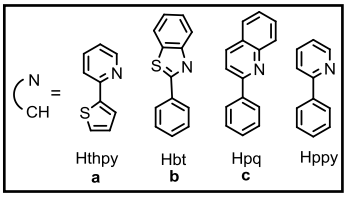
HC^N= Hthpy **1a**, Hbt **1b**, Hpq **1c**

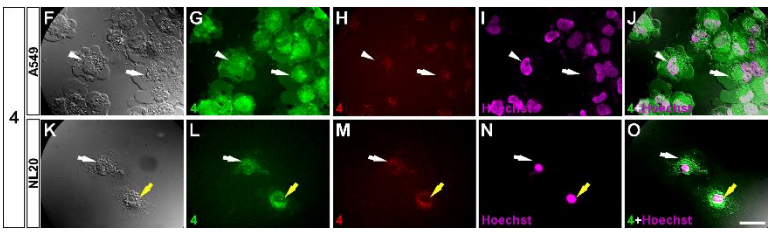


C^N= thpy **2a**, bt **2b**, pq **2c**



C^N= thpy **3a**, bt **3b**, ppy **4**





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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

NOVEL ACTIVATED GLYCODENDRIMER-BASED PHOTOSENSITIZERS DEVELOPED FOR PHOTODYNAMIC THERAPY

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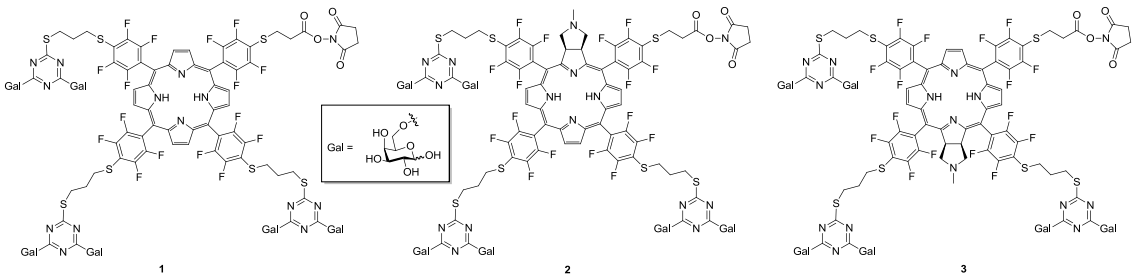
Keywords: *photosensitizers, photodynamic therapy, glycodendrimers, synthesis.*

Due to the inherent hydrophobic characteristics of most of the photosensitizers (PSs) and the formation of aggregates in aqueous or physiological medium, cores can be chemically modified with different motifs such as carbohydrates, biopolymers, amino acids or others to increase the biocompatibility, selectivity and solubility in photodynamic therapy (PDT) [1,2]. In this sense, photosensitizer-containing glycodendrimers are promising structures with excellent properties, being therefore improved by coupling of a specific antibody (photoimmunotherapy) [3,4]. Hence, we show the syntheses and characterization of asymmetric water-soluble porphyrin and chlorins (**1**-**3**) decorated with six D-galactopyranose units and NHS-ester on one-arm in high yields from the versatile building block, 5,10,15,20-tetrakis(2,3,4,5,6-pentafluorophenyl)-porphyrin (**$TPPF_{20}$**). Preliminary photophysical and photochemical studies suggest that these PSs may be excellent photodynamic therapeutic agents.



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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

OPTIMIZING THE LUMINESCENCE OF BIS-CYCLOMETALATED Pt(IV) COMPLEXES

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Keywords: *platinum, cyclometalating ligands, luminescence*

The excited-state properties of Pt(IV) complexes with heteroaromatic ligands remain largely unexplored, which contrasts with the extensive studies carried out on complexes of other d^6 ions, such as Re(I), Ru(II), Os(II) or Ir(III), or d^8 ions, such as Pt(II) or Au(III). Recently, we have reported a series of tris-cyclometalated Pt(IV) complexes of the type *fac*-$[Pt(C^N)_3]^+$, where C^N is *C*-deprotonated 2-(2-phenyl)pyridine (ppy) or related ligands, which exhibit efficient emissions from essentially ligand-centered (LC or π-π^*) triplet excited states, characterized by lifetimes of hundreds of microseconds and quantum yields up to 0.49 in fluid solution at room temperature.[1] Combined with their highly oxidizing character in the excited state, these characteristics make them very promising as photocatalysts.

Previous luminescence studies on bis-cyclometalated Pt(IV) complexes are limited to neutral complexes of the type $[Pt(C^N)_2(R)Cl]$ (R = CH_2Cl, $CHCl_2$), with quantum yields in the range 0.05-0.15 at room temperature,[2] and dicationic complexes of the type $[Pt(C^N)_2(N^N)]^{2+}$ (N^N = aromatic diimine), with quantum yields in the range 0.0005-0.035.[3] In this communication, we present a fundamental study on the luminescence of bis-cyclometalated Pt(IV) complexes of the types $[Pt(ppy)_2X_2]$ (X = halide, acetate, triflate), $[Pt(ppy)_2(E^E)]$ (E^E = catecholate, 1,2-benzenedithiolate), or $[Pt(ppy)_2(acac)]^+$. These complexes exhibit emissions from ^{3}LC states located on the ppy ligands. The ancillary ligands have little effect on the emission energy, but they strongly affect the quantum yield, which reaches a maximum in the fluorocomplex $[Pt(ppy)_2F_2]$ (Φ = 0.40 in CH_2Cl_2 solution at 298 K). The factors that determine the luminescence of these derivatives, including the extent of metal-orbital involvement in the excited state and the influence of deactivating excited states, have been analyzed with the aid of computational calculations.

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

ESTUDIO FOTOFÍSICO DE SONDAS FLUORESCENTES SOLVATOCRÓMICAS

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Palabras Clave: *Fluorescencia, sondas fluorescentes, transferencia de carga, dapoxyl.*

Las sondas fluorescentes han adquirido en años recientes una importancia creciente en muchos campos, especialmente en biología molecular, química analítica y química física. Entre los distintos tipos de sondas desarrollados, destacan por su gran versatilidad las sondas fluorescentes solvatocrómicas, que muestran una gran sensibilidad al medio y son capaces de detectar interacciones biomoleculares [1].

El conocimiento fotofísico de las sondas solvatocrómicas es un paso clave para entender su modo de acción, interpretar mejor la información que proporcionan y mejorar su diseño. En este trabajo nos hemos centrado en el estudio fotofísico de una sonda muy utilizada, el Dapoxyl® (véase la Figura 1) [2,3]. Hemos investigado el espectro de fluorescencia de esta especie en distintos disolventes, su tiempo de vida de fluorescencia y la polarización de su banda de emisión, con objeto de obtener información de los cambios estructurales que determinan la gran variación de su espectro de emisión en función de la naturaleza del medio. Hemos podido demostrar que esta especie sufre un proceso de transferencia de carga y cambios conformacionales en el estado excitado que determinan la alta sensibilidad al medio de su fluorescencia.

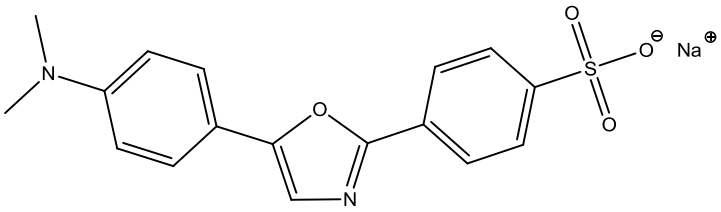

Figura 1. Estructura molecular del Dapoxyl®

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SÍNTESIS DE CARBON DOTS A PARTIR DE FORMALDEHIDO Y SU APLICACIÓN COMO MARCADOR CELULAR *IN VIVO*

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Palabras Clave: *Carbon Dots, Luminiscencia, marcador celular in vivo*

La familia de materiales denominados Carbon Dots (CD) han generado un gran interés debido a su solubilidad en agua, inercia química, baja toxicidad, facilidad de funcionalización, y resistencia a la foto-bleaching. CDs se componen generalmente de nanopartículas de carbono grafítico sp^2 y carbonilo superficiales. Debido a su bajo costo, baja toxicidad, biocompatibilidad y fotoluminiscencia razonable, CDs ofrecen una alternativa para reemplazar los tradicionales nanopartículas semiconductoras o Quantum Dots.

En este trabajo mostramos la síntesis de CDs a partir de formaldehido y su aplicación como marcadores celulares [1] en células de pre-osteoblasto de ratón. Las nanopartículas fueron localizadas selectivamente en el citoplasma sin funcionalización adicional y puede incorporarse por fagocitosis celular, de manera que la fluorescencia de los CD puede ser utilizada para visualizar células vivas in vitro.

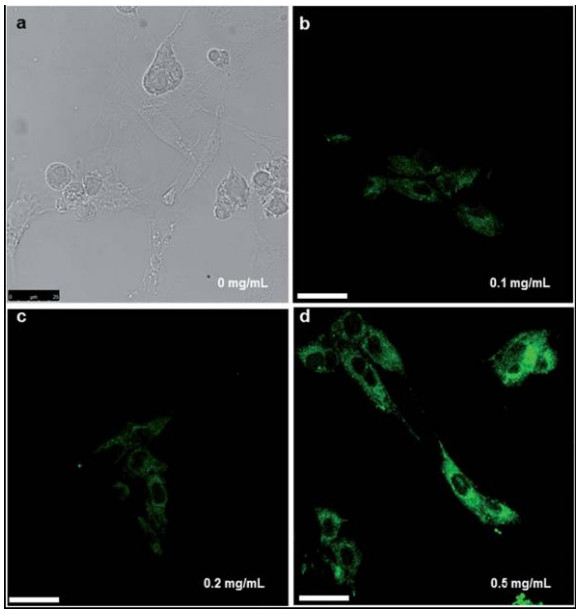

Imagen confocal de proteoblasto de ratón tratados con diferentes concentraciones de CD tras 24 horas de tratamiento. (a) Control; (b–d) Luminiscencia a diferentes concentraciones de CD.

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S1: *Sistemas Luminiscentes: Caracterización y aplicaciones*

NHC GOLD COMPLEXES WITH LUMINESCENT PROPERTIES

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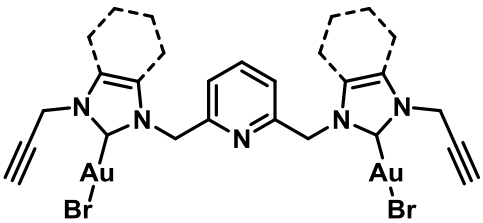
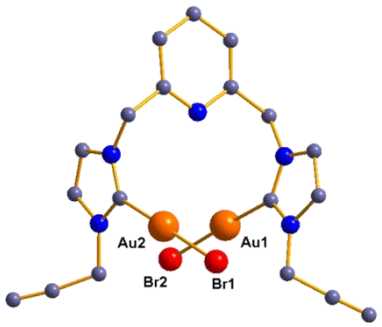
Keywords: *Gold, NHC, Allenyl, Imidazolium, Luminescence*

Allenyl-gold complexes derived from propargyl functionalised phosphonium salts are a novel class of organometallic compounds which were recently found to be stable and isolable, displaying an interesting regioselectivity[1]. N-heterocyclic carbene (NHC) complexes of gold are well-known and of great importance in organic and organometallic chemistry. They have attracted a lot of attention due to their diverse catalytic, biological, medicinal and optical properties[2-4]. Incorporation of the propargyl fragment into imidazolium salts allows the formation of a series of NHC precursors which also have the capability to form allenyl complexes. The introduction of an additional donor site, such as a pyridine, into the scaffold can provide stability to the complex through chelation but can also allow coordination of an additional metal ion, and thus the formation of polynuclear complexes with enhanced optical properties.

A series of NHC gold complexes have been prepared from propargyl functionalised imidazolium salts.





Further studies on the reactivity of the complexes in both the central carbene functionality and the propargyl side arms together with the emissive properties of the complexes have been carried out.

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

COMPUESTOS DE OSMIO CICLOMETALADOS CON PROPIEDADES LUMINISCENTES

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Palabras Clave: *osmio, luminiscencia*

El derivado hexahidruro $OsH_6(P^iPr_3)_2$ promueve la ruptura de enlaces C-H de moléculas orgánicas diversas.[1] La estrategia de asistencia por quelatación es crucial en estas reacciones, debido al elevado número de hidruros presentes en este compuesto. De entre los auxiliares de coordinación usados, el átomo de nitrógeno de heterociclos ha sido particularmente útil, y ha permitido la activación de enlaces C-H, no sólo aromáticos y olefínicos,[2] sino también la de enlaces $C(sp^3)$–H.[3]

Recientemente, partiendo de este derivado hexahidruro, hemos preparado nuevos compuestos homolépticos $Os(C_{NHC}C_{arilo}C_{NHC})_2$ y heterolépticos $Os(C_{NHC}C_{arilo}C_{NHC})(C_{NHC}C_{arilo'}C_{NHC})$ y $Os(C_{NHC'}C_{arilo}C_{NHC'})(C_{NHC}C_{arilo'}C_{NHC})$ que son fotoluminiscentes y emiten en el verde/azul con rendimientos cuánticos elevados.[4]

Siguiendo con esta línea de investigación, en este trabajo presentamos la síntesis de nuevos compuestos de osmio ciclometalados y el estudio de sus propiedades luminiscentes.

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S1: Sistemas Luminiscentes: Caracterización y aplicaciones

NOVEL FLUORESCENT POLYAZAMACROCYCLIC BIBRACHIAL RECEPTORS IN ORDER TO TARGET DNA AND RNA

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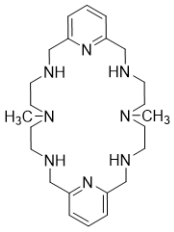
Keywords: *macrocyclic polyamines, binding affinity, intercalative binding, pH-dependence.*

In the last few years the field of DNA detection using new sensitive and selective species has increased remarkably and macrocyclic polyamines play an important role due to their modulation capability in order to selectively bind different guest species, from simple inorganic anions to biological molecules [1].

Therefore, a family of fluorescent bibrachial lariat aza-crown ethers have been synthesized. The ligands were prepared following an optimized synthetic route which consists in a dipodal (2+2) condensation between an α,ω-diamines as a precursor and an aldehyde[2]. The ligands L1, L2 and L3 are constituted by a common azamacrocyclic core appended with different arms. The fluorophoric units incorporated in the pendant arms permit to follow the association with guest species.

This project is focused in the study of the binding affinity between the ligands and polynucleotides. Ethidium bromide displacement assays and circular dichroism consistently support intercalative binding of L2 and L3 within base pairs, whereas L displays electrostatic interactions along the double helix. Moreover, the equilibrium constant values point toward an important impact of the number of positive charges in L1, L2 and L3 on the extent of interaction with DNA/RNA. However, the absence of pH-dependence in the CD experiments reveals that the protonation state of compounds has no significant influence on the structural features of the binding mode.



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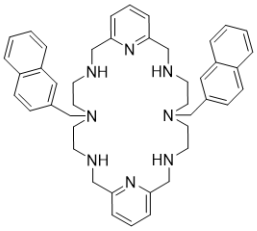

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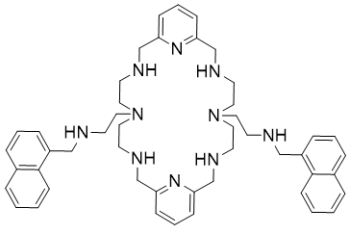

L3

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

ESTUDIO FOTOFÍSICO DE LA DESACTIVACIÓN DE LA FLUORESCENCIA DE NAFTALENO CON DERIVADOS HETEROMETÁLICOS DE Au^{I} Y Hg^{II}

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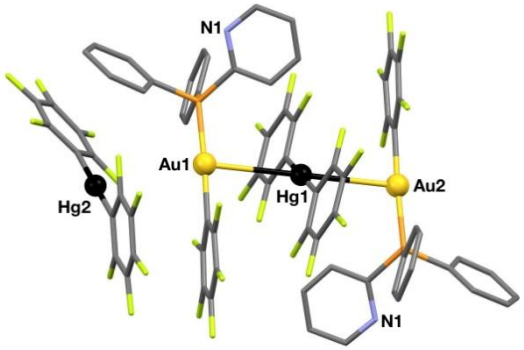
Palabras Clave: *Fluorescencia*, *Desactivación, Interacciones Metal-Metal*

Durante los últimos años un área de interés para nuestro grupo de investigación ha sido la preparación y estudio de compuestos heteronucleares de oro y mercurio. Así, se han sintetizado compuestos del tipo $\{[Hg(C_6X_5)_2](AuC_6X_5(PMe_3)_2\}$, en los que se dan interacciones metalofílicas $Au^{I}\cdots Hg^{II}$ y $Au^{I}\cdots Au^{I}$ no soportadas por ligandos. Una característica interesante de este tipo de derivados es que son capaces de atenuar en disolución la intensidad de emisión de moléculas orgánicas fluorescentes como el naftaleno, permitiendo así, el cálculo de diferentes parámetros termodinámicos.[1,2]

Por otro lado, y relacionado con la capacidad de desactivación fluorescente de emisores orgánicos, existen en la bibliografía varios ejemplos en los que moléculas nitrogenadas del tipo piridina también son capaces de actuar como desactivadores.

Así, en esta comunicación se describe la síntesis de derivados heterometálicos de oro y mercurio con el ligando difenilfosfinopiridina, en el que los grupos fosfina se coordinan a los centros de oro, mientras que el anillo de tipo piridínico aparece sin coordinar a ningún centro metálico. Además, también se describe un detallado estudio fotofísico en el que se analiza una posible competencia entre una desactivación por formación de complejos en el estado fundamental entre el fluoróforo y el metal y una desactivación en la que el responsable sea el resto nitrogenado.

Por último, para completar el estudio se han realizado cálculos teóricos DFT con el fin de confirmar y explicar observaciones experimentales.



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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

STUDYING METAL BINDING TO PHENANTHROLINE FLUORESCENCE SENSORS TO EVIDENCE AGGREGATES INVOLVED IN PROTEIN MISFOLDING DISEASES

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Keywords: *phenanthroline derivatives, fluorescence sensors, protein binding, metal association*

Some important pathologies, including type II diabetes, transmissible spongiform encephalopathies and Alzheimer´s and Parkinson´s diseases are associated to the formation of insoluble amyloid fibers. Several factors [1] (pH, metal ions and protein concentration) can contribute to shift the conformational transition from the native soluble structures exhibiting unfolded or partially α-helical conformation to insoluble amyloid aggregates, with a high β-sheet content. Search of new NIR fluorescence sensors for β-Ayloid plaques is a subject of interest [2].

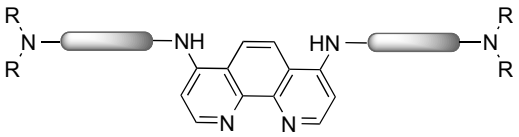

Figure 1: Chemical structure of the compounds studied

We describe here the synthesis and spectral study of a small library of phenanthroline derivatives designed as amyloid ligands with chelating properties, which were studied both as free bases and as hydrochloride salts (Figure 1). The fluorescence emission of the salts is notably shifted to the red region as a consequence of the protonation of the basic nitrogen. The fluorescence emission is also dependant on the polarity of the solvent. A batochromic (red) shift is observed in the fluorescence emission in water or organic polar protic solvents (alcohols) with regard to low-polarity organic solvents (dioxane). These changes are very useful to detect the transfer of the sensor from the aqueous phase to the hydrophobic environment of proteins, depending on their conformations. It has been established that amyloidgenic plaque formation is favoured as a consequence of the coordination of several cations Cu(II), Zn (II) by histidine residues in peptides *via* the stabilization of intermediate species key to the aggregation of amyloidogenic peptides. For this reason, we have explored the role of several cations in the interaction with proteins. The titration of our phenanthroline derivatives with cations causes significant changes in the emission spectra, as a consequence of ion chelation by the fluorescence sensor. Further studies on the exploitation of this selective chelating behaviour with therapeutic purposes are in progress.

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

DOSÍMETRO QUÍMICO PARA LA DETECCIÓN DE FORMALDEHÍDO

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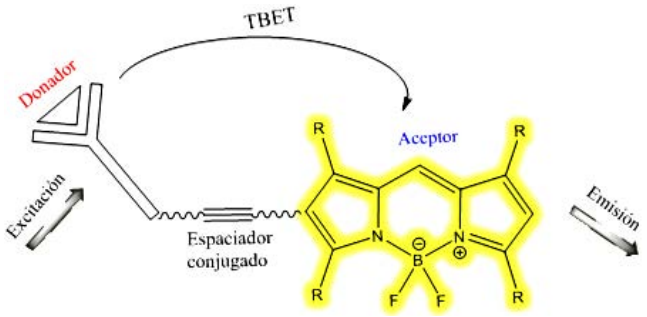
Palabras Clave: *Dosímetro, colorimétrico, fluorimétrico, formaldehído, BODIPY*

El formaldehído es uno de los compuestos orgánicos más importantes de la industria química. Se encuentra principalmente junto con urea, melamina o fenol, formando resinas destinadas a la industria del mueble y la madera. Diversas agencias dedicadas al estudio del cáncer como la IARC catalogan cada vez más al formaldehido como un producto carcinógeno e irritante. Los actuales sistemas de detección para este compuesto tienen como principal inconveniente la existencia de interferentes y la falta de sensibilidad, lo que los convierte en poco fiables, ésto genera la necesidad de disponer de sistemas capaces de detectar la presencia de formaldehído de forma rápida y fiable.

El presente trabajo hace uso de la reacción de Pictet-Spengler para diseñar un dosímetro basado en dopamina. Se sabe que la dopamina reacciona de forma rápida y selectiva con formaldehído, dando lugar a cambios en sus propiedades colorimétricas y fluorimétricas. Tras obtener unos límites de detección aceptables tanto en disolución como en fase gas, se decidió explorar la posibilidad de mejorar los resultados obtenidos utilizando los denominados “cassettes” y/o compuestos antena, combinando el dosímetro anterior con un núcleo de BODIPY. Ésta estrategia permitiría al fragmento de dopamina (donador) detectar el formaldehído y generar una señal que sería transmitida mediante una transferencia de energía a traves de enlace (TBET) hasta el nucleo de BODIPY (aceptor), que sería responsable de exhibir el cambio colorimétrico y/o fluorimétrico.



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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

SÍNTESIS DE ANTENAS LUMINISCENTES BASADAS EN HETEROCICLOS NITROGENADOS

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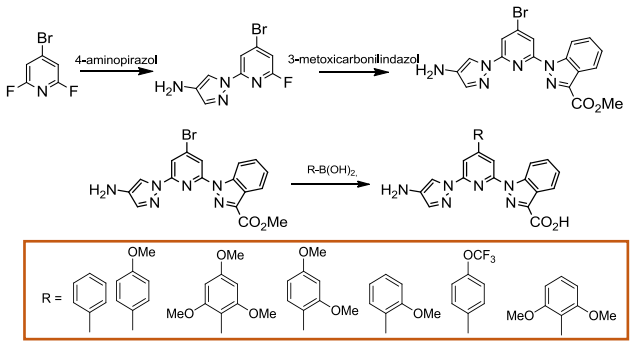
Palabras Clave: *Poliheterociclos, Luminiscencia, Lantánidos.*

Los ligandos poliheterocíclicos se han demostrado eficientes sensibilizadores de la luminiscencia de iones lantánidos [1].

Nuestro grupo de investigación trabaja con este tipo de ligandos, utilizándolos para el marcaje de oligonucleótidos en estudios de hibridación. Más concretamente, aplicándolos como método de diagnóstico rápido y selectivo de bacterias responsables de sepsis [2].

En esta comunicación se describe un nuevo método de síntesis de ligandos poliheteroaromáticos no descrito hasta la fecha. Más específicamente, para la síntesis de piridinas trisustituidas, por anillos de pirazol e indazol en las posiciones 2 y 6, donde el sustituyente en la posición 4 es introducido mediante una reacción de acoplamiento vía paladio [3].

Paralelamente se estudiaron las propiedades fotofísicas de los ligandos preparados, con diferente demanda electrónica sobre el sustituyente en posición 4, mediante la formación de complejos ternarios de Eu y Tb con éteres corona.



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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

COMPLEJOS FLUORESCENTES CON UNA IMINA-AMINA DERIVADA DE PERILENO

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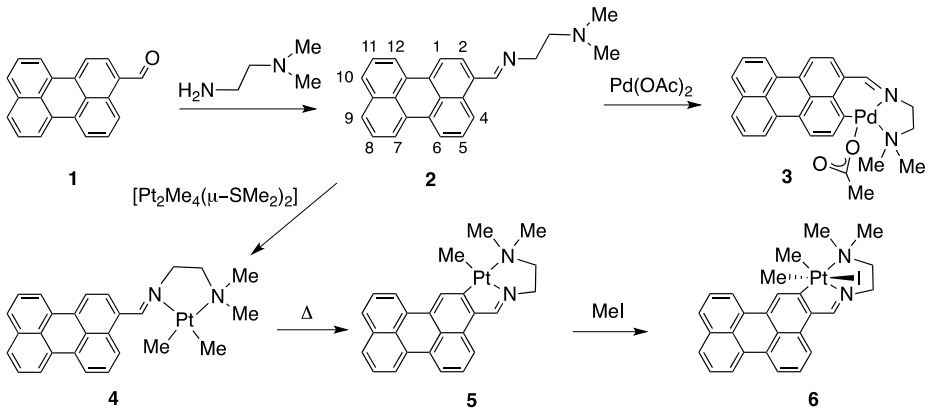
Palabras Clave: *Perileno, imina, paladio, platino, fluorescencia*

Las propiedades ópticas y electrónicas de los derivados de perileno hacen de ellos unos materiales de gran interés por sus variadas aplicaciones. La síntesis de diferentes derivados de perileno con grupos funcionales permite su coordinación a diversos metales y conocer los efectos en las propiedades fotofísicas producidos por la densidad electrónica de los grupos funcionales y de los centros metálicos con ligandos auxiliares adecuados [1]. Aquí presentamos derivados de perileno funcionalizados con un grupo imina-amina que actúa de conector a grupos ML_n.



La diferente posición de metalación de Pd y Pt ha sido confirmada por difracción de rayos X de los complejos **3** y **5**. Los complejos presentan en Vis-UV un desplazamiento hacia el rojo de las longitudes de onda de los máximos de absorción y emisión del ligando, y muestran la fluorescencia característica del perileno con rendimientos cuánticos en disolución ($0.03 < \Phi_{fl} < 0.34$) que dependen de la posición del metal, de su naturaleza y de su estado de oxidación.

Agradecimientos: Este trabajo ha sido realizado con el apoyo económico del Ministerio de Economía y Competitividad (Proyecto CTQ2014-52796-P) y de la Junta de Castilla y León (Proyecto VA302U13).

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S1**:** *Sistemas Luminiscentes: Caracterización y Aplicaciones*

Na^+ ION CONCENTRATION EFFECT ON THE STABILITY OF *p*-SULFONATOCALIX[6]ARENE COMPLEXES

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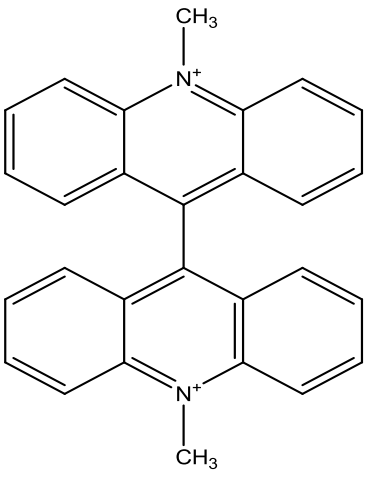
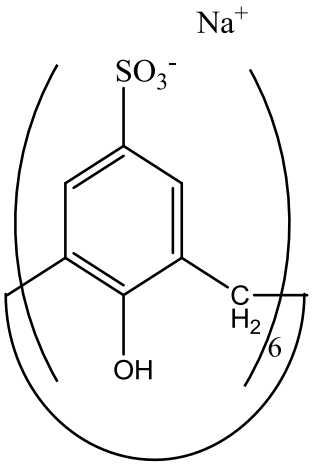
Keywords: Calixarene,Lucigenin

Host-guest complexes of calixarenes posses high importance in sensor development studies and many members of p-sulfonatocalix[n]arenes have been studied widely but the properties of p-sulfonatocalix[6]arene has not explored fully.

In present study we explored the behaviour of p-sulfonatocalix[6]arene towards a fluorescence probe Lucigenin. Experimental titrations have been carried out by fluorescente, ITC and NMR showing the formation of 1:1 and 1:2 host:guest complexes. These stoichimetries were determined by Job´s Method. Binding constant for the 1:1 complex being almost 10^2 times higher than for the 1:2. The influence of sodium concentration as a competitive guest have been studied allowing a model where two sodium cations can be bounded by the calixarene.



Lucigenin



p-sulfonatocalix[6]arene

S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

MESOMORFISMO COLUMNAR Y PROPIEDADES FLUORESCENTES DE COMPUESTOS CON FORMA DE ESTRELLA

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Palabras Clave: *mesógenos fluorescentes, solvatofluorocromismo.*

La auto-organización molecular es de gran interés debido al orden estructural impartido. En este contexto, mesógenos con mesofases columnares presentan un orden bidimensional que produce canales de flujo unidimensionales,[1] estos materiales son muy atractivos para ser utilizados en la fabricación de dispositivos optoelectrónicos como OLEDs, OFETs y celdas orgánicas fotovoltaicas.[2] En general los mesógenos carecen de fluorescencia considerable, sin embargo, la incorporación apropiada de grupos fluoróforos en la estructura molecular a conducido a mesógenos con alta fluorescencia.[3] El presente trabajo muestra el estudio de las propiedades fluorescentes de diez compuestos con forma de estrella sintetizados (figura 1).

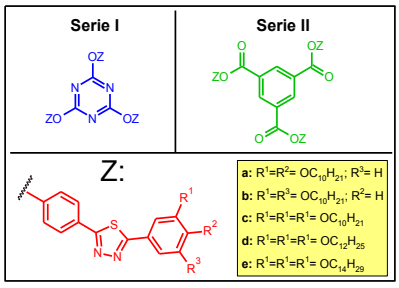

Figura 1. Estructuras compuestos.

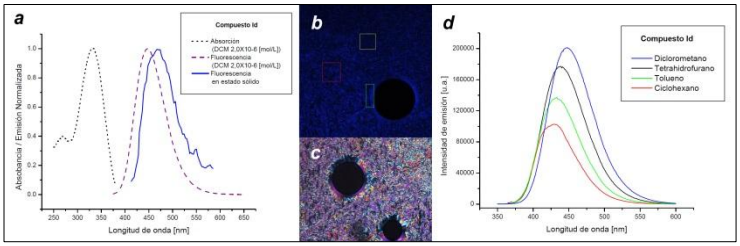

Figura 2. Espectros de absorción/emisión (a), microfotografía de fluorescencia (b), microfotografía POM (c) y solvatofluorocromismo (d) de **Id**.

Los compuestos $\mathbf{I_b}$, $\mathbf{I_c}$, $\mathbf{I_d}$, $\mathbf{II_c}$ y $\mathbf{II_d}$ presentan mesofases columnares hexagonales en amplios rangos de temperatura. La fluorescencia de los compuestos sintetizados es modulada por el tipo de núcleo trifuncional, el número, posición y largo de las cadenas alcoxídicas y por la polaridad del entorno (solvatofluorocromismo), presentando rendimientos cuánticos entre bajos y moderados (0,01 y 0,36). La fluorescencia en estado sólido mostró un desplazamiento batocrómico de los máximos de emisión y atenuación de la intensidad de emisión mediante *quenching*. Los tiempos de vida media de fluorescencia variaron entre 1.093 [ns] y 2.152 [ns].

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

COMPLEJOS DE Au(I) Y Au(III) CON TERPIRIDINA: PROPIEDADES FOTOFÍSICAS Y REDOX

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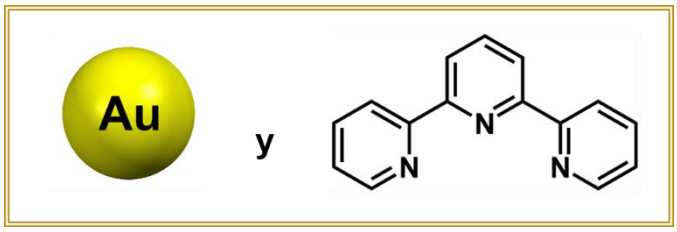
Palabras Clave: *terpiridina, oro*

Los ligandos aromáticos N-dadores han sido ampliamente empleados en la química de coordinación, debido a su versatilidad coordinativa y la estabilidad que proporcionan a los compuestos que forman, pero también porque en muchas ocasiones promueven a estos compuestos interesantes propiedades fotofísicas y electroquímicas.[1,2]

Entre ellos, el ligando 2,2':6',2''-terpiridina contituye una molécula muy versátil y de gran interés. En los últimos años se han publicado compuestos en los que este ligando se coordina a gran variedad de metales.[3] Desde el punto de vista estructural el ligando terpiridina suele actuar como tridentado, pero también se conocen algunos ejemplos en los que se comporta como mono- y bidentado. Por otra parte, se han llevado a cabo numerosos estudios fotofísicos y electroquímicos de complejos de metales de transición coordinados a este ligando, en cambio no hay muchos ejemplos de este tipo de estudios en complejos oro-terpiridina.

Así, en esta comunicación se presenta la síntesis, caracterización espectroscópica y las propiedades fotofísicas y electroquímicas de compuestos organometálicos de oro en estados de oxidación +1 y +3 coordinados al ligando 2,2´:6´,2´´-terpiridina. También se ha analizado su comportamiento, tanto en disolución como en estado sólido, y su inteconversión química y electroquímica.



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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

FOTOÁCIDOS FLUORESCENTES COMO SENSORES DE LA TRANSFERENCIA PROTÓNICA AL DISOLVENTE: ESTUDIO DINÁMICO DE LA FOTODISOCIACIÓN DEL 2-(3'-HIDROXI-2'-PIRIDIL)BENCIMIDAZOLIO

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Palabras Clave: *Fotoácidos, transferencia protónica, fluorescencia, fotodisociación*

La absorción de luz provoca en las especies fotoácidas un incremento súbito de su acidez, que conduce a su disociación si existe una base en el medio capaz de captar el protón y que facilita el estudio dinámico del proceso a través de técnicas de fluorescencia con resolución temporal. Cuando el disolvente actúa como base, los fotoácidos facilitan el estudio de procesos muy rápidos de transferencia protónica al disolvente.

Nuestros estudios anteriores sobre fotoácidos fuertes o muy fuertes demostraron que la transferencia protónica al disolvente tiene como primer paso un proceso reversible en el que se forma un par de encuentro entre el fotoácido disociado y la base protonada, estando este proceso controlado por la solvatación para los fotoácidos más fuertes [1,2,3]. El par de encuentro se separa para dar los productos en un proceso controlado por difusión para los fotoácidos más fuertes, siendo algo más lento para ácidos de fortaleza media.

En este trabajo mostramos los resultados sobre la transferencia protónica al disolvente del fotoácido 2-(3'-hidroxi-2'-piridil)bencimidazolio en metanol y agua, obtenidos por medio de espectroscopia de fluorescencia resuelta en el tiempo. Esta especie tiene la particularidad de poseer un N piridínico cuya basicidad aumenta en el estado excitado [4]. Así, tras la fotodisociación del grupo hidroxilo en el estado excitado, el protón puede revertir a su posición original o protonar el N piridínico, la posición más básica en el estado excitado. El estudio de este proceso proporciona por tanto información relevante para conocer los detalles moleculares del proceso de recombinación entre el protón y la base conjugada, un aspecto profusamente discutido en la bibliografía [5]. Los resultados obtenidos indican que la recombinación se produce únicamente sobre el O, lo que parece indicar que el par de encuentro es un intermedio unido por enlace de hidrógeno.

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

INFLUENCE OF THE LIGANDS AND MODIFICATION PROCEDURES ON THE LUMINESCENT FEATURES OF CdSe/ZnS QUANTUM DOTS

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Keywords: *CdSe/ZnS quantum dots, characterization, capillary electrophoresis, ligands*

The use of quantum dots for analytical purposes is nowadays one of the most challenges in the analytical chemistry area. The vast majority of analytical applications involve the use of several methodologies for surface modification of QDs for a particular application [1-4]. However, according to intended use, it is necessary to take in account that the modification of the QDs surface by different ligands and by using different modification procedures can be drastically changed the initial properties of colloidal QDs (total QDs size, quantum yield, bioavailability, chemical and photochemical stability, etc), affecting in many cases the quantum efficiency of the quantum dots. Therefore, in this communication, the optical properties of the modified QDs with different surface coating ligands, using different procedures and surrounding environments, were studied and the results were compared. In addition, capillary electrophoresis (CE) with diode array and fluorescence detection, as one of the most powerful separation techniques resulting in advantages of fast, simple, low sample consumption and high separation resolution, was used in order to provide valuable information about the distribution of sizes, as well as surface charge resulting from the modified QDs.

Acknowledgements: Financial support from the Spanish Ministry of Economy and Competitiveness (CTQ2013-48411-P), and JCCM (PEIC-2014-001-P) are gratefully acknowledged.

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

SÍNTESIS DE CRISTALES LÍQUIDOS CON ESTRUCTURAS 1,3-bis (α-CIANO-4-ALCOXIESTIRENIL)BENCENOS Y 1,3-bis (β-CIANO-4-ALCOXIESTIRENIL)BENCENOS. ESTUDIO DE LAS PROPIEDADES TÉRMICAS Y FOTOLUMINISCENTES.

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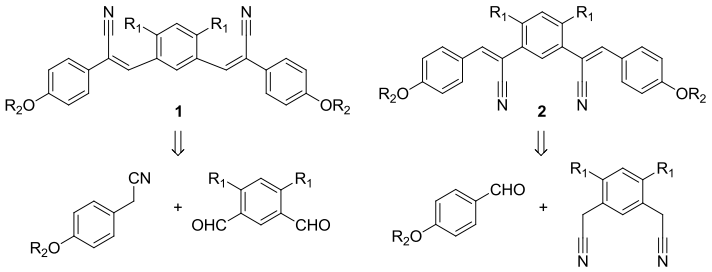
Palabras Clave: *síntesis, cristales líquidos, fluorescencia, 1,3-bis (a-ciano-4-alcoxiestirenil)bencenos, 1,3-bis (β-ciano-4-alcoxiestirenil)bencenos*

En las últimas décadas se han desarrollado oligómeros y polímeros que sufren cambios en sus propiedades ópticas (fluorescencia), provocados por estímulos químicos o físicos. Debido a esta característica estos compuestos pueden ser utilizados como sensores en diversos campos tecnológicos [1]. Dentro de los materiales mecanocrómicos, la familia de moléculas de estructura 1,4-bis (α-ciano-4-alcoxiestirenil)bencenos desarrollada por el profesor Weder constituye un éxito notable [2]. Recientemente diversos grupos han centrado su investigación en oligómeros y polímeros con estructura *m*-fenileno vinileno al presentar estos compuestos diferentes propiedades ópticas [3].

En nuestro trabajo se presenta la síntesis y el estudio de las propiedades ópticas y térmicas de las moléculas de estructuras 1,3-bis (α-ciano-4-alcoxiestirenil)bencenos y 1,3-bis (β-ciano-4-alcoxiestirenil)bencenos. La síntesis se realizará mediante una reacción de Knoevenagel entre el nitrilo y el aldehído adecuado.



Agradecimientos: Este trabajo ha sido financiado por el MEC y FEDER (MAT2013-42425-R).

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

FLUOROGENIC MATERIALS FOR THE DETECTION OF MERCURY SPECIES

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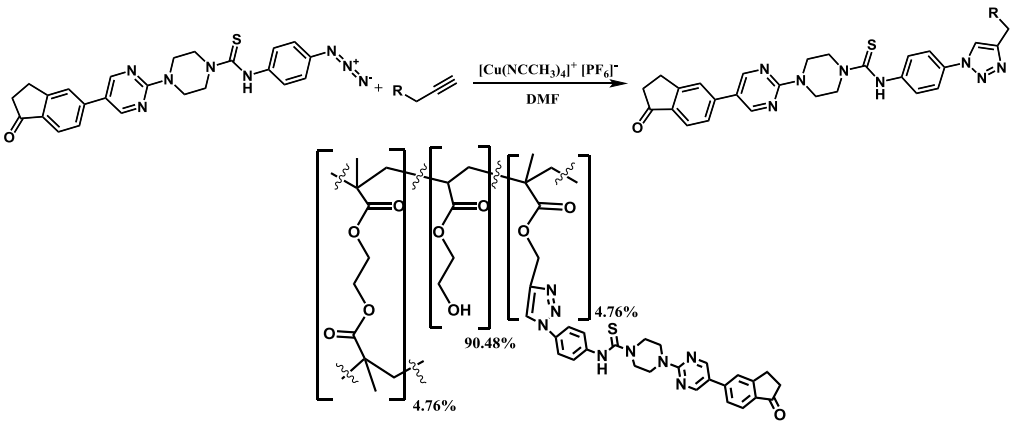
Keywords: *fluorogenic probes, mercury(II) species, polymers*.

Mercury (Hg) is a toxic element and one of de the most hazardous pollutants in the world that is emitted to the environment by the human action. Of the mercury(II) species which can be found in the environment, the most important is the methylmercury(II) cation, a lipophilic cation that tends to be accumulated in living organisms such as fish. By this way, mercury(II) is introduced in the food chain, creating a risk because its neurotoxicity and teratogenicity.

Some time ago we developed a chromogenic probe to detect mercury(II) and methylmercury(II) species. [1] Now we report new fluorogenic materials in which a fluorogenic probe was anchored, by means of a click reaction between an azide group and a terminal triple bond, to solid polymers with water affinity as well as to water soluble polymers. These new fluorogenic materials are able to detect neurotoxic mercury(II) compounds in water or biological environments, for example, by direct contact between the polymer layer and real fish samples.



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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

A NEW FLUOROGENIC PROBE FOR THE DETECTION OF BIOGENIC AMINES IN FOOD

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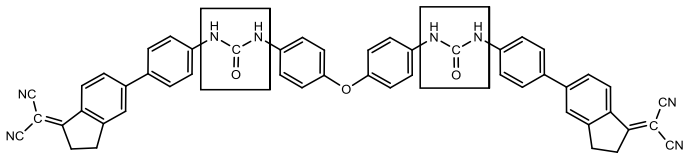
Keywords: *biogenic amines, fluorogenic probes*

Biogenic amines are part of a large group of compounds of great interest in food industry due to its influence on the product quality and its toxic effects. Thus, their presence is a matter of concern for food safety, so it is of the most importance to find a method that allows its quick, sensitive and accurate detection. Whereas the usual methods for the determination of biogenic amines in food are expensive, require specialized equipment and long analysis time, the implementation of new sensitive and rapid methods is necessary. Chemical sensors are a good solution to these problems, and among them, the fluorogenic probe [1] shown in the figure exhibits high selectivity and good response to this type of molecules, allowing a fast and effective analysis of their presence.



One of the advantages provided by the use of this probe is that it has the ability to interact with amines in the gaseous state, which makes this technique faster and easier than conventional techniques. It is also a highly sensitive method because it presents detection limits of 8 ppm, 5 ppm, 2 ppm and 1 ppm respectively for cadaverine, histamine, putrescine and pyrrolidine. While performing this work, it has been found a spectrophotometrically measurable response (Fluorescence) of the probe when biogenic amines from degradation of proteins are present in real samples of fish.

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

HETEROMETALLIC LUMINESCENT MACROCYCLES FOR MOLECULAR RECOGNISING PURPOSES

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Keywords: *supramolecular chemistry, macrocycle, fluorescence*

Macrocycles have been commonly used as receptors in supramolecular chemistry which can host inside specific molecules [1]. Regarding this, heterometallic water soluble M(II) (M = Pt, Pd) -Zn(II) macrocycles have been synthesized from polyamine ligands by self – assembly reactions. These ligands contain N-atoms at terminal position [2] (Figure 1). Their empty inner cavities and luminescent properties make them potential candidates to act as luminescent sensors. The synthesis is based on the firstly coordination of Zn(II) to the polyamine chain at the adequate determinate pH allowing the coordination of the terminal nitrogens to the square planar metal atom.

The observed enhancement of luminescent produced by zinc(II) coordination and the empty inner cavity open the way to design heterometallic fluorosensors for anions [3], whose recognition processes are based on the metal–ligand interaction and/or weak interactions.

Full geometry optimitzations of the macrocycles have been performed by theoretical calculations.

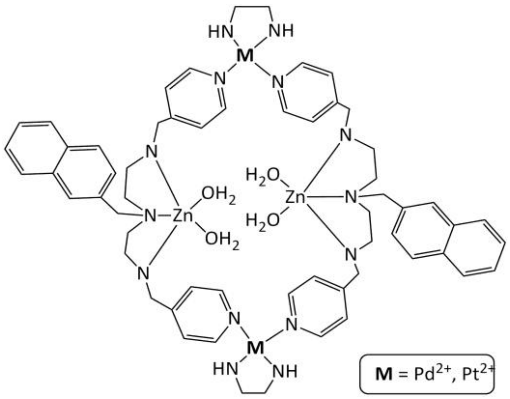

Figure 1: Heterometallic macrocycle formed from a nitrogenated polyamine ligand

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

MÉTODO FLUORESCENTE COMPETITIVO PARA LA DETECCIÓN DE GLIFOSATO (ROUNDUP)

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Palabras Clave: *sensor, poliamina, glifosato.*

Cada día hay una mayor conciencia medio ambiental y es necesario el diseño y síntesis de moléculas o sistemas capaces de reconocer y cuantificar sustancias de interés en un medio tan importante como es el agua. Concretamente este trabajo está centrado en el reconocimiento del herbicida glifosato (Figura 1A) por ser uno de los más usados a nivel mundial. Se ha empleado la poliamina tripodal *N-{2-[Bis(2-aminoetil)amina]etil}-5-(dimetilamino)naftalen-1-sulfonamida* (**TDS**) (figura 1B) [1] por su versatilidad en disolución acuosa ya que puede interaccionar tanto con metales como aniones.

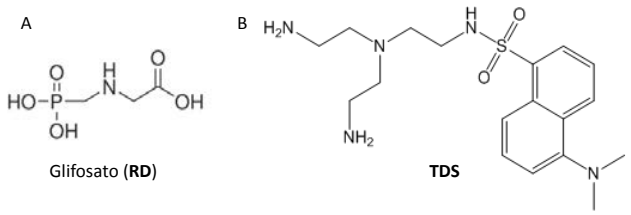
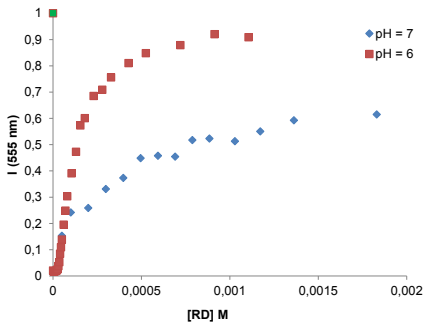


Figura 1. A) analito de interés.B) ligando poliamínico fluorescente.

De hecho, el sistema que funciona como sensor de desplazamiento es el complejo formado por el **TDS** con Cu(II) relación 1:1.

En la Figura 2 se muestra la variación de la intensidad del máximo fluorescencia a 555 nm cuando a una disolución que contiene solo **TDS** (punto verde) se le añade un equivalente de Cu(II) (intensidad cero) y a continuación cantidades crecientes de analito (**RD**).

Figura 2. Cambios en la emisión fluorescente del sistema TDS:Cu:RD a pH 6 y pH 7.



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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

PHOTOPHYSICS OF A SILICON-SUBSTITUTED XANTHENE DYE

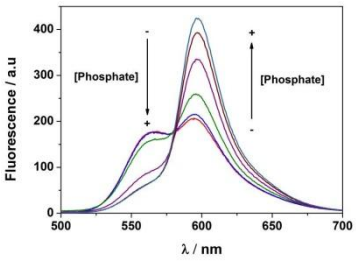
J. Valverde[1], S. Resa[2], L. Crovetto[1], D. Miguel[2], J. M. Paredes[1], J. M. Cuerva[2], E. M. Talavera[1]

[1]Physical Chemistry Department, Campus of Cartuja, Granada University. [2]Organic Chemistry Department, Campus of Fuentenueva, Granada University.

Keywords: *Silicon-Substituted dyes.Excited-state proton-transferreactions.*

Fluorescence imaging is one of the most powerful techniques for visualizing biological phenomena in living cells, and many fluorescent probes have been developed. Recently, silicon-substituted xanthene fluorophores have been reported to emit strong fluorescence red shifted with respect to the corresponding xanthene derivative.Due to the utility of some xanthenes dyes for sensing phosphate ions inside living cells by means of the phosphate-mediated excited-state proton transfer reaction, ESPT, interconverting two different prototropic forms at near-neutral pH, we have decided to explore the ability of this silicon-substituted dyes to undergo the above ESPT reaction.

For this purpose we have synthesized thedye 9-[1-(2-methyl-4-methoxyphenyl)]-6-hydroxy-3H-Si-xanthen-3-one, and the rate constants describing the dynamic behaviour of the system, along with the spectral parameters, were studied in detail by steady-state and time-resolved fluorescence measurements. The underlying kinetic rate constants have been determined using global compartmental analysis (GCA) of the multi-dimensional fluorescence decay surface collected as a function of excitation and emission wavelength, pH, and phosphate buffer concentration.



The figure shows the recorded fluorescence spectra (exciting at 475 nm) from solutions of the dye with different concentrations of phosphate buffer at pH 6.15. As can be observed, the increase in the phosphate buffer concentration resulted in a pronounced increasing in the fluorescence at 600 nm. Since the 475 nm wavelength almost exclusively excites the less fluorescent neutral form, the experimental results indicate the increase in the phosphate buffer concentration at constant pH, promotes the formation of the more fluorescent excited anion molecules due to the ESPT reaction [2].

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S1: *Sistemas Luminiscentes: Caracterización y Aplicaciones*

IRIDIUM COMPLEXES WITH NHC-LIGANDS AS SOLAR ANTENNAS IN GREEN HYDROGEN PRODUCTION PROCESSES

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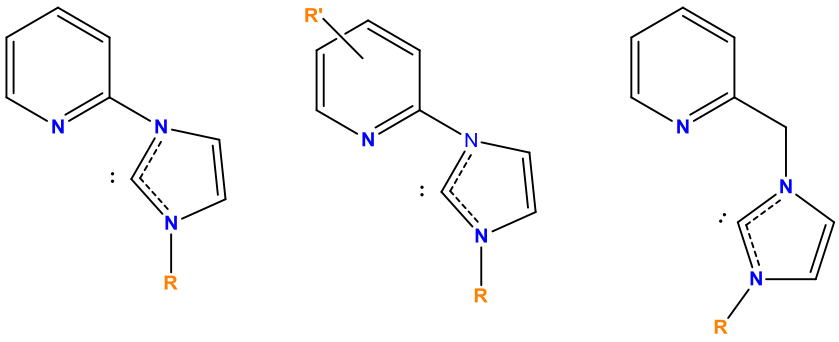
[2] Fundación Parque Científico y Tecnológico de Castilla-La Mancha (Fundación PCTCLM). Bulevar Rio Alberche s/n. 45007, Toledo.

Keywords: *Iridium, NHC ligands, carbene, organometallic chemistry, fluorescence, hydrogen production.*

Iridium complexes C-Ir bonded are known to have good optical and photochemical properties, which make interesting their use in catalytical processes involving light. Ligands exhibiting ortometalated rings or N-heterocyclic carbenes provide organometallic complexes with good optical properties.[1] One of the reasons that make those complexes attractive is their high fluorescence (indicator of their facility to be excited with light), long lifetimes (indicator of the stability of their reactive triplet state) and the ability to tune the excitation and emission of the complexes by simple modifications of the ligands as required.
One promising system studied in this field that benefits from the use of these solar-antennas is the hydrogen generation from water using visible or near-ultraviolet light as a source of energy (abundant in the atmosphere). Hydrogen is a promising fuel alternative to petroleum when it is obtained from water and sunlight as they are renewable sources.

Having this in mind, our group has prepared a batch of different N-heterocyclic carbene ligands based on pyridine and imidazole rings, and we have coordinated them to iridium complexes containing ortometalated phenylpyridine molecules as auxiliary ligands. The products exhibit good fluorescent properties in intensity and lifetimes of their excited state.



Generic structure of the carbene ligands used in the antennas.

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S2. Nanociencia y Materiales Moleculares (NMM) / Nanoscience and Molecular Materials

Este simposio tiene por objeto aunar las diferentes áreas de investigación que conforman la multidisciplinar actividad en materiales funcionales basados en moléculas. Hoy día dichos materiales moleculares se han enfocado, en gran parte, en el campo de la nanociencia, o nanociencia molecular. La otra gran rama que ocupan estos materiales moleculares, la (opto)electrónica orgánica, la constituye las aplicaciones en dispositivos electrónicos, fotónicos y opto-electrónicos. La puesta en común e intercambio de ideas, así como la generación de colaboraciones en este campo entre los diferentes actores nacionales es el objetivo final de este simposio.

The objective of this symposium is to bring together the different research areas working in the multidisciplinary field of molecular-based functional materials. Nowadays, molecular materials play a main role in the field of nanoscience, or molecular nanoscience. Furthermore, molecular materials find a key application in the field of organic electronics (in electronic, photonic and opto-electronic devices). This symposium offers a unique opportunity to share and exchange ideas, and to promote collaborations among the active national research groups in the field of molecular materials and molecular nanoscience.

Organizadores:

Ángela Sastre (UHM)

Juan Casado (UMA)

e-mail de contacto: asastre@umh.es

Lunes 20 de Julio 2015

08:40 – 09:40	**PL-2**	***Conferencia Plenaria*** (Común a todos los simposios) **Tomás Torres Cebada** *"Phtalocyanines: Old Dyes, New Molecular Materials"*

Chairman: Ángela Sastre-Santos

10:00 – 10:30	**S2-IL-01**	**Shunichi Fukuzumi** *"New Strategies for Artificial Photosynthesis"*
10:30 – 10:40	**S2-OC-01**	**Fernando Fernández Lázaro** *"Perylenediimides with Optoelectronic Applications"*
10:40 – 10:50	**S2-OC-02**	**David González Rodríguez** *"Polar Self-Assembled Molecular Materials"*
10:50 – 11:00	**S2-OC-03**	**Isabel Pastoriza-Santos** "*Nanoparticle-Loaded Filter Paper: A versatile Platform for Catalysis and Sensing*"
11:00 – 11:30		Pausa Café

Chairman: Fernando Langa

11:30 – 12:00	**S2-IL-02**	**Jean Francois Nierengarten** "*Clickable Scaffolds for the Preparation of Nano-Materials*"
12:00 – 12:10	**S2-OC-04**	**Pilar de la Cruz** "*Thiophene-Functionalized Porphyrins for Efficient Bulk Heterojunctions Solar Cells*"
12:10 – 12:20	**S2-OC-05**	Jose Lorenzo **Alonso-Gómez** "*Chirality Transfer from Single Molecules to Surface-Confined Nanostructure*"
12:20 – 12:30	**S2-OC-06**	**Beatriu Escuder** "*Peptide-Based Functional Molecular Gels*"
12:30 – 12:40	**S2-OC-07**	**José L. Zafra** "*Tiggering Chromic Effects in a New Naphtodithiophene Derivative. Role of Diradical Character and Pro-Aromaticity in the Formation of Intermolecular Weak σ-Bonds*"
12:40 – 12:50	**S2-OC-08**	**M. Monge** "*Ultrathin Gold-Silver Nanorods and Nanowires Stabilized with Oleic Acid: Synthesis and Plasmonic Properties*"
12:50 – 13:00	**S2-OC-09**	**Reynaldo Villalonga** "Máquinas Mesoporosas Controladas por Enzimas"
13:00 – 13:10	**S2-OC-10**	**Victor Blanco** "*Rotaxane-Based Switchable Organocatalysts*"
13:10 – 13:20	**S2-OC-11**	**Rosa Mª Girón** "*Materiales de Tipo n con Actividad Catalítica Basados en Fullerenos*"
13:20 – 13:30	**S2-OC-12**	**Rubén Chico** "*Columnar Arrangement of Metal Complexes Induced by Their Anchorage to a Triphenylene-Based Mesogenic Moiety: Pd(II) and Pt(II) Metallomesogens*"
13:30 – 15:30		Comida

Lunes 20 de Julio 2015

Chairman: Tomás Torres

15:30 – 16:00	**S2-IL-03**	**Jaume Veciana** *"Intramolecular Charge Transport Through Organic Radicals"*
16:00 – 16:10	**S2-OC-13**	**Aurelio Mateo Alonso** *"Twisted Polycyclic Aromatic Hydrocarbons with Pyrazine Rings: From Molecular to Low-Dimensional Materials"*
16:10 – 16:20	**S2-OC-14**	**Delia Miguel** *"Towards Multiple Conductance Pathways with Heterocyclic-Based Oligo(Phenyleneethynylene) Derivatives"*
16:20 – 16:30	**S2-OC-15**	**Pilar Cea** *"Presentation of the TIDOC Method (Thermal Induced Decomposition of Organometallic Compound) for the Fabrication of Metal/Molecule/Metal Electronic Devices"*
16:30 – 17:00		Pausa Café

Chairman: Juan Teodomiro López-Navarrete

17:00 – 17:10	**S2-OC-16**	**Félix Freire** *"Nanopartículas Poliméricas Quirales"*
17:10 – 17:20	**S2-OC-17**	**Javier Montenegro** *"Self-Assembly of Ag_3 Atomic Quantum Metal Clusters on Cyclic Peptide Nanotubes "*
17:20 – 17:30	**S2-OC-18**	**Juan C. Otero** *"Dual Estructura Electrónica de Híbridos Cargados Metal-Molécula y Procesos de Transferencia de Carga"*
17:30 – 17:40	**S2-OC-19**	**Emilia Iglesias** *"The New Approach for Captopril and s-Nitrosocaptopril Detection Using Gold Nanoparticles"*
17:40 – 17:50	**S2-OC-20**	**Teresa Pineda** *"Characterización de Bioconjugados Formados con Nanopartículas de Oro y Proteínas"*
17:50 – 18:00	**S2-OC-21**	**Marek Grzelczak** *"Plasmon-Driven Photoregeneration of Cofactor Molecules"*
18:00 – 18:30	**S2-IL-04**	**Francesco Stellacci** *"Nanomaterials and Transmissible Diseases"*

18:30	***Sesión de Pósteres***

Comunicaciones Invitadas (IL)

S2: *Nanociencia y Materiales Moleculares*

NEW STRATEGIES FOR ARTIFICIAL PHOTOSYNTHESIS

Shunichi Fukuzumi

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Faculty of Science and Engineering, ALCA and SENTAN, Japan Science and Technology Agency (JST), Meijo University, Nagoya, Aichi 468-0073, Japan
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Keywords: *artificial photosynthesis, hydrogen peroxide, fuel cell*

Sustainable and clean energy resources using solar energy are urgently required in order to solve global energy and environmental issues. This lecture presents our new strategies for artificial photosynthesis, focusing on combination of photocatalytic production of hydrogen peroxide from seawater and dioxygen (O_2) in the air as a solar fuel and hydrogen peroxide fuel cells.

We have developed a variety of photosynthetic reaction center models composed of organic electron donors and acceptors linked by covalent or non-covalent bonding, which undergo efficient charge separation and slow charge recombination.[1] The efficient charge-separation step has been successfully combined with the catalytic water reduction step with earth-abundant metal catalysts to develop efficient photocatalytic hydrogen evolution systems.[2,3] The photocatalytic oxidation of water with O_2 in the air to produce H_2O_2 has been achieved,[4,5] together with the development of H_2O_2 fuel cells.[6-9] The photocatalytic oxidation of water with O_2 in the air was found to be enhanced significantly in seawater. Thus, the combination of the photocatalytic H_2O_2 production from seawater and O_2 using solar energy with one-compartment H_2O_2 fuel cells provides on-site production and usage of H_2O_2 as a more useful and promising solar fuel than H_2, supplying the 21st century's demands for sustainable energy resources.

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S2: *Nanociencia y Materiales Moleculares*

CLICKABLE SCAFFOLDS FOR THE PREPARATION OF NANOMATERIALS

J.-F. Nierengarten

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Keywords: *fullerene, nanomaterials, click reactions*

Click reactions largely crossed the borders of organic synthetic chemistry and are now at the forefront of many interdisciplinary studies at the interfaces between chemistry, physics and biology. As part of this research, our group is involved in a research program on the development of clickable fullerene building blocks and their application to the preparation of a large variety of new advanced materials and bioactive compounds.[1,2] Importantly, the introduction of the click chemistry concept in fullerene chemistry allowed us to produce compounds that would be hardly accessible by using the classical tools of fullerene chemistry. This is particularly the case for the conjugation of fullerenes with other carbon nanoforms such as carbon nanohorns and graphene. It is also the case for most of the sophisticated molecular ensembles constructed from clickable fullerene hexa-adduct building blocks. In this contribution, our ongoing progresses in this particular field will be summarized.

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S2: *Nanociencia y Materiales Moleculares*

INTRAMOLECULAR CHARGE TRANSPORT THROUGH ORGANIC RADICALS

J. Veciana

Institut de Ciencia de Materials de Barcelona (CSIC) - Networking Research Center on Bioengineering, Biomaterials and Nanomedicine (CIBER-BBN),
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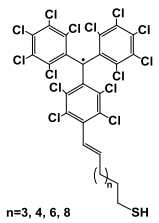
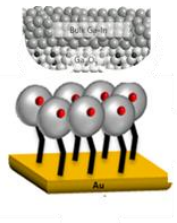
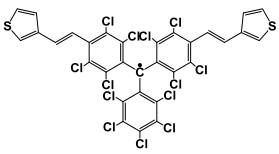
Keywords: *free radicals, charge transport, spintronics*

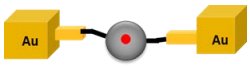
Organic free radicals are neutral molecules exhibiting magnetic properties due to the presence of an unpaired electron. This property together with their low spin-orbit couplings and weak hyperfine interactions make them good candidates for molecular spintronics insofar the radical character is preserved in solid state.

In the present contribution, the charge transport through molecules containing persistent polychlorinated triphenylmethyl (PTM) radicals will be presented. These studies have been made with self-assembled monolayers (SAMs) of PTM derivatives grafted on gold surfaces using conducting AFM or contacting the SAMs with top liquid electrodes of eutectic gallium-indium.[1-3] Also the transport through a single PTM radical molecule with a two- (mechanically-controlled break junction) and three-terminal (electromigrated break junction) solid-state devices will be reported.[4] In all cases the conductance through the radical molecules is enhanced two orders of magnitude due to a resonant tunnelling assisted by one of the MOs of these open-shell molecules. Furthermore, the magnetic property of radicals is manifested by a Kondo anomaly in these measurements.









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S2: *Nanociencia y Materiales Moleculares*

NANOPARTICLES AND TRANSMISSIBLE DISEASES

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Keywords: *nanoparticles, viruses, transmissible diseases*

In this talk I will highlight a large number or recent experiments from my group and from collaborators where the interactions of nanoparticles with viruses are studied. I will show how a large number of different interactions can be observed when particles and viruses are mixed together. The understanding of these interactions is underway, what is currently understood will be presented.

Comunicaciones Orales (OC)

S2: *Nanociencia y Materiales Moleculares*

PERYLENEDIIMIDES WITH OPTOELECTRONIC APPLICATIONS

F. Fernández-Lázaro, N. Zink-Lorre, S. Pla, D. Gutiérrez-Moreno, E. Font-Sanchis, A. Sastre-Santos

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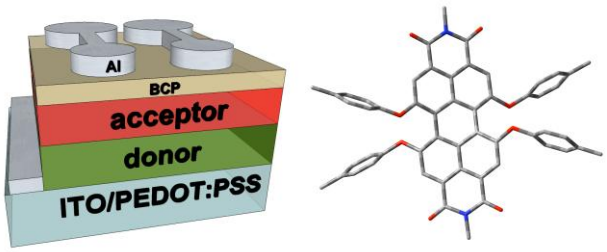
Keywords: *perylenediimide, optoelectronics, solar cell*

Among π-materials, perylenediimides (PDIs) show special significance due to their extremely high stability, intense absorption in the UV-vis., fluorescence quantum yields close to unity, strong electron-accepting character and high electron mobilities. [1] These characteristics have promoted their extensive use in optoelectronics as molecular materials for field effect transistors, [2] solar cells, [3] light-emitting displays [4] and lasers. [5] The electronic and optic properties of PDIs can be modulated over a wide range by introducing substituents at the aromatic core.

In the present contribution, we will describe our new results in the synthesis of PDIs with different substitution patterns and the application of these materials in the preparation of field effect transistors and solar cells.



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S2: *Nanociencia y Materiales Moleculares*

POLAR SELF-ASSEMBLED MOLECULAR MATERIALS

David González-Rodríguez,*[1] Julia Guilleme,[1,2] Tomás Torres[2] and Maria Jose Mayoral[1]

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Keywords: *Self-assembly, liquid crystals, subphthalocyanines, advanced nanomaterials*

Columnar nanostructures and liquid crystals are an important class of self-assembled organic materials that are making great impact in several optoelectronic technologies like transistors, solar cells, ferroelectric switches or light-emitting diodes. These materials are typically produced by the ordered stacking of functional molecules with a discotic shape (Fig. 1A). We have here studied related assemblies from a unique class of molecules, Subphthalocyanines,[1] having instead a rigid conical shape and a strong axial dipole moment (Fig. 1B). In solution, these molecules organize into non-centrosymmetric supramolecular columnar polymers[2,3] that show intriguing dual-mode self-assembly and chiral self-sorting processes, as a result of the intrinsic monomer chirality. In condensed phases, the generation of liquid crystalline materials[3,4] that can be efficiently aligned in the presence of electric fields and that exhibit permanent or switchable net polarization is observed. This is a novel and appealing attribute that may have important implications in, for instance, technologies that require an efficient directional transport of charges or memory devices combining ferroelectric and semiconducting properties.

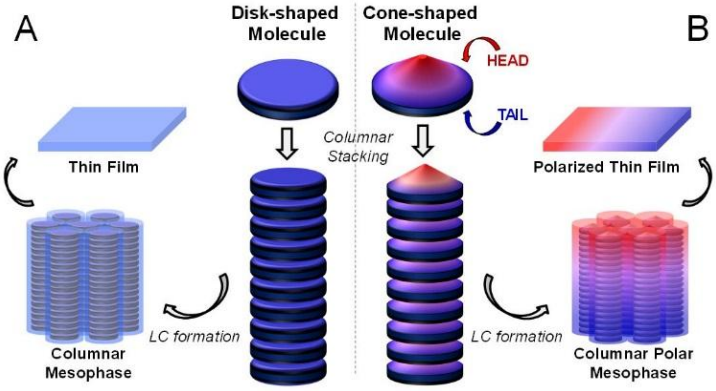

Fig. 1

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S2: *Nanociencia y Materiales Moleculares*

NANOPARTICLE-LOADED FILTER PAPER: A VERSATILE PLATFORM FOR CATALYSIS AND SENSING

G. Zheng,[1] L. Polavarapu,[1] L.M. Liz-Marzán,[1,2] J. Pérez-Juste,[1] Isabel Pastoriza-Santos[1]

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Keywords: *Metal nanoparticles, Supported catalyst, Sensing, SERS*

Cellulose-based materials are widely used in analytical chemistry as platforms for chromatographic and immunodiagnostic techniques. The numerous advantages (3D porous structure, flexibility, biocompatibility and biodegradability, low cost, among others) presented by this material make a valuable substrate for sensing, catalysis, etc. With the aim of developing a versatile platform, we present a simple and general strategy for the immobilization of metal nanoparticles on filter paper; where the strong van der Waals forces and hydrophobic interactions between the particles and the substrate are responsible of the nanoparticle permanent immobilization. The final application of these cellulose based substrates is determined by the nature of the nanoparticles. For instance, we have demonstrated that the self-assembly of Ni/NiO nanoparticles on filter paper allows the selective immobilization of proteins containing polyhistidine tags (His-tag) and its further use for immune-capture of live bacteria or for performing enzymatic reactions. In the case of doping with Pd nanoparticles, the hybrid platform have been tested for several model reactions displaying efficient catalytic activity and excellent recyclability and reusability.[1] Additionally, the use of Au nanoparticles has allowed to obtain a bifunctional platform with catalytic and, at the same time, sensing capabilities allowing the real-time monitoring of chemical reactions on its surface through Surface Enhanced Raman Scattering (SERS) technique. [2]

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S2: *Nanociencia y Materiales Moleculares*

THIOPHENE-FUNCTIONALIZED PORPHYRINS FOR EFFICIENT BULK HETEROJUNCTION SOLAR CELLS

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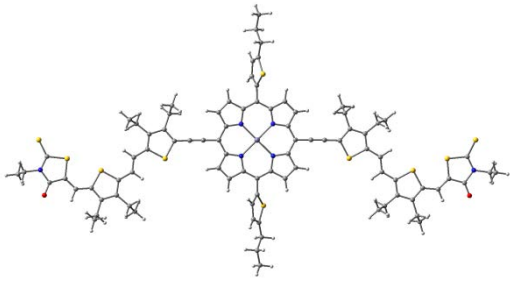
Keywords: *Photovoltaics, bulk heterojunction solar cells, small molecule, porphyrin*

Mimicking the photosynthesis, where chlorophylls absorb light for energy conversion, porphyrin and their derivatives can be suited as panchromatic photosensitizers being excellent building blocks in the construction of molecular architectures for light harvesting. Thus, porphyrins are among the most significant types of sensitizers for Dye Sensitized Solar cells (DSSCs) [1] showing record breaking performances as high as 13% [2]. However, utilization of porphyrins as active material in solution-processed BHJ has been scarce [3] despite the natural tendency of porphyrins to form aggregates by π-π stacking and then favour intermolecular interactions and, consequently, the efficiency of the device.

In this communication, we will present the design, synthesis and characterization of several novel porphyrin derivatives where the porphyrin is covalently linked to different thiophene-based moieties. The photophysical properties of these novel conjugates, as well as their application in photovoltaic devices (BHJ) afford information on the structure-efficiency relationship.



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S2: *Nanociencia y Materiales Moleculares*

CHIRALITY TRASFER FROM SINGLE MOLECULES TO SURFACE-CONFINED NANOSTRUCTURES

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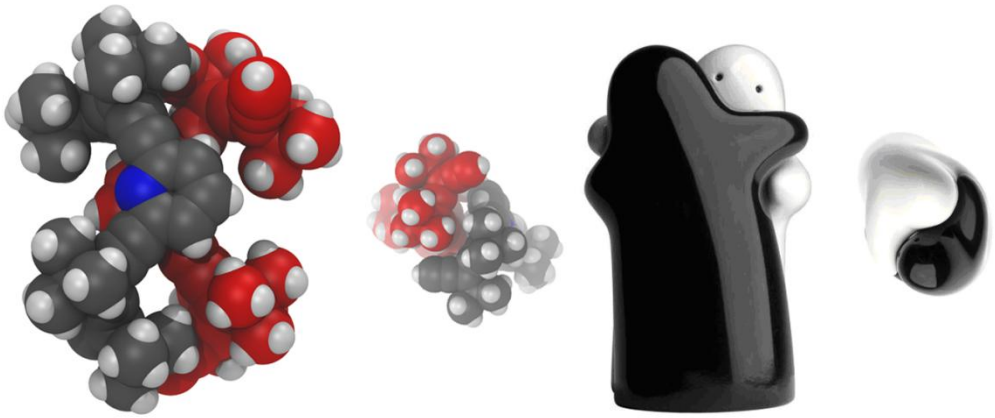
Keywords: *axial chirality, self-assembly, chiral surfaces*

Single chiral molecules (0D chirality) can be design to form 2D self-assemblies on surfaces.[1] We use frameworks bearing chiral axis and aromatic spacers for the construction of surface-confined **Upstanding Chiral Architectures** (**UCAs**).[2] Gas-phase characterization, low-temperature scanning tunneling microscopy and molecular-dynamics simulations reveal that the dominance of molecule–molecule over molecule–substrate interactions leads to regular diastereomeric domains of **UCAs** with the optically active units being largely decoupled from the substrate. The outstanding chiroptical responses presented by these axially chiral derivatives[3] along with the opportunity to further functionalization via the terminal alkyne exposed on top of the monolayer-thin architectures make such **UCAs** promising key ingredients for chiroptical sensing applications.



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S2: *Nanociencia y Materiales Moleculares*

PEPTIDE-BASED FUNCTIONAL MOLECULAR GELS

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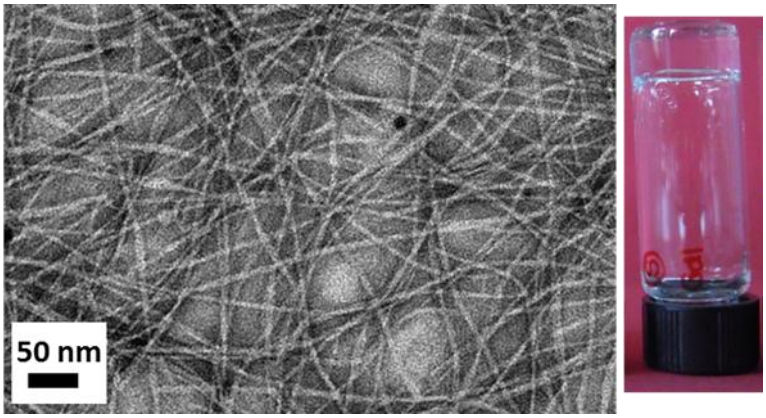
Keywords: *self-assembled materials, molecular gels, peptides, nanofibers*

The field of peptide-based molecular hydrogels has emerged in the last times at the borders of Biomaterials Science and Supramolecular Chemistry.[1] Molecular gels are soft materials formed by self-assembly of low-molecular weight compounds through non covalent interactions and represent an example of the bottom-up hierarchical construction of soft matter in which the information programmed at the molecular level is transferred into the nano- and micro-scale leading to a functional material.[2] In particular, gelators based on small peptides are easy to prepare, have a rich self-assembly behavior – well established for their natural counterparts – and are biocompatible. Additionally, new functional features may emerge after self-assembly such as pKa shifts, new catalytic activity or multivalent recognition among others. Here some recent examples of functional molecular hydrogels with an emphasis on their bioinspired self-assembly and function will be presented.[3]



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S2: *Nanociencia y Materiales Moleculares*

TRIGGERING CHROMIC EFFECTS IN A NEW NAPHTODITHIOPHENE DERIVATIVE. ROLE OF DIRADICAL CHARACTER AND PRO-AROMATICITY IN THE FORMATION OF INTERMOLECULAR WEAK σ-BONDS.

José L. Zafra [1], N. Yanai [2], T. Mori [2], I. Osaka [2], L. Qiu [3], J. T. López Navarrete [1], M. Kertesz [3], K. Takimiya [2], and J. Casado [1]

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Keywords: *Open-shell, Diradicals, pro-aromaticity, Raman spectroscopy, DFT, aggregation, molecular electronics*

Multifunctional materials require of molecular building blocks able to easily and reversibly tune their chemical structure in response to soft external stimuli. In this regard, chromism is a valuable property for functional materials often related to π-conjugated organic dyes in which the alteration of the π-molecular structure gives rise to different electronic shapes before and after the color mutation. There are plenty of good examples of thermo- and electro-chromic polymers, however, only a few cases based on small molecules, being these mainly related to mono-radicals. Even more uncommon examples are those related to diradicals, like phenalenyl based ones that forms stair-chain oligomers [1] or a tetrafluorobisimidazol diradical with a strong photochromism mediated by a double dimerization. [2]

With this communication we present a spectroscopic study of the reversible diradical σ–dimerization/oligomerization of a new naphtodithiophene derivative, depending on different external mild conditions, that is accompanied by a strong chromism originated by the transition from quinoidal to aromatic cores during the process.

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S2: *Nanociencia y Materiales Moleculares*

ULTRATHIN GOLD-SILVER NANORODS AND NANOWIRES STABILIZED WITH OLEIC ACID: SYNTHESIS AND PLASMONIC PROPERTIES

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Keywords: *gold, silver, ultrathin nanostructures, plasmonic properties*

The control of the characteristics of nanostructures is a fundamental prerequisite for the exploration of their properties, which change with size, shape and surface state. The use of organometallic complexes has permitted to achieve a plethora of well controlled metal nanostructures that have been obtained through the precise knowledge of the chemical structures and molecular chemistry of this type of metal precursors.[1]

We have developed an organometallic approach that allows a controlled chemical reduction of perfluoroaryl Au(I)-Ag(I) precursors.[2] Bimetallic one-dimensional gold-silver alloy nanostructures have been obtained through the reduction of these complexes obtained when oleic acid is used as capping agent. When oleic acid is used as solvent and capping ligand ultrathin nanorods (UNRs) and ultrathin nanowires (UNWs) are obtained. These UNRs and UNWs display a length-dependent broad band in the mid IR region that is related to the longitudinal mode of the surface plasmon resonance (SPR) of these ultrathin nanostructures.

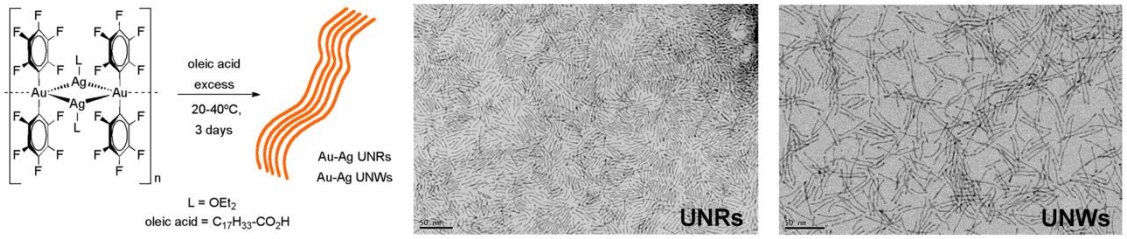

Figure 1. Synthesis of UNRs and UNWs and TEM micrographs.

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S2: *Nanociencia y Materiales Moleculares*

NANOMAQUINAS MESOPOROSAS CONTROLADAS POR ENZIMAS

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Palabras Clave: *Nanopartículas de sílice mesoporosa, Enzimas, Liberación controlada, Nanopartículas Janus*

El desarrollo de nuevos sistemas nanométricos de liberación controlada de fármacos y otros compuestos constituye una prioridad en la Química de los materiales y la farmacología aplicada. En este trabajo se describen diversas estrategias orientadas al ensamblaje de nanomáquinas inteligentes para la liberación bajo demanda de compuestos químicos basadas en nanopartículas de sílice mesoporosas mecanizadas con enzimas, en los cuales los biocatalizadores actúan como sistemas de control del proceso de liberación mediante el biorreconocimiento y transformación de los estímulos químicos del entorno. Estas estrategias incluyen:

- El uso dual de enzimas artificialmente glicosidadas como puertas biomoleculares y sistemas de control para el diseño de nanomáquinas, basadas en nanopartículas de sílice mesoporosas, capaces de efectuar la liberación estímulo-dependientes de compuestos mediante mecanismos de entrega en un solo paso o a través de procesos pulsátiles químicamente programados [1].
- La preparación de originales nanopartículas Janus de oro y sílice mesoporosa, y su empleo como "hardware" para el ensamblaje de nanomáquinas químicamente programadas por enzimas o combinaciones de estos biocatalizadores capaces de operar como puertas lógicas Booleanas (Fig.1) [2].

Estas nanomáquinas fueron evaluadas *ex vivo* como sistemas inteligentes para la liberación del fármaco antitumoral doxorrubicina en células HeLa de cáncer cérvico-uterino.

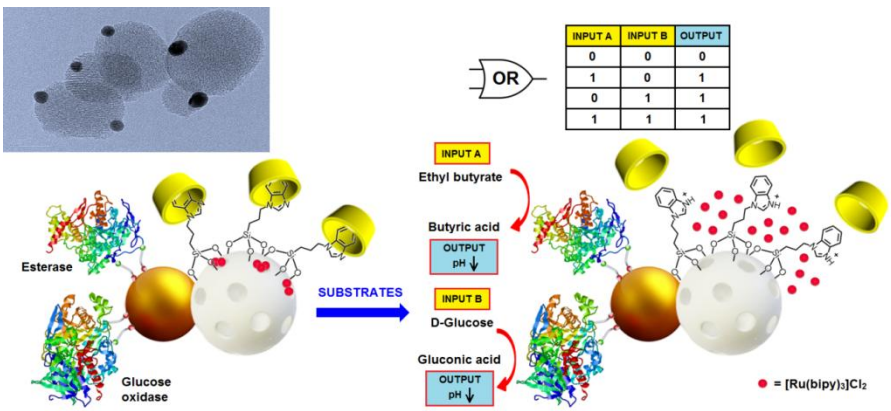

Figura 1. Esquema del funcionamiento de la nanomáquina Janus operada por una puerta enzimática OR.

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S2: *Nanociencia y Materiales Moleculares*

ROTAXANE-BASED SWITCHABLE ORGANOCATALYSTS

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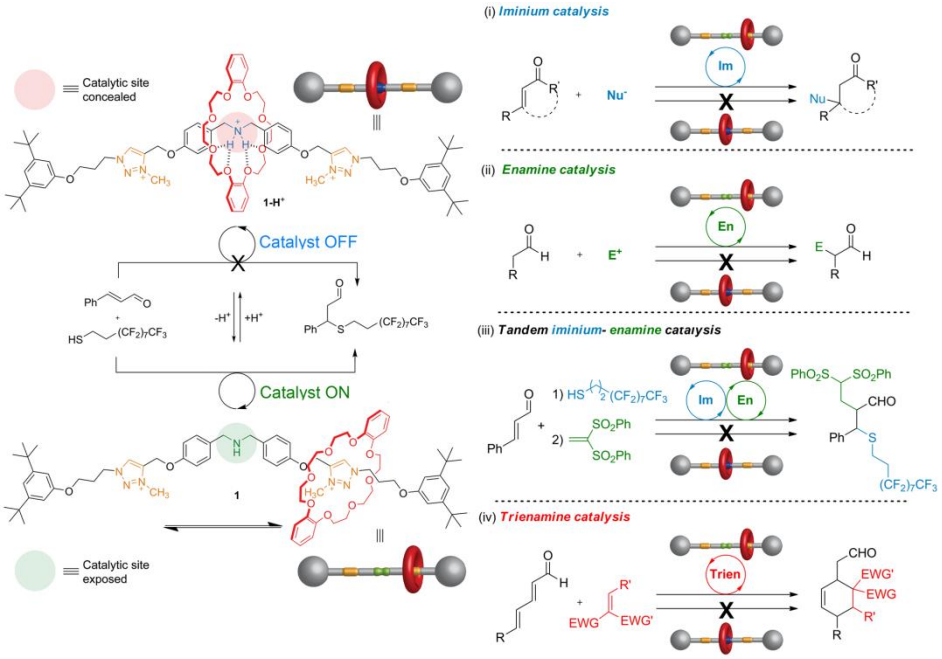
Keywords: *Rotaxanes, molecular machines, switchable catalysts, organocatalysis.*

Enzymes are often regulated in Nature through trigger-induced effects, processes that are inspiring a growing number of synthetic catalysts for which an external stimulus can turn "on" or "off" the catalytic activity or change the stereochemical outcome of the system. We described a switchable organocatalyst based on a rotaxane (**1**) able to control the rate of the Michael addition of an aliphatic thiol to *trans*-cinnamaldehyde (Figure, left) through an acid/base-promoted change of the position of the macrocycle between a secondary amine/ammonium catalytic unit and a triazolium ring.[1a] Recently, we studied the scope of the system as a switchable aminocatalyst, exploring its efficacy in a variety of activation modes, including iminium, enamine, and trienamine catalysis, and in tandem iminium-enamine reactions (Figure, right).[1b] A modification in the catalytic unit or in the auxiliary binding site led to systems that can promote asymmetric Michael addition reactions[2a] or generate different products from a mixture of building blocks.[2b]



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S2: *Nanociencia y Materiales Moleculares*

MATERIALES TIPO N CON ACTIVIDAD CATALÍTICA BASADOS EN FULLERENO

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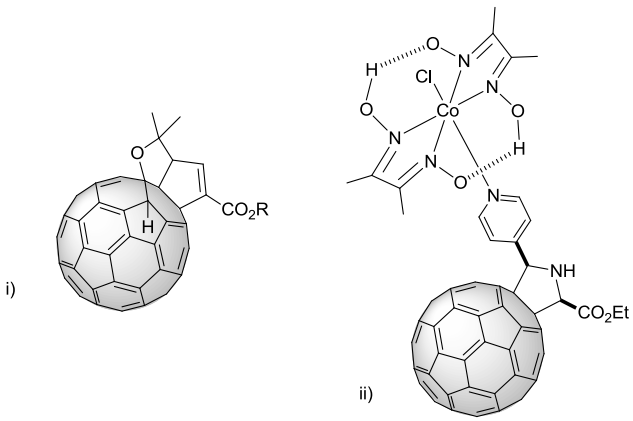
Palabras Clave: *Fullereno, Catálisis, Síntesis asimétrica, Complejo metálico.*

En los últimos años, entre las aplicaciones más importantes de los fullerenos ha destacado su empleo en dispositivos fotovoltaicos orgánicos como consecuencia de su interesante potencial.[1,2]

Su elevada eficiencia en procesos de transferencia electrónica y su comportamiento como portadores de carga de tipo n, les confiere gran interés como aceptores orgánicos en células solares poliméricas junto con polímeros dadores.[3]

Hoy en día existe un amplio rango de herramientas sintéticas disponible para la preparación de derivados fullerénicos con un elevado control de sus propiedades optoelectrónicas.

En este aspecto, la química de fullerenos se ha orientado a la síntesis de derivados fullerénicos que contengan sitios catalíticos donde podrían llevarse a cabo procesos de reducción. Dicha estrategia está dirigida a la preparación de: i) catalizadores fullerénicos carbonados y, ii) compuestos híbridos metalo-fullerénicos en los que el fullereno está unido a metales activos tales como el cobalto. Además, el efecto de la introducción de quiralidad en estos derivados también es un aspecto evaluable con interesantes aplicaciones.



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S2: *Nanociencia y Materiales Moleculares***s**

COLUMNAR ARRANGEMENT OF METAL COMPLEXES INDUCED BY THEIR ANCHORAGE TO A TRIPHENYLENE-BASED MESOGENIC MOIETY: Pd(II) AND Pt(II) METALLOMESOGENS

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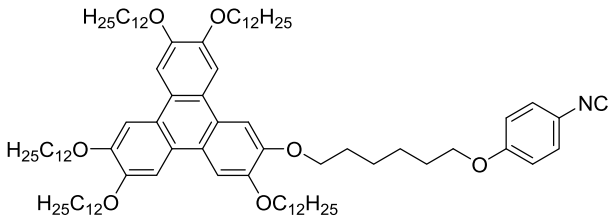
Keywords: *nanomaterials, liquid crystals, metallomesogens, organometallic chemistry*

Soft materials based on discotic liquid crystals exhibiting columnar mesophases have gained attention in the last decades because these anisotropic fluidic systems are useful in the synthesis of nanoscale conductive devices, field-effect transistors or photovoltaic solar cells [1]. In this regard, substituted triphenylenes have been widely used for this purpose and many reported works are aimed at studying the influence of the molecular constitution and stacking of the mesogenic triphenylene-based molecules in the mesophase, mostly on conventional organic liquid crystals. However, there are less examples of such studies on metal-containing liquid crystals (metallomesogens) [2].

We have prepared the isocyanide ligand (CN-L) and its corresponding organometallic complexes *cis* or *trans*-[MX_2(CN-L)$_2$] (M = Pd, Pt; X = Cl, Br, I; M = Pt, X = CN).



Free isocyanide ligand (CN-L).

Although the *trans* complexes are not liquid crystals, all the *cis* derivatives exhibit columnar mesophases, revealing the importance of the dipolar moment in the metallic fragment for the appearance of the mesophase. The incorporation of two triphenylene moieties in the complexes also facilitates the formation of the liquid crystal state. The luminescent properties in solution, in the mesophase and in the solid state of the free ligand and some of the complexes have also been studied.

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S2: *Nanociencia y Materiales Moleculares*

TWISTED POLYCYCLIC AROMATIC HYDROCARBONS WITH PYRAZINE RINGS: FROM MOLECULAR TO LOW-DIMENSIONAL MATERIALS

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Keywords: *polycyclic aromatic hydrocarbons, nanoribbons*

Polycyclic aromatic hydrocarbons (PAHs) are receiving a great deal of attention because of their increasingly better performance in organic electronic applications. Among these, PAHs containing N atoms (N-PAHs) are particularly interesting since their electronic structure, stability, solubility, and supramolecular organization can be modulated by varying the number and position of N atoms.

In general, PAHs are planar structures but they can adopt twisted conformations as the result of the steric strain induced by overcrowding or congestion in key positions of the aromatic core. *twisted*-PAHs have shown enhanced solubility and unique optoelectronic and chiroptical properties as an effect of their distorted molecular structure.

We have developed a general strategy that provides access to a new family of *twisted*-N-PAHs (0D) with different twist angles by introducing silyl groups with different size and rigidity, providing direct experimental correlation between twist size and properties. In addition, this methodology has been successfully implemented in the preparation of low-dimensional materials (1D and 2D). The most recent advances of these materials including synthetic routes, optoelectronic properties, self-organising properties, and potential applications will be discussed.

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S2: *Nanociencia y Materiales Moleculares*

TOWARDS MULTIPLE CONDUCTANCE PATHWAYS WITH HETEROCYCLIC-BASED OLIGO(PHENYLENEETHYNYLENE) DERIVATIVES

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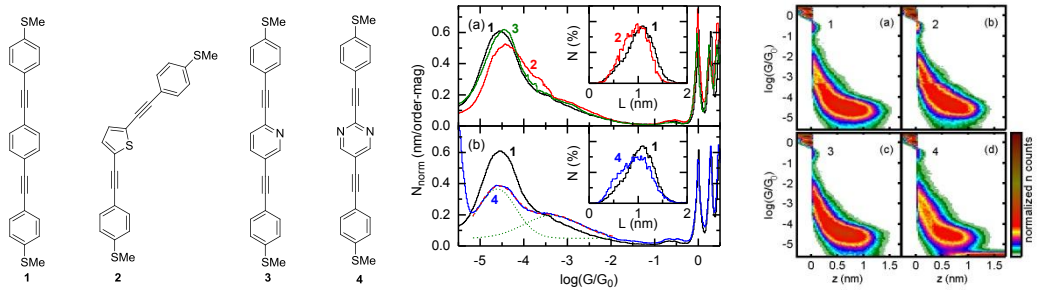
Keywords: *molecular junctions, STM-BJ, heterocyclic oligophenyleneethynylenes*

The idea of encoding information in organic molecules opens the possibility to construct electronic devices with new or improved properties. Very recently some groups have demonstrated the possibility of using organic molecules with multiple pathways to connect electrode leads, mainly based on oligosilanes [1], thiophene[2] and fullerene derivatives [3] and folded molecular wires [4]. In this work we have systematically studied how the replacement of a benzene ring by an heterocyclic compound in OPE derivatives affects the conductance of a molecular wire using the scanning tunneling microscope-based break junction technique. We described for the first time that OPE derivatives with a central pyrimidine ring can efficiently link to gold electrodes by two pathways presenting two different conductance ($\log(G/G_0)$) values, that can be observed in the 1D and 2D histograms of the figure. We have demonstrated that this effect is associated to the presence of two efficient conductive pathways of different length. It is worth noting that our strategy represents one of the scarce examples in which two defined conductive states can be set up in a single molecule without the aid of external stimulus.



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S2: *Nanociencia y Materiales Moleculares*

PRESENTATION OF THE TIDOC METHOD (THERMAL INDUCED DECOMPOSITION OF AN ORGANOMETALLIC COMPOUND) FOR THE FABRICATION OF METAL/MOLECULE/METAL ELECTRONIC DEVICES

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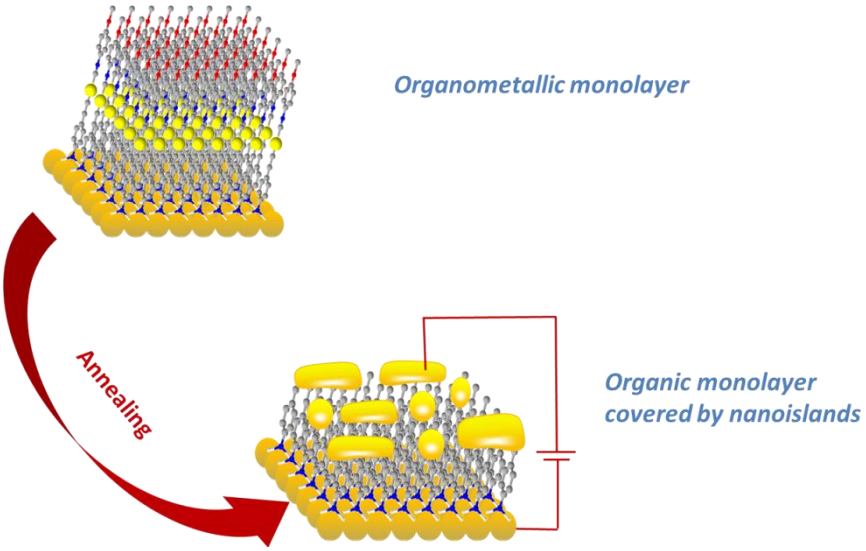
Keywords: *Molecular Electronics, Chemistry of Surfaces.*

In this contribution, a novel method [1] for the fabrication of the top contact electrode in a metal|organic monolayer|metal device is presented. The procedure used consists in the thermally induced decomposition of an organometallic compound that we have abbreviated as the TIDOC method. Monolayers incorporating metal organic compounds (MOCs), namely [[4-{(4-carboxy)ethynyl}phenyl]ethynyl]-(triphenylphosphine)-gold, **1**, and [1-isocyano-4-methoxybenzene]-[4-amino-phenylethynyl]-gold, **2**, were annealed at moderate temperatures (1:150 °C for 2h and 2: 100 ºC for 2 h), resulting in cleavage of the Au-P or Au-C bond and reduction of Au(I) to Au(0) as metallic gold nanoparticles (GNPs). These particles are distributed on the surface of the film which leads to the formation of metal|molecule|metal devices. Electrical properties of these nascent devices were determined by recording I-V curves with a conductive-AFM using the Peak Force Tunneling AFM (PF-TUNA™) mode. The obtained results rule out the formation of short-circuits evidencing that the TIDOC method is an effective procedure for the fabrication of molecular junctions.



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S2: *Nanociencia y Materiales Moleculares*

NANOPARTÍCULAS POLIMÉRICAS QUIRALES

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Palabras Clave: *polímero helicoidal, quiralidad, cation-pi, nanoestructuras*

Los polímeros helicoidales dinámicos del tipo poli(fenilacetileno) (PPAs), presentan propiedades muy interesantes debido a la posibilidad de modular el sentido de giro de la hélice una vez que han sido sintetizados. Así, un polímero de tipo PPA que posee como sustituyente la anilida del ácido (*R*)-*α*-metoxi-*α*-fenilacético, presenta una estructura helicoidal muy dinámica cuando se disuelve en distintos disolventes orgánicos (DCM, Acetona, THF, …), dando lugar a un polímero racémico desde el punto de vista macroscópico con actividad óptica nula (CD = 0).[1] La adición de iones metálicos permite amplificar el sentido de giro de la hélice hacia hélices de tipo *P* o *M*, dependiendo de la valencia del metal utilizado, ya que iones metálicos de tipo mono--- o divalentes se coordinan de distinta forma a la unidad de MPA del polímero amplificando sentidos de giros opuestos.[2-4] El uso de iones metálicos para realizar la amplificación de quiralidad de polímero, puede ser utilizada también para generar nanoestructuras quirales basadas en este tipo de compuestos, ya que los metales pueden actuar como agentes de entrecruzamiento.[2-4] Además, en nuestro grupo de investigación hemos diseñado otros polímeros que pueden dar lugar a otro tipo de nanoestructuras basados en otros tipos de interacciones supramoleculares como son los enlaces de hidrógeno.[5,6]

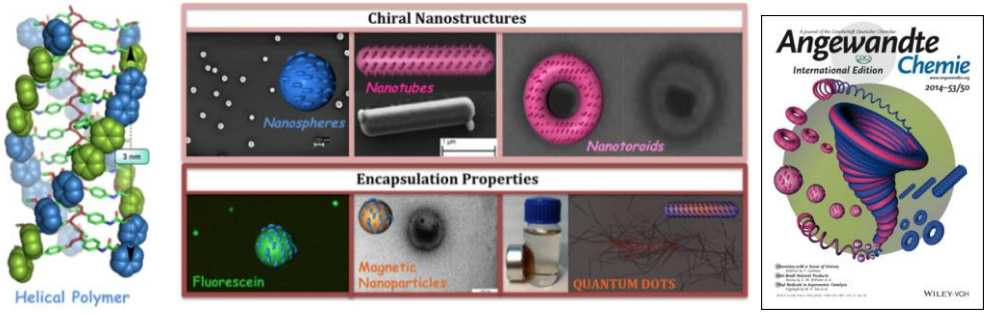

Figura. Nanoestructuras quirales a partir de complejos Metal/Polímero helicoidal.

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S2: *Nanociencia y Materiales Moleculares*

SELF-ASSEMBLY OF AG_3 ATOMIC QUANTUM METAL CLUSTERS ON CYCLIC PEPTIDE NANOTUBES

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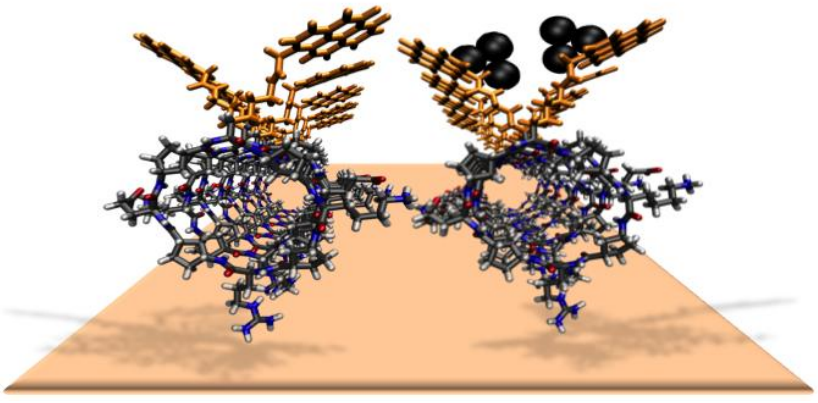
Keywords: *Self-assembly, Subnanometric Metal Clusters, Supramolecular Chemistry*

Quantum effects dominate metals when the particle size approaches the Fermi wavelength of an electron.[1] At this level, subnanometric metallic clusters behave like real molecular entities and they display magnetic, luminescent and catalytic activities. However, positional control and hierarchical arrangements of these novel and prospective materials have remained elusive. Theoretically attractive and experimentally discernable, van der Waals forces and/or other non-covalent interactions at the metal/organic interfaces will be crucial to understand and influence the next generation hybrid nanotechnology and materials science. Here, we present clear-cut experimental and theoretical evidences of the sensitivity of atomic quantum clusters (AQCs) towards non-covalent interactions and their application to obtain 1-D arrangements of Ag_3 clusters on ditopic self-assembling cyclic peptide nanotubes (SCPNs).[2] Atomic force microscopy, fluorescence experiments and computational simulations verified the occurrence of induced non-covalent interactions between silver clusters and the aromatic residues of the peptidic tubular ensembles. These findings constitute the first example of the supramolecular 1D patterning of atomic quantum clusters and in the long-term outline and generalize the unlimited possibilities that non-covalent interactions will have in the emerging field of subnanometric molecular metal clusters.



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S2: *Nanociencia y Materiales Moleculares*

DUAL ESTRUCTURA ELECTRÓNICA DE HÍBRIDOS CARGADOS METAL-MOLÉCULA Y PROCESOS DE TRANSFERENCIA DE CARGA

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Palabras Clave: *transferencia de carga, materiales híbridos, estructura electrónica*

Aunque la transferencia de carga (CT) entre metales y moléculas es uno de los procesos más simples, interesantes y estudiados de la química, hay comportamientos que no se pueden entender utilizando esquemas muy populares y similares al representado en la Figura 1. Sobre la base de resultados experimentales (Surface-Enhanced Raman Scattering, SERS) y teóricos hemos demostrado que la sutil estructura electrónica del híbrido cargado determina la energética de los procesos CT. La transferencia electrónica metal-molécula directa e inversa no son perfectamente simétricas como se deduciría de la Figura 1, sino que presenta una compleja dependencia con la naturaleza y la carga del complejo superficial [1].

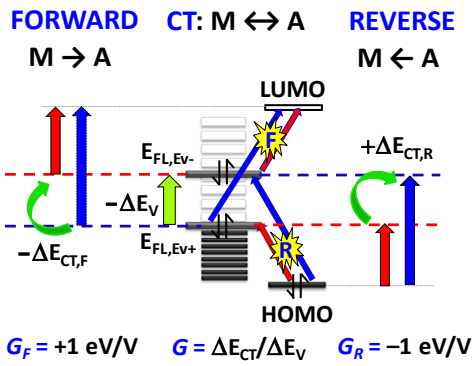

Figura 1: Simple esquema energético para los procesos CT directo (F) e inverso (R).

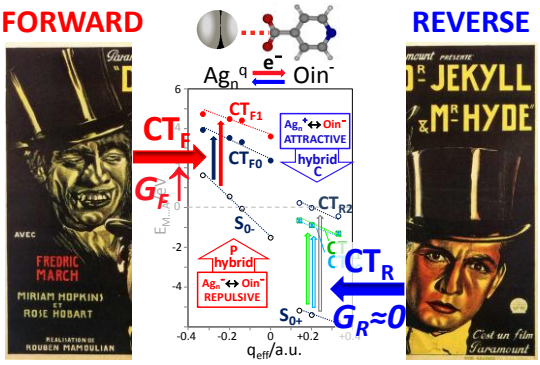

Figura 2: Dependencia de las energías de los estados S_0 y CT del sistema Ag-Isonicotinato con la densidad de carga por átomo metálico.

En el caso de moléculas cargadas, como el anión isonicotinato usado como modelo, se predice una doble estructura electrónica seleccionada por el signo de la carga del metal (Figura 2), mostrando los estados CT_F metal-molécula una gran sensibilidad con el potencial de electrodo, mientras que los estados CT_R molécula-metal no dependen en absoluto del exceso de carga[2].

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S2: *Nanociencia y Materiales Moleculares*

THE NEW APPROACH FOR CAPTOPRIL AND S-NITROSOCAPTOPRIL DETECTION USING GOLD NANOPARTICLES

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Key words: *captopril, gold-nanoparticles, manganese ions, reversible assembly.*

The optical properties of colloidal gold-nanoparticles (AuNPs) depend strongly on their surface chemistry and on the interparticle interactions [1]. This contribution reports results regarding reactivity and assembly of AuNPs mediated by captopril (cap) and S-nitrosocaptopril (NOcap), in comparison with the well studied cysteine (cys). The original gold-nanoparticles were efficiently modified by small concentrations of Mn^{+2} ions (<0.2 mM) in mild acid medium ([acetic acid]≤10 mM) [2]. Manganese ions adsorb onto the surface of 15.4 nm citrate-capped gold nanoparticles; the resulting new particles are highly sensitive and afford a rapid colorimetric detection method for thiols, see Figure.

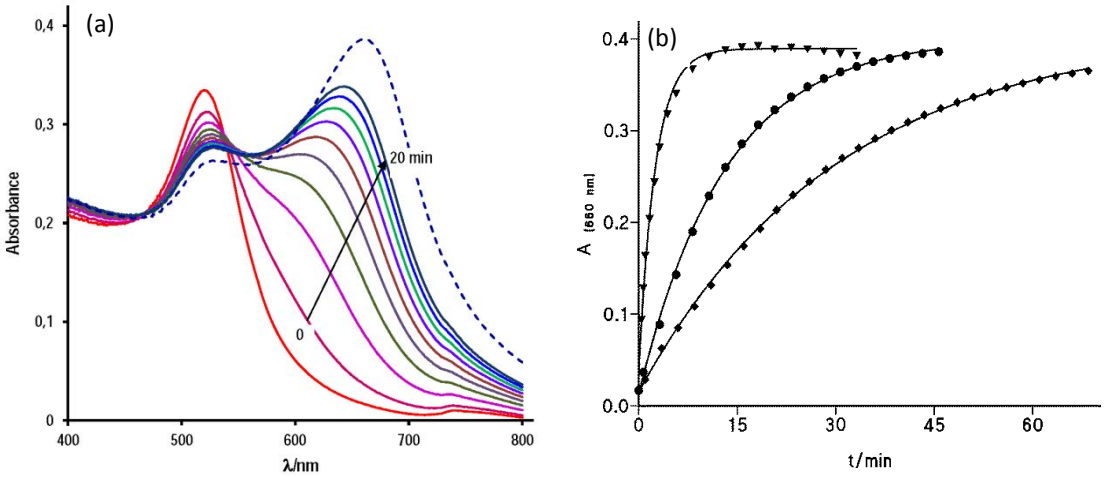

Figure. *(a)*UV-vis spectra of AuNPs at 10 mM acetic acid and 34 μM of cys recorded as a function of time; scan red correspond to AuNPs; dashed scan is after 50 min; *(b)*A increase as a function of time for (◆) [Cys]=34 μM, [AcH]= 5.5 mM; (●)[Cys]=34 μM, [AcH]=10 mM, and (▼[Cys]=34 μM, [AcH]=5.5 mM, [Mn^{+2}]=0,12 mM.

The assembly of thiol-capped AuNPs can be explained by electrostatic interactions between zwitterionic amino acids when using cys as the ligand or by hydrogen bonding when the ligand is captopril or S-nitrosocaptopril. In the last two cases the process is fully reversible when the pH is increased to basic levels. On the other hand, the binding of NOcap molecules to AuNPs implies the RS–NO bond cleavage, which makes citrate-stabilized gold nanoparticles as a efficiently platform to regulate NO release, a small molecule that plays key roles in biological processes, such as neurotransmission, vasodilation, or hormone secretion in living bodies.

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S2: *Nanociencia y Materiales Moleculares*

CARACTERIZACIÓN DE BIOCONJUGADOS FORMADOS CON NANOPARTÍCULAS DE ORO Y PROTEÍNAS

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Palabras Clave: *nanopartícula, proteína, bioconjugado, estabilidad.*

La utilización de nanomateriales en el campo de la salud ha encontrado una barrera importante en el desconocimiento de la interfase entre los materiales y el medio biológico. Los aspectos a destacar son la composición superficial del nanomaterial, la interfase sólido-líquido y la zona de contacto de esta última con el medio biológico.[1] En el medio biológico se encuentran presentes numerosas proteínas y pequeñas moléculas a altas concentraciones que se pueden adsorber a la superficie de la nanopartícula formando una nube de proteínas agregadas conocida como "corona" de proteínas.[2] Este fenómeno es imposible de evitar y está presente siempre que un nanomaterial se encuentre en contacto con un fluido biológico.[3]

Es, por tanto, de gran importancia el estudio de estos sistemas con el objeto de conocer tanto su estructura como la estabilidad en diferentes entornos. La estabilidad, en particular, depende de la funcionalización superficial del nanomaterial.

En este trabajo se aborda el estudio de la funcionalización superficial de nanopartículas de oro, tanto de forma esférica como cilíndrica y de su interacción con material proteico. Se hace énfasis en las diferencias encontradas en función de la forma de las partículas y como estos aspectos se relacionan con la estabilidad de las dispersiones de estos nanobioconjugados en medios acuosos. La utilización de diferentes técnicas de caracterización como son las espectroscopías FTIR, UV-visible, Fluorescencia y Dicroismo circular permiten obtener información sobre la naturaleza de la capa molecular protectora del nanomaterial así como sobre la estructura y conformación de las proteínas que forman parte de la *corona*.

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S2: *Nanociencia y Materiales Moleculares*

PLASMON-DRIVEN PHOTOREGENERATION OF COFACTOR MOLECULES

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Keywords: *gold nanoparticles, plasmonic nanochemistry*

Spurred by outstanding optical properties, metallic nanoparticles gain progressive attention as photocatalysts. Large absorption cross-sections and chemical stability allow metal nanoparticles to efficiently harvest light over the UV-Vis-NIR spectral range and use it to catalyse reduction/oxidation reactions. These photo-chemical processes are mediated by plasmon resonances, which lead to production of strong enhancement of the optical near field, which increase the efficiency of chemical reactions. For example, non-enzymatic regeneration of cofactor molecules, which is a biologically relevant reaction, but still remains as a challenging task. We found that gold nanorods functionalized with metallic platinum can reduce NAD^+ to NADH using visible and IR light.[1] Gold nanorods were randomly distributed on glass substrate to fabricate centimeter-scale plasmonic substrates consisting of homogenously distributed nanoparticles (Figure 1). Morphological integration of the substrates allows their manipulation in different media. The control over the spatial distribution of cocatalyst (Pt) on gold nanorods surface – either on the tips or the latter parts – is crucial element when designing nanoparticles for photochemical applications. Our results suggest promising use of plasmonic particles in biochemical reactions

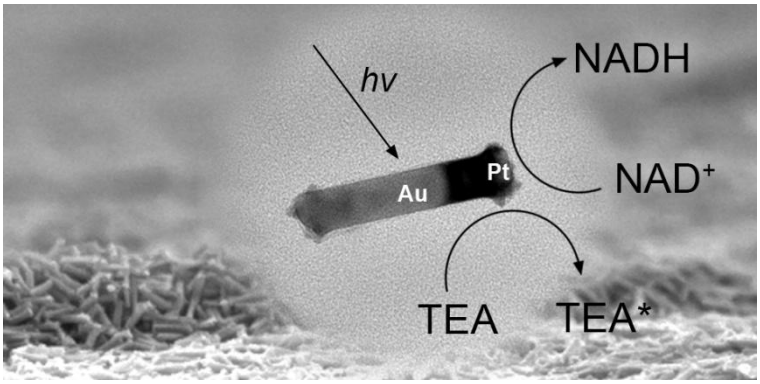

Figure 1. Platinum-doped gold nanorods are able to regenerate cofactor molecules under visible and infrared light irradiation.

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Presentaciones Póster (PP)

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S2: *Nanociencia y Materiales Moleculares*

PREPARACIÓN DE SISTEMAS NANOESTRUCTURADOS PARA LA LIBERACIÓN CONTROLADA DE ALENDRONATO Y DERIVADOS

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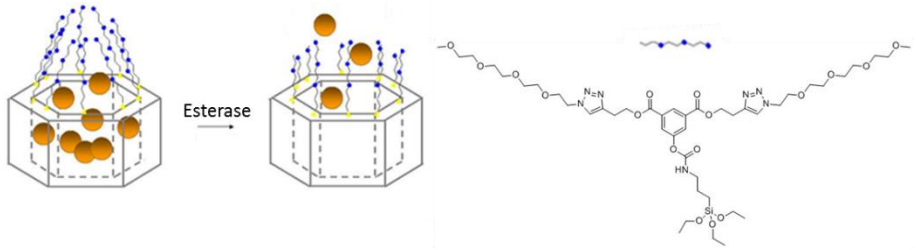
Palabras Clave: *nanopartículas de sílice, puertas moleculares, liberación controlada, alendronato*

Para maximizar la eficacia terapéutica y minimizar los efectos adversos, se están intentando diseñar sistemas de liberación de fármacos que puedan transportar la medicación de forma segura hasta las células o tejidos diana evitando su degradación o liberación antes de tiempo [1]. En los últimos años se han desarrollado nuevos sistemas de liberación controlada de fármacos basados en un soporte de sílice mesoporosa con una puerta molecular anclada, capaz de liberar su contenido selectivamente en determinadas condiciones [2].



En este proyecto, se ha diseñado y se ha sintetizado la molécula 1 que es capaz de actuar como puerta molecular sobre el material mesoporoso MCM-41. Los primeros estudios de liberación por medio de una esterasa se han realizado cargando el sistema con un colorante y bloqueando los poros con el compuesto 1 para comprobar la eficacia del mismo. Se han realizado los estudios de liberación del colorante mediante medidas de la fluorescencia en presencia y ausencia de enzima esterasa [3]. Una vez comprobada la eficacia de nuestro sistema se han realizado los estudios de liberación del fármaco.

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S2: *Nanociencia y Nanomateriales*

INTERACCIÓN CATIÓN-π EN POLÍMEROS HELICOIDALES Y NANOESTRUCTURAS QUIRALES

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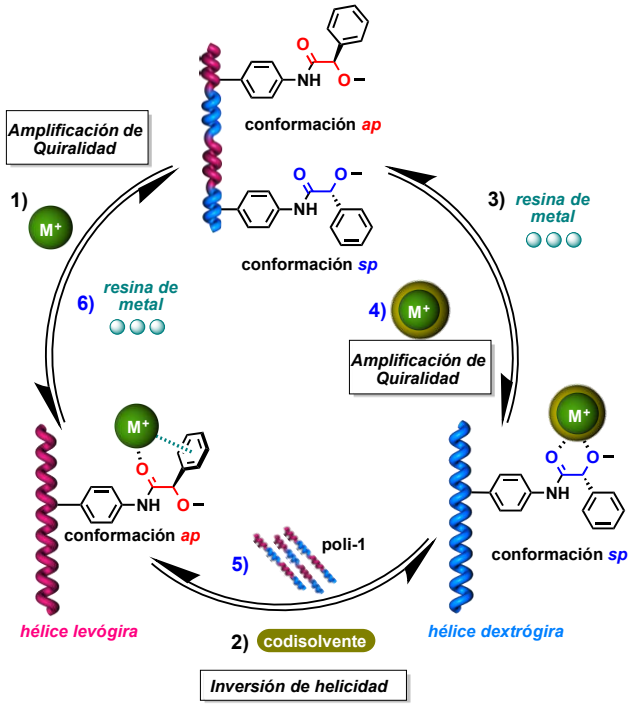
Palabras Clave: *Polifenilacetileno, Interacción catión-π, Nanoestructuración, Amplificación de quiralidad.*

Los poli(fenilacetilenos) (PPAs) son un tipo de polímeros helicoidales que responden a diferentes estímulos externos como son la temperatura, polaridad, iones metálicos, etc. En esta comunicación se presenta un nuevo concepto de un derivado de PPA, ópticamente inactivo (DC nulo), que incorpora MPA (ácido metoxifenilacético) en la unidad monomérica. La formación de complejos metal monovalente polímero helicoidal inducirá un sentido de giro de tipo *P* o *M*, debido a la presencia/ausencia de interacciones de tipo catión-π desactivadas/ activadas mediante un codisolvente.



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S2: *Nanociencia y Materiales Moleculares*

ISOCIANURO-COMPLEJOS DE Au(I) DERIVADOS DE PERILENO. LUMINISCENCIA Y PELÍCULAS DELGADAS.

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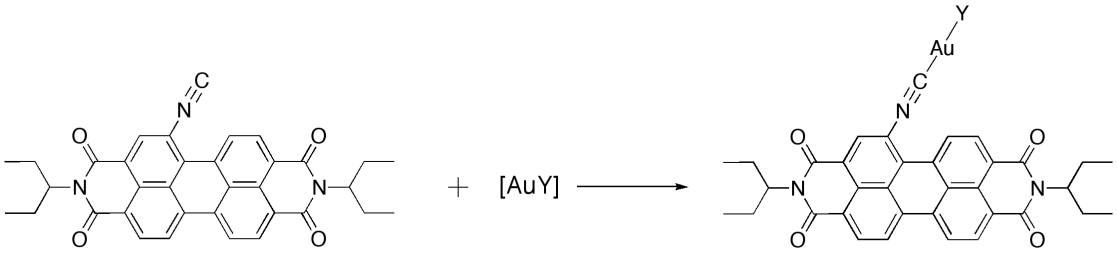
Palabras Clave: *Perilenodiimida, oro, isocianuro, películas delgadas, luminiscencia*.

La química de derivados de perileno está ampliamente desarrollada y entre ellos se encuentran las perilenocarboxidiimidas (PDI) cuyas propiedades ópticas y electrónicas les convierten en excelentes candidatos para la preparación de polarizadores, dispositivos electroluminiscentes y semiconductores de tipo n. Una posibilidad muy flexible para modificar o inducir nuevas propiedades en estos sistemas es la incorporación de un fragmento metálico al sistema perilénico.[1] Con este objetivo, se ha funcionalizado una PDI con un grupo isocianuro en una posición bahía y se han preparado una serie de derivados de Oro(I) con este ligando funcional (ver esquema). El uso de diferentes fragmentos de oro [AuY], permite analizar la influencia del grupo Y sobre las propiedades del sistema. Se ha encontrado que el efecto global que ejercen los sustituyentes del oro sobre los niveles energéticos del anillo perilénico es mínimo y que la coordinación del metal al ligando CN-PDI no supone una distorsión significativa de la planaridad y rigidez del cromóforo.



CN-PDI **[Y-Au-CN-PDI]**

Y = Cl, CC-C_6H_4-C_9H_{19}, C_6F_5, $C_6F_4OC_6H_{13}$, (μ-4-4'-$C_6F_4C_6F_4$)

Se ha estudiado la capacidad de agregación para formar películas delgadas, que generalmente presentan las PDI,[2] tanto en el isocianuro libre (CN-PDI) como en el derivado [C_6F_5-Au-CN-PDI]. En ambos casos se han obtenido, mediante la técnica de Langmuir, monocapas estables en la interfase aire-agua con una disposición *edge-on* de las moléculas. Las correspondientes películas de Langmuir-Blodgett y Langmuir-Schaefer se comportan como materiales dicroicos.

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S2: *Nanociencia y Materiales Moleculares*

PHOTORESPONSIVE GOLD NANOPARTICLES BY USING AN AZO ISOCYANIDE LIGAND

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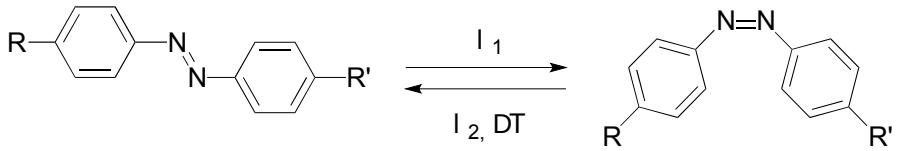
Keywords: *azo, gold, nanoparticles, isocyanide, photoresponsive.*

In recent years intensive work has been focused on the synthesis and properties of gold nanoparticles, with narrow size distributions and well controlled surface states. On the other hand, the reversible light induced *trans-cis* photoisomerization of the azo group has been exploited to modify systems by inducing chemical and physical changes under irradiation. The phenomenon consists of the isomerization of the most stable *trans* configuration to the bent *cis* configuration upon UV irradiation (Scheme 1). The reverse transformation can be brought about thermally, or by illuminating with visible light [1].



Scheme 1. *Trans-cis* photoisomerization.

The use of a photoresponsive azo isocyanide ligand bearing an alkoxy chain OC_nH_{2n+1} allow us to synthesize photoresponsive gold(I) compounds. Gold nanoparticles have been obtained by reduction of $HAuCl_4$ in the presence of this ligand, or alternatively, by direct reduction of the gold(I) compounds. The isocyanide functional group is a good ligand for gold, while the azo remains free and able to make *trans-cis* azo isomerization in the presence of UV light, even for the gold nanoparticles.

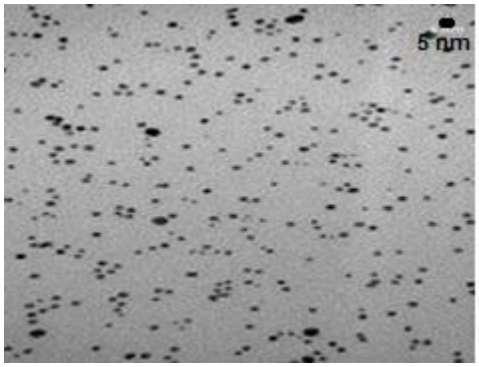


Fig. 1. TEM image of gold nanoparticles.

Different gold nanoparticles have been prepared and characterized. Morphology, size and size distribution has been studied by transmission electron microscopy (TEM, Fig. 1), and dynamic light scattering (DLS). The optical and mesogenic properties have been studied, and also the behavior under UV light.

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S2: *Nanociencia y Materiales Moleculares*

PREPARATION OF $YBa_2Cu_3O_{7-x}$ NANOPARTICLES

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Key words: *nanoparticles, superconductors,* $YBa_2Cu_3O_{7-x}$

Nanoscience is one of the most explored fields due to the different properties exhibited by materials prepared in this scale [1]. It is not yet clear, though, if HT superconductivity is much affected by the particle size. Clearly, deep investigation is needed to establish such a correlation and explore other features as the coexistence of low ferromagnetism and superconductivity in the case of small particles. [2] The already well-known $YBa_2Cu_3O_{7-x}$ material has been taken as reference to initiate this investigation and it has been prepared by the sol-gel method using citric acid as quelatant [3]. Once the water is evaporated, the cations are distributed within a blue gel and after calcination, the Ybacuo nanoparticles are obtained. The use of soft conditions allows one obtaining smaller particles than those prepared through the ceramic route. In order to make samples with different particle size to correlate this parameter with the properties, the experimental conditions such as temperature, time and citric acid concentration, have been modified. For instance, it has been observed the drastic influence of the temperature in the particle size; as shown in the Figure, particles below 100 nm can be obtained at 750 ºC. Work is continuing to fully characterize the magnetic and transport properties of the prepared samples.

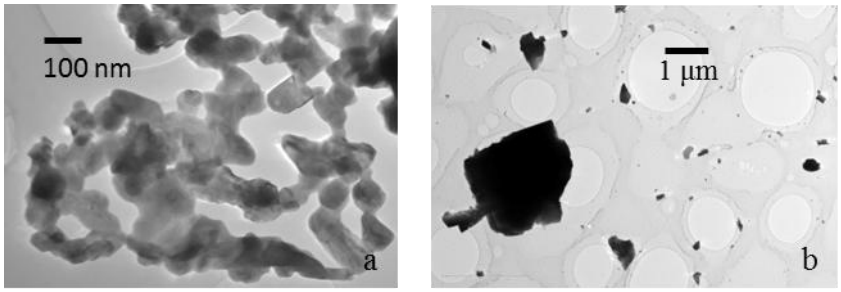

Figure. YBCO particles obtained at 750 (a) and 900 ºC (b) for a same time of treatment.

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S2: *Nanociencia y Materiales Moleculares*

TOWARDS RATIONAL DESIGN OF SYNTHETIC EXOSOMES FOR ANTITUMOR THERAPY

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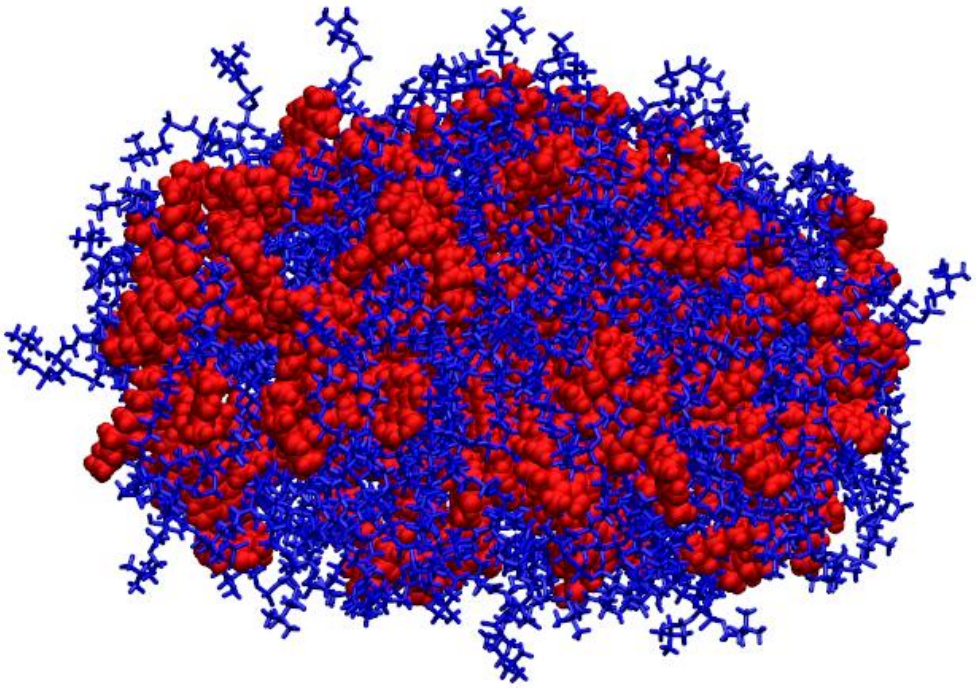
Keywords: *Exosomes, nanometric vesicles, Molecular Dynamics simulations*

Exosomes are nanometric vesicles (40-100 nm) secreted by every cellule in the organism. In pathological states such as cancer, a number of key proteins and microRNAs are released and hosted into exosomes, which are transported from a tumor cell to another one. [1] Given their role in intercellular communications, exosomes have many of the characteristics of an ideal drug delivery vehicle, since they are able to cross membranes and show a great ability to reach target tissues and release their contents. [2] Nanotechnology opens the door to the development of exosome-mimetics, capable of targeting selectively to tumor cells and transporting therapeutic elements thus opening the door to numerous applications in clinic studies.



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S2: *Nanociencia y Materiales Moleculares*

MAGNETIC PHOTOSWITCHES BASED ON DINUCLEAR COPPER(II) COMPOUNDS

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Keywords: *photoswitch; magnetic properties; copper(II) compounds*

Molecular switches have attracted the attention to scientists because of several applications, such as data storage, drug delivery or sensors. They are characterized by a reversible interconversion of the chemical and physical properties due to an external stimulus (light, pH, electrical current…). Among all, magnetic photoswitches are an important class, in which their magnetic properties can be tuned by light irradiation.

Previously, dinuclear copper(II) compounds have been developed in our research group with oxamate ligands bearing photoactive groups such as antracene.[1] This group undergoes under a [4+4] photocycloaddition reaction. As a result, the relatively strong antiferromagnetic coupling between the copper(II) ions vanishes.

Following this research line, new ligands bearing photoswitchable groups, *i.e.* stilbene and azobenzene, have been designed. In this work, the synthesis and characterization of dinuclear copper(II) compounds with these new ligands are presented.

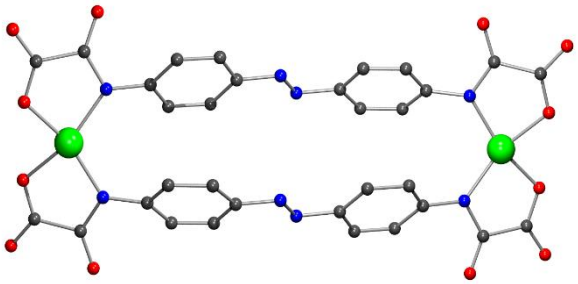

Figure 1. Anionic part of the dinuclear copper(II) compound with a photoactive azobenzene derivative ligand.

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S2: *Nanociencia y Materiales Moleculares*

SUPRAMOLECULAR METAL-ORGANIC FRAMEWORKS (SMOFs) AS AN ALTERNATIVE TO MORE CONVENTIONAL METAL–ORGANIC FRAMEWORKS (MOFs)

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Keywords: *MOFs, nucleobases, hydrogen bonds*

The present work reports a synthetic strategy to obtain supramolecular metal–organic frameworks (SMOFs) based on base pairing interactions with potentially accessible voids as an alternative to more conventional metal–organic frameworks (MOFs). [1-3] This goal can be achieved by considering three key factors: (i) the use of rigid building units, (ii) the establishment of predictable and rigid synthons between the building units and (iii) the non-coplanarity of functional groups involved in the predictable synthons. Throughout this report we demonstrate the suitability of this synthetic strategy supported by several SMOFs based on metal-nucleobase entities which fulfill the above stated requirements.

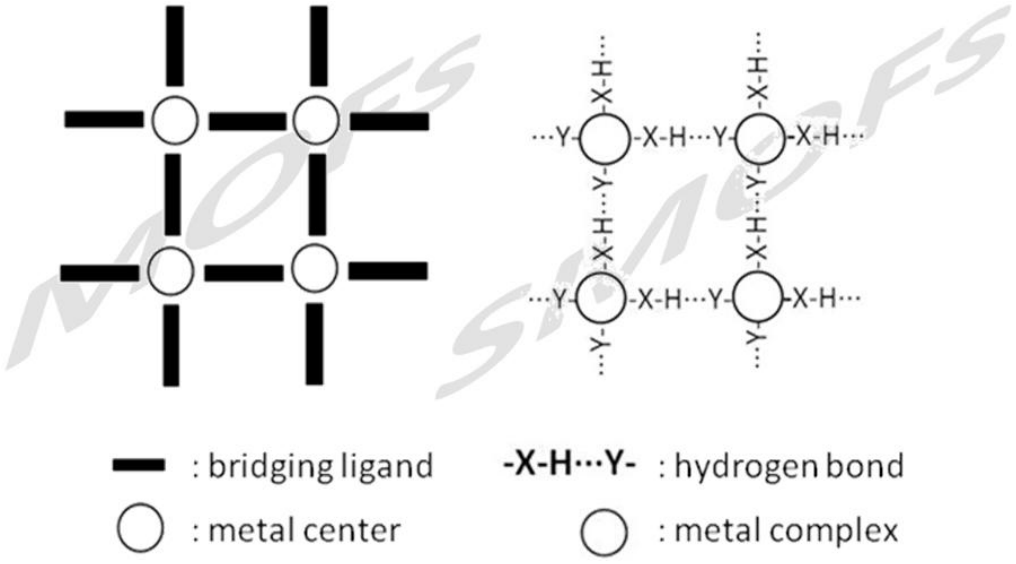

Figure **1**: Comparison between (a) coordination bonds and (b) hydrogen bonding interactions as structure directing agents.

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S2: *Nanociencia y Materiales Moleculares*

RHODIUM NANOPARTICLES FOR SELECTIVE HYDROGENATION

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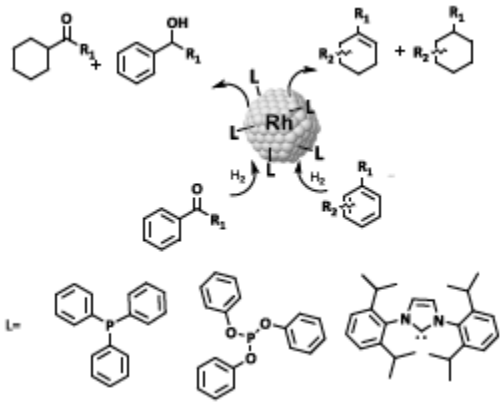
Key words: *Nanoparticles, Ligands stabilization, Catalysis, Hydrogenation*

Over the last decades, transition metal-nanoparticles (M-NPs) have received a great deal of attention as catalysts since they potentially combine the advantages of heterogeneous and homogeneous catalysts. The stabilization of M-NPs can be realized in the presence of polymers, surfactants or ligands, which allows the control of their size, shape and dispersion as well as their surface state. In the last decade ligands such as phosphines, phosphites and NHC-carbenes were shown to efficiently stabilize metal nanoparticles that are catalysts in the hydrogenation of various substrates.[1] However, to date, the fine tuning of the properties of this type of catalysts to achieve specific selectivities remains a challenge.

Recently, our research group reported the synthesis of M-NPs (M= Ru, Rh, Ir) stabilized by diphosphites and their application in the catalytic hydrogenation of arenes with high selectivity.[2] To gain understanding into the role and influence of the stabilizing ligands in catalysis, a series of Rh-nanoparticles stabilized by phosphines, phosphites and NHC-carbenes were synthesized, characterized and their catalytic performances evaluated in the selective hydrogenation of several substrates such as arenes[3] and aromatic ketones.[4] Comparison of the catalytic results using the corresponding Ru-NPs is also included. The results show that the nature of the ligand, its hapticity and steric properties clearly influence the catalytic performances of the nanocatalysts.



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S2: *Nanociencia y Materiales Moleculares*

RATIONALLY BOSTING THE WATER OXIDATION CAPACITY OF METAL OXIDE NANOPARTICLES

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Keywords: *water oxidation, ruthenium nanoparticles, immobilization*

Molecular hydrogen is a promising candidate for replacing fossil fuels as energy sources. However, its renewable and clean generation is still a great challenge. A particularly attractive solution is the production of this gas from water splitting (WS) by sunlight as driving force (Figure 1, right).[1] Therefore, an enormous progress has been recently made on the development of catalysts to speed up the involved semi-reactions; the oxidation of water to O_2 (WOC) and the reduction of protons to H_2 (PRC). The decomposition of homogeneous species into heterogeneous systems of non-controlled size, composition and reactivity, is a common phenomenon in catalysis.[2] Particularly, several examples of *in situ* formed oxides and colloidal species acting as rugged, low-overpotential WOCs and PRCs have been recently reported.[3] However, the factors controlling their efficiency are still not rationally understood.

In this context, a family of Ru and RuO_2 NPs of different sizes stabilized by pyridine-based ligands, has been prepared by means of the organometallic approach (Figure 1, left),[4] and their WO activity when dispersed in aqueous solution or immobilized into ligand functionalized carbon-based supports have been analyzed.

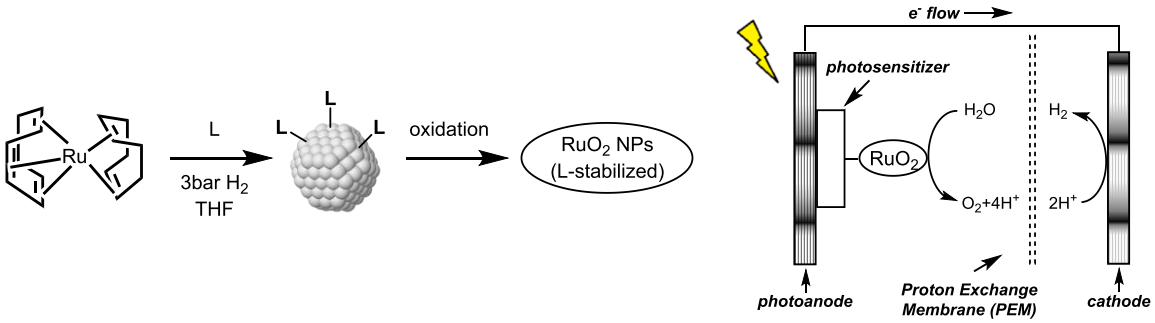

Figure 1. On the left side, synthesis of RuO_2 NPs by the organometallic approach and, on the right, a basic photoelectrochemical cell type with RuO_2 NPs as WOC.

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S2: *Nanociencia y Materiales Moleculares*

REDES ELECTROPOLIMERIZADAS DE NANOPARTICULAS DE ORO POLIFUNCIONALIZADAS PARA LA CONTRUCCION DE BIOSENSORES ELECTROQUÍMICOS

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Palabras Clave: *Nanopartículas, Redes electropolimerizadas, Biosensores*

El diseño de nuevas plataformas biosensoras altamente sensibles y reproducibles, con bajos límites de detección e interferencias, de fácil manejo, robustas y miniaturizadas, constituye el principal reto de la Química Bioelectroanalítica moderna.

En este trabajo se describe la preparación electroquímica de superficies electródicas nanoestructuradas, mediante la formación de enlaces tipo bis-anilina, de redes tridimensionales de nanopartículas de oro polifuncionalizadas.[1] Estas superficies se emplean para la inmovilización específica de diferentes proteínas mediante interacciones supramoleculares[1a,c], covalentes[1b] y de afinidad[1d]. La estrategia se basa fundamentalmente en el diseño y la síntesis de pequeñas nanopartículas de oro (2.5 a 5.7 nm de diámetro), polifuncionalizadas específicamente con tres derivados de tiol diferentes: p-aminotiofenol como unidad polimerizante, ácido 2-mercaptoetanosulfónico como residuo solubilizante y un tercer ligando tiolado (Ácido 3-mercaptofenil borónico[1a], Dendrímero PAMAM-Cisteamina [1b],1-Adamantanotiol [1c] y Biotina tiolada [1d]) para la inmovilización selectiva de biomoléculas.

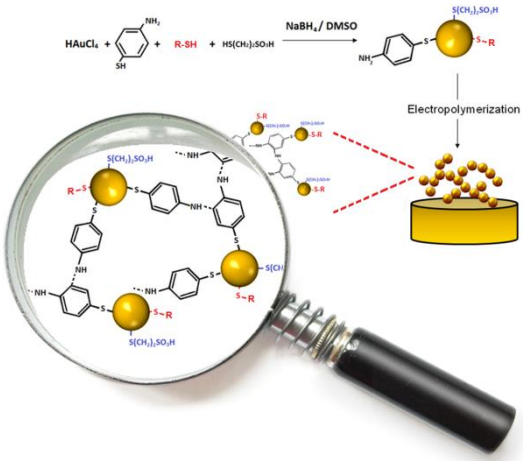

Figura. Esquema de la preparación de nanopartículas de oro polifuncionalizadas y su electropolimerización a través de la formación de enlaces bis-anilina.

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S2: *Nanociencia y Materiales Moleculares*

NEW CONJUGATED OLIGOMERS: TOWARDS THE SATURATION LIMIT

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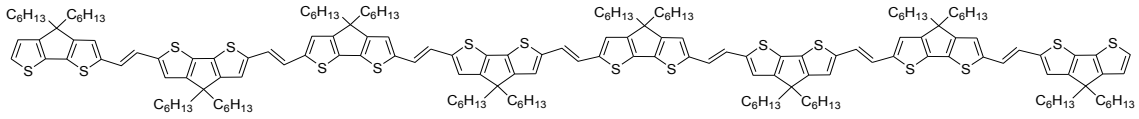
Keywords: *oligomer, thiophene, band-gap*

Conjugated oligomers and polymers have attracted considerable research interest in recent years owing to their utility in a variety of electronic devices as photovoltaic cells, light-emitting diodes (LED), field-effect transistors (FET) or chemical sensors. Significant experimental and computational efforts have been devoted to studying the electronic properties of conjugated polymers. However, such studies are quite complicated, because polymers do not have well-defined structures, many of them are insoluble and polydisperse, and computational techniques are significantly less developed for infinite polymers than for well-defined molecules.

Linear π-conjugated oligomers as molecular wires in molecular electronics or nanoscopic systems have attracted particular attention. Although most of the work in these two areas has involved oligomers of intermediate chain length, the synthesis of highly extended π-conjugated oligomers is of crucial importance. In particular, thiophene derivative oligomers and their functional derivatives have been extensively studied and have allowed us to develop materials with specific electronic properties, which arise from both the backbone and the functional groups.[1-7]

Continuing our research on molecular wires, in this work we have designed, synthesized and characterized a new family of oligomers based on cyclopentadithiophene linked by vinylenes in order to study their behavior as molecular wires. Oligomers as long as 8 nm have been prepared and studied.



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PREPARACIÓN Y CARACTERIZACIÓN DE BIONANOCOMPOSITES DE ÁCIDO POLILÁCTICO, PLA, CON NANOTUBOS DE DIÓXIDO DE TITANIO

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Palabras Clave: *Bionanocomposites, extrusión, propiedades térmicas mecánicas y barrera*

La adición de nanocargas a los materiales bioplásticos, permite mejorar el comportamiento en uso de los mismos, por lo que el objetivo de este trabajo es el estudio de las propiedades térmicas, mecánicas y barrera en materiales compuestos de PLA y nanotubos de dióxido de Titanio.

Se prepararon filmes mediante moldeo por compresión a temperaturas de 200 º C, 30 bar y enfriamiento rápido desde el fundido a partir de los materiales previamente extruidos: PLA comercial con un contenido en isómero D del 6% (Ingeo^{TM}2003D, Natureworks) y PLA modificado con un 2% en peso de TiO_2.

Mediante DSC, se estudió el efecto de la velocidad de enfriamiento/calentamiento; el efecto de la temperatura de cristalización (tratamientos de templado a temperaturas por encima de la temperatura de transición vítrea, T_g); y la evolución con el tiempo, cuando dichos materiales están a temperaturas inferiores a la T_g, analizando, a su vez, la influencia en la generación de la fase cristalina y su repercusión en las propiedades finales.

El PLA y el PLA-TiO_2 no cristalizan desde el fundido a ninguna de las velocidades en estudio. Sin embargo, durante el calentamiento presentan el proceso de cristalización en frio y el correspondiente proceso de fusión de dichas entidades. Cuando las muestras se cristalizan isotérmicamente, a temperaturas superiores a 80 ºC desde el estado sólido, son capaces de cristalizar en tiempos relativamente cortos. El proceso de fusión muestra la presencia de polimorfismo en el PLA, la forma α' evoluciona a la forma α, esta última de mayor estabilidad y/o procesos de fusión y recristalización, según el tratamiento térmico. La presencia de los nanotubos de TiO_2 repercute en las propiedades mecánicas (esfuerzo-deformación y microdureza), disminuyendo la rigidez del PLA de partida.

Agradecimientos: Se agradece al MINECO MAT 2013-47972C2-1P-2P su financiación.

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SISTEMAS MESOPOROSOS MODIFICADOS QUÍMICAMENTE PARA EL TRANSPORTE Y LIBERACIÓN CONTROLADA DE FÁRMACOS SOBRE LA MUCOSA COLÓNICA

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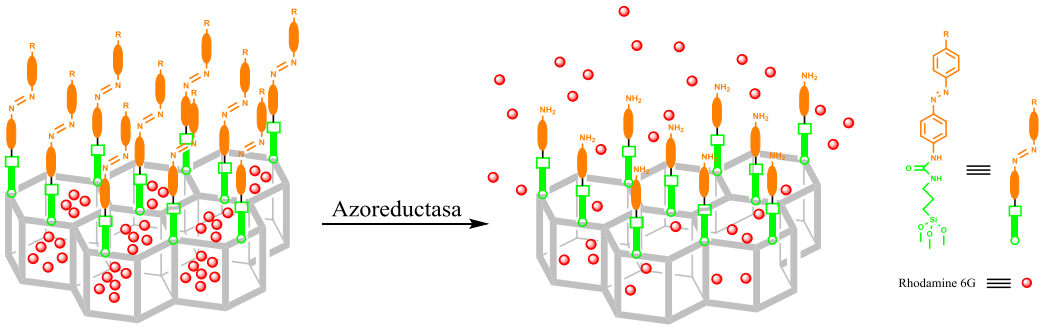
Palabras Clave: *MCM-41, mucosa colónica, liberación controlada.*

Los materiales mesoporosos de sílice, como el MCM-41 han demostrado recientemente ser sistemas adecuados para la encapsulación y liberación de fármacos.[1] Un nuevo avance en la liberación controlada de fármacos en lugares específicos es el uso de los llamados "materiales inteligentes", inspirados en bio-canales y bio-puertas.[2]

Para conseguir una liberación controlada de distintos tipos de fármacos (5-ASA, budesonida o azatioprina) para el tratamiento de la *Colitis Ulcerosa* y *Enfermedad de Crohn* (enfermedades autoinmunes producidas en el íleo y colon) se han diseñado y desarrollado materiales microestructurados basados en MCM-41 modificados químicamente, que incorporan puertas moleculares conteniendo grupos *azo*. Es sabido que el enlace *azo* se rompe específicamente por la acción de la flora bacteriana autóctona (enzimas azoreductasas) en el intestino grueso por lo que una puerta molecular que contuviera dicho grupo funcional sería útil para la liberación controlada del fármaco en la mucosa colónica.[3] Las puertas moleculares han sido cargadas con un colorante (Rodamina 6G) con el objetivo de estudiar la liberación en condiciones reductoras mediante UV-vis.



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COVALENT LINKAGE OF SELF-ASSEMBLING CYCLIC PEPTIDES

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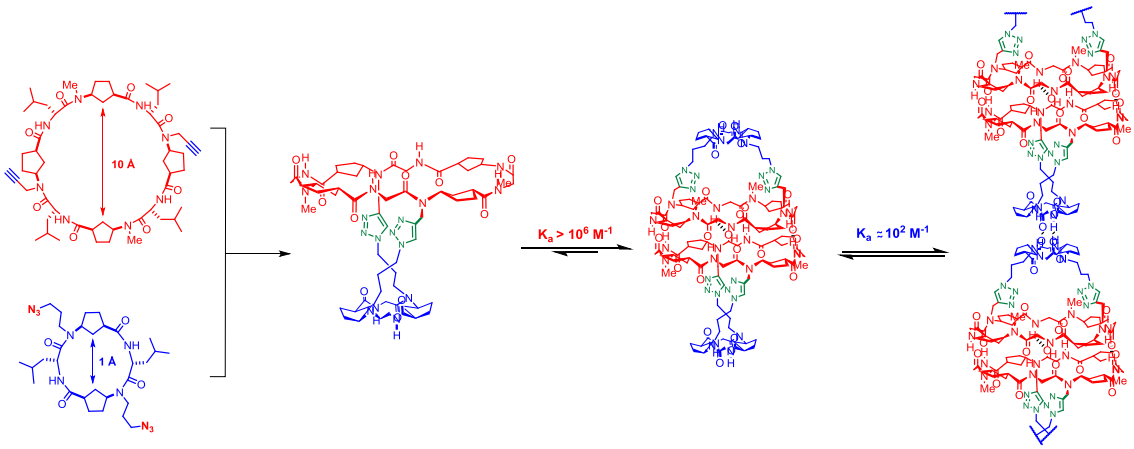
Keywords: *nanoscience, nanotube, cyclic peptide, supramolecular chemistry*

Having access to molecular materials with defined properties and dimensions in the nanometer scale is becoming a goal of crescent interest nowadays due to the recent advances in several disciplines, such as nano-electronics,[1a] nano-optics[1b] or nano-medicine[1c].

Particularly, peptide nanotubes present remarkable advantages over other tubular nanostructures (especially inorganic).[2] They can exhibit different properties on the inner and outer surface and the diameter can be precisely adjusted depending on the type and/or number of amino acids contained in the cyclic peptide.[3]

In this work, we present a novel alternative for the formation of peptide nanotubes with filter areas by alternating dimers of different sizes. For this purpose, covalent linked α,γ-cyclic peptides were designed. With this design, it is still possible to achieve the supramolecular stacking of two cyclic peptides through non-functionalized faces. The minimal component of these new nanotubes are molecular capsules that can eventually self-assemble into a nanotube.



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BOWL MEETS BOWL: SUPRAMOLECULAR COMPLEXATION BETWEEN BUCKYBOWLS AND CONCAVE TRUXENE-DERIVATIVES

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Keywords: *Buckybowls, truxTTF, supramolecular complexation.*

Some carbon nanoforms, namely fullerenes, carbon nanotubes and graphene, have attracted a great deal of attention in different areas of research due to their singular and extraordinary properties. The molecular fragments of these carbon nanoforms have been significantly less studied, despite the interest they raised as new curved and electroactive species. Up to now, the coordination of metal cations by fullerene fragments had been studied and these fragments had also been used to construct concave receptors for fullerenes. However, supramolecular complexation studies of fullerene fragments by other organic hosts have not been so widely investigated. In this communication, we present the first reported study of a supramolecular association of a fullerene fragment, the hemifullerene $C_{30}H_{12}$ with a bowl-shaped electron donor molecule based on a truxene core to which three dithiole rings are covalently attached (truxTTF), to form heteromolecular bowl-bowl donor-acceptor complexes.[1] Furthermore, we will discuss the formation of four new truxene-derivative•buckybowl heterodimers among the truxene derivatives truxTTF and its electron-acceptor analogue trux6CN with the buckybowls $C_{32}H_{12}$, $C_{30}H_{12}$ and $C_{38}H_{14}$, to form the truxTTF•$C_{32}H_{12}$, the truxTTF•$C_{38}H_{14}$, the trux6N•$C_{30}H_{12}$ and the trux6CN•$C_{32}H_{12}$ supramolecular heterodimers. To carry out these studies, where the π–π interactions primarily act between the curved species, UV-vis titrations were performed. Theoretical calculations, (revPBE0-D3 functional) for structural and energetic characterization, and photophysical studies nicely complement this work.

Studied (truxene-derivative•buckybowl) heterodimers

truxTTF•$C_{30}H_{12}$ truxTTF•$C_{32}H_{12}$ truxTTF•$C_{38}H_{14}$ trux6CN• $C_{30}H_{12}$ trux6CN• $C_{32}H_{12}$

Calbo, J. Aragó, R. Krick-Calderón, F. H. Líquido, T. Iwamoto, A. K. Greene, E. A. z, E. Ortí, D. M. Guldi, L. T. Scott, N. Martín, *Angew. Chem., Int. Ed.* **2014**, *53*, 2170-

S2: *Nanociencia y Materiales Moleculares*

NEW HOLE TRANSPORTING MATERIALS FOR PEROVSKITE SOLAR CELLS

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Keywords: *holetransportingmaterials, perovskite, photovoltaics*

Because of the pollution, global warming and degradation of our planet, a new era base on non-contaminating renewable energies is currently a priority. In this regard, the Sun represents the most powerful source of energy available in our solar system and therefore, its use for providing energy to our planet is one of the most important challenges in science. [1]

Recently, the organometal halide perovskites (CH3NH3PbX3, X = Cl, Br, I) have attracted great attention due to their direct band gap, large optical absorption and high mobility. Recently, an impressive photovoltaic performance has been achieved using 2,2',7,7'-tetrakis-N,N-di (4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD) as hole transporting material (HTM). Actually, a power conversion efficiency surpassing 20% has been achieved.[2] However, the high synthetic cost of spiro-OMeTAD is a serious problem for commercialization.[3] Therefore, the development of cost-effective HTMs with high efficiency along with a better stability is an important task to address. We report on four new hole transporting compounds based on diphenylamino or carbazole electron-donor units covalently connected through tetraphenylethene[4] or 9,9'-bifluorenylidene[5] as shown in figure 1.

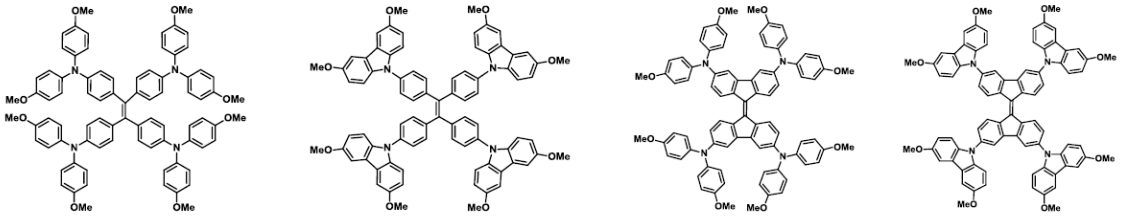

Figure 1. Chemical structures of four new HTMs.

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S2: *Nanociencia y Materiales Moleculares*

PREDICTION OF HYDRODYNAMIC PROPERTIES OF DILUTE SUSPENSIONS OF PLANAR NANOPARTICLES OF ARBITRARY SHAPE

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Key words: *Flat nanoparticles / Nanosheets / Platelets / Diffusion coefficients / Suspension viscosity / Hydrodynamics / Modelling /*

The development of theoretical/computational methodologies for calculating hydrodynamic properties of macromolecules and colloidal particles in dilute conditions has been, since the pioneering studies of Einstein, an essential goal in colloid and polymer science, biophysics, and nowadays in the new field of nanotechnology. Our group has pursued this goal over the years, employing the so-called bead-modelling methodologies. For rigid particles of arbitrary shape, we have developed procedures that are easily applicable to 3D structures [1] Garcia de la Torre The relevance of that development for the interpretation of hydrodynamic properties of well-defined clusters of nanoparticles has been demonstrated recently [2,3]. Flat, thin essentially 2D nanoparticles are well known in colloid science as typical structures for some clays (gibbsite, bentonite, etc) and are being presented by newly obtained metal and graphene-like materials. The design of efficient, robust and user-friendly computational tools able to predict properties of such planar nanoparticles is complicated by their high aspect ratio (surface to thickness), and requires a different approach than in 3D. We have developed computational procedures for making such modelling work accessible. The high-aspect-ratio problem has been solved in terms of a convenient combination of particle's surface area and thickness. The computational tools developed for this purpose, which are ancillary programs that interface with HYDRO++ [1], will be of public domain, available from our software repository [4]

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S2: *Nanociencia y Materiales Moleculares*

SOFT MATERIALS BASED ON SELF-ASSEMBLED DENDRONS BY HYDROGEN BONDS AND/OR METAL COMPLEXATION

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Keywords: *liquid crystal, molecular gel, supramolecular polymer, H-bond, gold.*

Liquid crystals and molecular gels are fascinating examples of soft matter in which the molecules self-assemble into complex systems through non-covalent interactions such as π-stacking, H-bond or van der Waals forces. There is an increasing interest in their study as they give rise to supramolecular architectures with a control at the nanoscale, and potentiality to respond to different external stimuli such as temperature, pressure, pH, light, etc, which are beneficial attributes to reach efficient responsive materials for sensors, organic electronics or biomedicine [1,2].

Our interest in this kind of structures [3,4] have led us to design novel dendron-like molecules with a 3,5-dimetil-1*H*-pirazol at the focal point, due to the versatility of the pyrazole ring to interact by hydrogen bonding, or act as a ligand in coordination compounds. In particular, several gold group cyclic trinuclear complexes using pyrazolate dendrons and other basic pyrazoles have also been prepared. Liquid crystal phases in which the molecules arrange in columns giving rise to hexagonal columnar mesophases by supramolecular interactions are observed.

In addition, the pyrazole dendrons are excellent organogelators, due to the formation of fibers able to entrap large quantities of organic solvents (supergelators). In addition, they show fluorescence in the visible spectra with aggregation induced enhanced emission (AIEE).

Acknowledgement

The authors thank the Gobierno de Aragón - Fondo Social Europeo (FSE) (research group E04), the Spanish Ministerio de Economia y Competitividad (MINECO) - Fondo Europeo para el Desarrollo Regional (FEDER) (projects CTQ2012-35692, CTQ2011-22516, and MAT2012-38538-CO3-01) and Cátedra IQE for financial support.

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S2: *Nanociencia y Materiales Moleculares*

INTERFACIAL SELF-ASSEMBLY OF PLASMONIC NANOPARTICLES

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Keywords: *Nanoparticles, Plasmon coupling, SERS, Interfaces*

The air/liquid interface is an advanced platform for self-assembling large monolayers of inorganic nanoparticles.[1] A broad range of size and shapes of nanoparticles can be self-assembled given the adequate functionalization. The nanoparticles assembled using this route yield close-packed monolayers with small interparticle distance. This architecture promotes a large plasmon coupling, of huge interest for the application of these monolayers in surface-enhanced spectroscopy, such as SERS.

We design plasmonic substrates based on self-assembly of functionalized plasmonic nanoparticles at the air/water interface by two approaches. First, a PVP polymer coating of Au nanotriangles.[2] Second, a combination of hydrophobic thiols with PEG polymer.[3] In both cases, the self-assembled monolayers have been transferred to solid substrates. The SERS features of these plasmonic substrates are assessed.

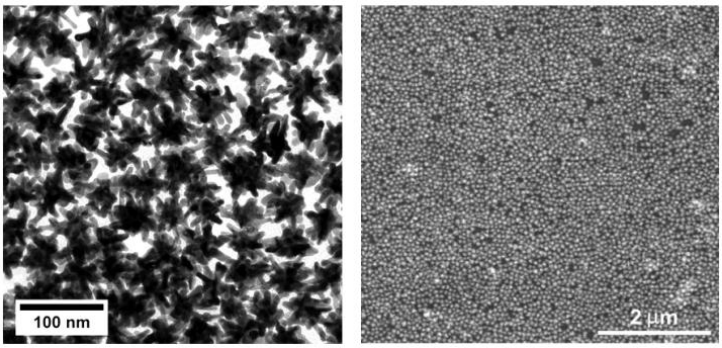

Figure Self-assembled plasmonic substrates of Au nanostars. Left and right, TEM and SEM images, respectively.

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S2: *Nanociencia y Materiales Moleculares*

THERANOSTIC NANOMATERIAL: DINUCLEAR Gd(III) COMPLEX BASED MAGNETIC RESONANCE IMAGING AND pH-CONTROLLED ANTICANCER DRUG DELIVERY

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Keywords: *gadolinium; doxorubicin; nanomaterials; theranostic; pH*

Recent studies have focused on the development of nano and bio-functionalized metal complexes as delivery vehicles for imaging and therapy applications [1]. Since many nanomaterials enter cancer cells via endocytosis and coordination bonds are pH-sensitive, the use of nanomaterials based on metal complexes offers excellent potential for pH-controlled drug release [2]. Release of drugs at low pH is highly desirable considering that tumors and intracellular organelles, such as endosomes and lysosomes, are acidic. Recently, it was reported that Gd(III) complexes containing two 2,2',2''-(1,4,7,10-tetraazacyclododecane-1,4,7-triyl) triacetic acid (DO3A) units linked by the 4,4'-dimethyl-2,2'-bipyridyl spacer aggregate to form stable Gd(III) nanosized coordination particles (GdNPs) in aqueous solutions with excellent properties for magnetic resonance imaging [3]. Here we report the use of specific moieties within these self-assembled dinuclear Gd(III) complexes as carrier sites with capability of coordinating and releasing the anticancer drug (doxorubicin, DOX) in response to small pH variations. The conjugation of DOX to GdNPs is demonstrated by UV-vis and fluorescence spectroscopy studies. These studies indicate that the resulting drug conjugate GdDOX is stable at physiological pH with DOX being released at mildly acidic pH. Transmission Electron Microscope (TEM) and Dynamic Light Scattering (DLS) measurements of GdDOX reveal the presence of clusters composed of nanoparticles of *ca.* 14 nm in diameter. Cytotoxicity studies show that the GdNPs are not toxic in prostate cancer cells (PC3). In contrast, GdDOX show similar IC_{50} to the free drug, suggesting rapid and efficient drug transport and release. Flow cytometry studies confirm that GdDOX allows rapid intracellular drug delivery. T1-weighted images as well as relaxometric studies show that GdNPs and GdDOX provide higher r_1 (12 $mM^{-1}.s^{-1}$ and 8 $mM^{-1}.s^{-1}$, respectively) than current clinical Gd(III) chelates (Gadovist®; $r_1 \approx 4$ $mM^{-1}.s^{-1}$). Thus, GdDOX exhibits several desirable properties for the combination of cancer therapy and imaging-based diagnosis (theranostics).

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S2: *Nanociencia y Materiales Moleculares*

NEW SERS SUBSTRATES MADE OF POLYMERS AND ALUMINIUM

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Keywords: *SERS and Al, PFPE, Ormocers, Nanostructures, plasmonics, UV-NIL*

Surface Enhanced Raman Scattering (SERS) uses nanoparticles or structured metal surfaces typically made of noble metals, commonly gold or silver. Laser excitation of these metal nanostructures resonantly drives the metal surface charges creating highly localized plasmonic light fields at these photonic structures, which we know as hot-spots [1]. When a molecule is bonded, adsorbed or lies close to the enhanced field of a hot-spot at the surface, a large enhancement in the Raman signal can be observed, -usually of several orders of magnitude- thereby making it possible to detect concentrations as low as 10^{-18}M of target molecules [2]. The main problem to use SERS as everyday lab technique is the lack of appropriate substrates. Available commercial substrates are scarce, expensive and quite unstable, requiring to keep them in controlled atmospheres and a careful handling to maintain their enhanced properties. Important research efforts try to provide cheap and reliable substrates [3]

In this work we show our results testing home-made SERS substrates based in an easy and cheap fabrication process comprising just two steps: a replica molding based on a UV-NIL like process, and coating of a thin metal layer. As supporting material we synthesized a crosslinkable tetrafuntional perfluoropolyether derivate [4], and a commercial ormocer photoresist. The experiments show an uniform SERS enhancement of several orders of magnitude over the structured substrates when tested with organic dyes, antibiotics, graphene and others, using a excitation laser of 785nm working at 1 or 0.1mW . Signal enhancement is comparable or higher than that obtained with commercial substrates. Aluminum coated substrates with comparable or even better signal enhancement respect to the same substrates made of gold reduce cost of these substrates. Additionally no change in the intensity of the spectra was observed after a month of storage at room conditions.With this simple, fast and versatile molding process, it is possible to produce polymer SERS substrates with extremely low cost, high throughput, and in a highly repeatable way.

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S2: *Nanociencia y Materiales Moleculares*

COPOLÍMEROS DE BLOQUE CON DENDRONES RÍGIDOS

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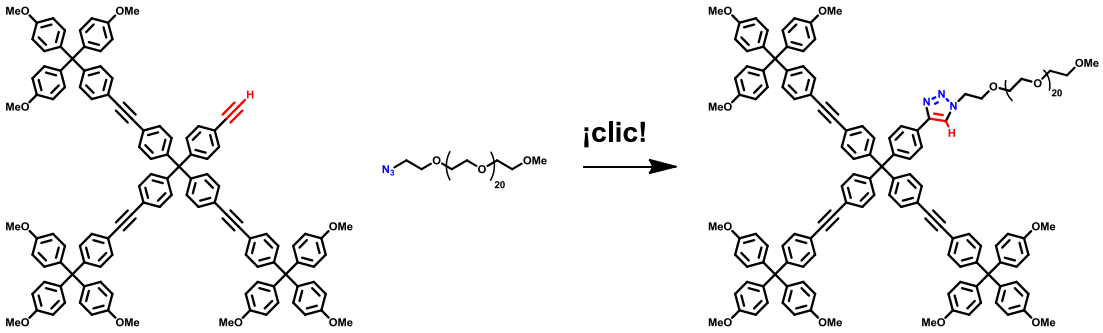
Palabras Clave: *copolímero, química clic, dendrón, polietilenglicol, autoensamblaje, nanotecnología*

Dentro del área de los copolímeros de bloque, en los últimos años están despertando gran interés los copolímeros en los que al menos uno de los bloques tiene estructura dendrítica [1].

En nuestro trabajo sintetizamos copolímeros de bloque con estructuras dendrítico-lineal (DL) [2] y dendrítico-lineal-dendrítico (DLD). Para uno de los bloques empleamos dendrones derivados de tetrafenilmetano, que poseen forma globular persistente y un alquino terminal en su punto focal [3]. Mediante química clic se une el bloque lineal de polietilenglicol mono- o difuncionalizado con azidas terminales. La unión de estos bloques con propiedades diferentes origina híbridos copoliméricos capaces de formar distintas morfologías autoensambladas que dependen de las dimensiones de cada uno de los bloques.

El interés de estos compuestos no solo radica en sus estructuras fascinantes, si no que se trata de prometedores materiales para diversas aplicaciones avanzadas en el campo de la nanotecnología.



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S2: *Nanociencia y Materiales Moleculares*

PREPARACIÓN Y COMPORTAMIENTO MAGNETICO DE FERRITAS $Fe_{1-x}M_xFe_2O_4$ (M = Ni, Mn) CON APLICACIONES BIOMÉDICAS

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Palabras Clave: *nanopartículas, ferritas, superparamagnetismo, hipertermia, citotoxicidad.*

Las nanopartículas magnéticas son materiales muy prometedores en áreas como la biomedicina, almacenamiento energético o catálisis. Concretamente, su comportamiento superparamagnético a nivel nanométrico posibilita aplicaciones tanto terapeúticas como en diagnosis, en las áreas de transporte y liberación de fármacos, hipertermia magnética o imagen [1]. La hipertermia magnética, basada en el calentamiento producido por estos materiales cuando son sometidos a un campo magnético alterno, puede aplicarse en terapias para la generación de un calentamiento local en zonas tumorales sin dañar los tejidos sanos adyacentes, para lo cual es imprescindible un control exhaustivo del tamaño medio del núcleo magnético, su forma y cristalinidad. El trabajo que presentamos se enmarca en este contexto y tiene como objetivo la preparación de ferritas con altos valores de imanación y biocompatibilidad.

Así, se presenta la optimización de un proceso sintético basado en la descomposición térmica de precursores de hierro (y níquel o manganeso dependiendo de la estequiometría) en dibencil éter, en presencia de 1,2-hexadecanodiol, ácido oleico y oleilamina para la obtención de nanopartículas (NP) magnéticas con tamaños controlados en el intervalo de 10 – 20 nm. Las nanopartículas sintetizadas han sido transferidas a agua mediante la incorporación de un ligando anfifílico. Se ha llevado a cabo la caracterización química, estructural y morfológica mediante análisis termogravimétrico, difracción de rayos X, scattering de luz dinámico (tamaño y potencial Z) y microscopia de transmisión electrónica (TEM).

Las muestras presentan un comportamiento superparamagnético con valores de imanación próximos a 90 emu/g$_{Fe_3O_4}$ y que varían con el contenido de níquel o manganeso. La espectroscopía de resonancia magnética electrónica (EMR) muestra una relación directa entre la posición del campo resonante (H_{ef}) y la anchura de linea pico a pico con el tamaño con el tamaño y la monodispersidad de las muestras. Finalmente, para el caso de las nanopartículas con mejor respuesta magnética se ha estudiado su citotoxidad en un medio celular.

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S2: *Nanociencia y materiales moleculares*

SILICA SUPPORTED Rh-NPs STABILIZED BY P-BASED LIGANDS FOR SELECTIVE HYDROGENATION REACTIONS

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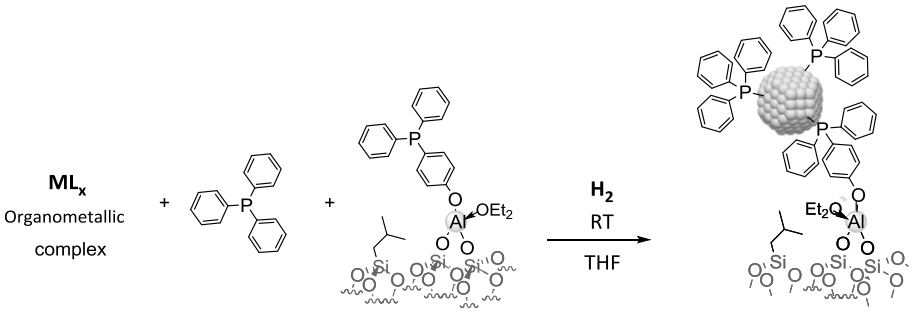
Keywords: *Nanoparticles, supported, hydrogenation*

In the last decade, P-based ligands were also shown to efficiently stabilise metal nanoparticles (M-NPs) that catalyse the hydrogenation of various substrates.[1] However, to date, the fine tuning of the properties of this type of catalysts to achieve specific selectivities remains a challenge. Recently, the synthesis of Rh-NPs stabilised by P-donor ligands and their application in the partial hydrogenation of arenes and in the selective hydrogenation of aromatic ketones was reported.[2]

In this project, surface organometallic chemistry (SOMC) approach was used to support metal NPs stabilised by P-based ligands as it provides accurate synthetic strategies to obtain well defined supported catalysts.[3] The main objective of this approach is the transfer of concepts and tools from molecular chemistry to surface science, affording heterogeneous catalysts able to perform selective chemical transformations. Surface organometallic chemistry provides relevant information for supported catalytic systems with the formation of well defined species, which allows a better understanding of their reactivity/selectivity.[4]

This work, describes the anchoring of metal nanoparticles synthesized using the organometallic approach [5] in presence of a phosphine anchored on silica. The nanoparticles have small diameter (~2nm) and are well dispersed on the support. This strategy could be applied to several metals (Rh, Ru, Pt, Au) and the materials obtained could be use as catalysts for hydrogenation of arenes for instance.



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S2: *Nanociencia y materiales moleculares*

CARBON-BRIDGE OLIGO-p-PHENYLENEVINYLENES: MOLECULAR INSIGHTS FROM SPECTROSCOPY

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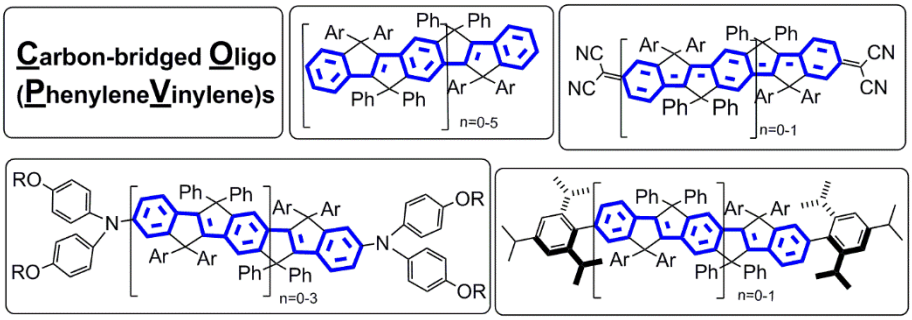
Keywords: *COPVs, molecular electronics, Raman spectroscopy, spectroelectrochemistry, spectrochemistry, density functional calculations.*

Linearly fused aromatic systems are attacting much interest because of their utility in organic electronic devices. In this line, carbon-bridged oligo-*p*-phenylenevinylenes (COPVs) [1] have resulted in outstanding molecular wires [2] because of the high responsiveness to doping and photoexcitation as well as their great chemical stability [3,4].



Hereby we present an extensive spectroscopic study (including Raman spectroscopy, spectrochemistry and spectroelectrochemistry jointly with theoretical calculations) of the unsubstituted COPV family (from monomer to hexamer) highlighting the effects of planarization, fusion and ring strain in their electronic structure. For the charged species, mixed-valence behavior and biradical character will be addressed. To complete the analysis, COPV derivatives with quinoidal structures are also analyzed.

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S2: *Nanociencia y Materiales Moleculares*

COLORIMETRIC SENSING OF DICARBOXYLATES USING FUNCTIONALIZED GOLD NANOPARTICLES

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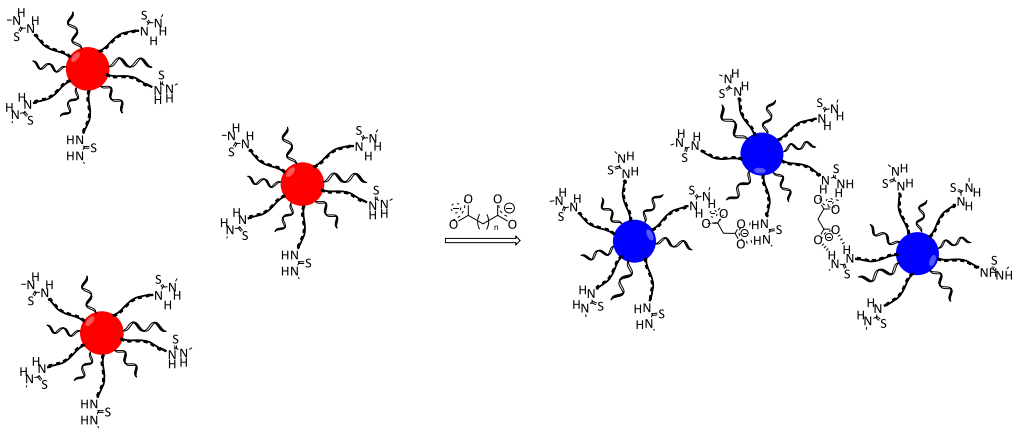
Keywords: *Dicarboxylates, sensors, gold nanoparticles, molecular recognition.*

In recent years, functionalized gold nanoparticles (AuNPs) have attracted growing attention in colorimetric sensing in the chemical and biological sciences owing to their tunable photophysical properties.[1] The visual-sensing ability of AuNPs relies on changes in the surface plasmon resonance (SPR), which is dependent on the aggregation state and the surface morphology. Generally, the aggregation of AuNPs in solution through analyte-triggered interparticle cross-linking leads to a change in color from red to blue or purple, which is useful for observing molecular-recognition events. The interparticle cross-linking requires a "three-body" molecular-recognition event between a ditopic analyte and two nanoparticles.[2] Such molecular interactions can be dependent on the directionality of two interacting end groups of the analyte, and thus may be used for specific sensing purposes such as the selective sensing of organic compounds.

Dicarboxylate anions are biologically important molecules and their detection in aqueous media is of high interest.[3] We have synthesized gold nanoparticles functionalized with thiourea derivates as a colorimetric sensing system for dicarboxylate recognition in aqueous media. The sensing paradigm is depicted in the Figure.



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POSTSYNTHETIC IMPROVEMENT OF THE PHYSICAL PROPERTIES IN A METAL-ORGANIC FRAMEWORK THROUGH A SINGLE CRYSTAL TO SINGLE CRYSTAL TRANSMETALLATION

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Keywords: *Metal-Organic Frameworks, Transmetallation, Magnetism, Gas Adsorption*

In this work, we report the synthesis, structural characterization, and the magnetic and gas sorption properties of a novel oxamato-based three-dimensional (3D) Metal-Organic Framework (MOF) of formula $Ni^{II}_2\{Ni^{II}_4[Cu_2(mpba)_2]_3\}\cdot 50H_2O$, where mpba is the *N,N'*-1,3-phenylenebis(oxamate) ligand. This system was obtained by a single-crystal to single-crystal transmetallation process from the previously synthesized ancestor of formula $Na_4\{Mn_4[Cu_2(mpba)_2(H_2O)_4]_3\}\cdot 72.65H_2O$ [1]. After the complete replacement of the Mn^{II} ions within the covalent network and the Na^{I} ions hosted in the large octagonal channels of $Na_4\{Mn_4[Cu_2(mpba)_2(H_2O)_4]_3\}\cdot 72.65H_2O$ by Ni^{II} ions (Figure 1), an increase of the robustness occurs in the resulting 3D MOF, which is also reflected in a drastic improvement of the magnetic and gas sorption properties. [2]

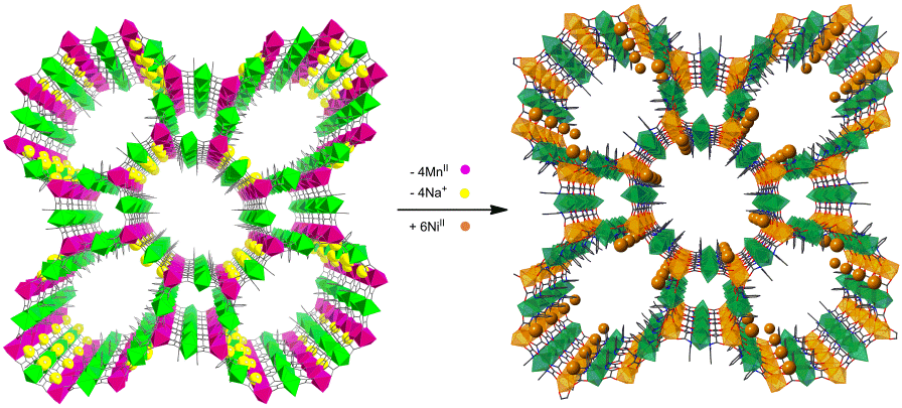

Figure 1. Perspective view of $Na_4\{Mn_4[Cu_2(mpba)_2(H_2O)_4]_3\}\cdot 72.65H_2O$ and $Ni^{II}_2\{Ni^{II}_4[Cu_2(mpba)_2]_3\}\cdot 50H_2O$ along the crystallographic c axis.

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SYNTHESIS, CHARACTERIZATION AND MAGNETIC PROPERTIES OF OCTAHEDRAL Mn(III)-PORPHYRINATO COMPLEXES

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Keywords: *Mn(III)-Porphyrinato complexes, Magnetic properties, HFEPR*

There are few examples of mononuclear manganese(III) complexes exhibiting slow magnetic relaxation effects which are typical of molecular nanomagnets. By analogy, these new kind of systems are called single-ion magnets (SIMs).[1]

In this communication, we report a complete study on the synthesis and structural characterization, spectroscopic and magnetic properties, and theoretical calculations of 0D and 1D Mn(III) compounds: $[Mn^{III}(TPP)(py)_2]BPh_4$ (**1**), $\{[Mn^{III}(TPP)(\mu\text{-bipy})]BPh_4\}_n$ (**2**) and $\{[Mn^{III}(TPP)(\mu\text{-dpbz})]ClO_4\}_n$ (**3**) [H_2TPP = 5,10,15,20-tetraphenylporphine, py = pyridine, bipy = 4,4'-bipyridine, dpbz = 1,4-di(pyridine-4-yl)benzene] (Figure 1). This study increases the number of octahedral Mn(III) systems with porphyrinato ligands and allows to compare the effect of the coordination environment of the metal ion on the magnetic properties.[2]

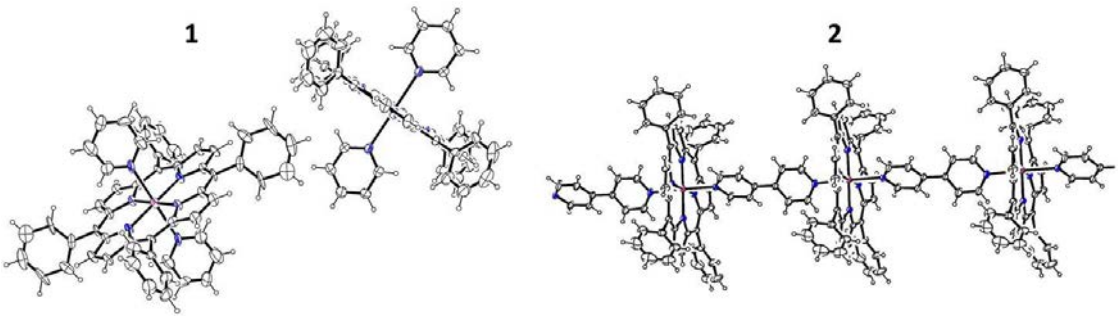

Figure 1. Crystal structures of complexes **1** and **2**

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S2: *Nanociencia y Materiales Moleculares*

SYNTHESIS, PHOTOPHYSICAL AND ELECTROCHEMICAL STUDIES OF NOVEL PUSH-PULL PYRIMIDINE CHROMOPHORES

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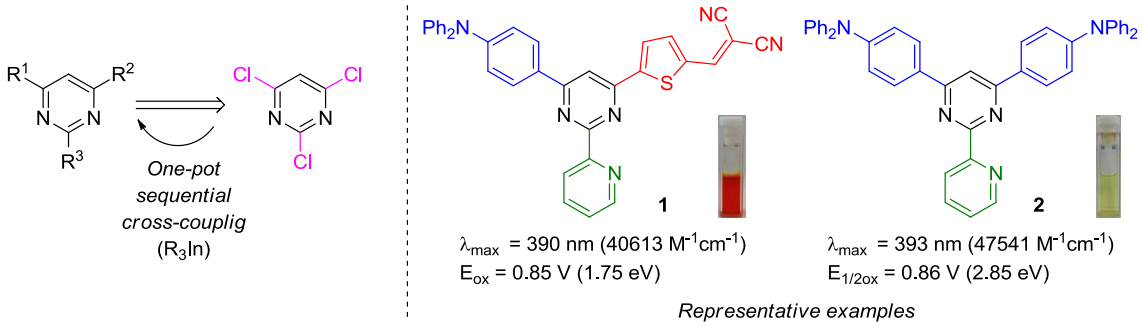
Keywords: *push-pull, pyrimidine, chromophores, cross-coupling, triorganoindium reagents.*

Push-pull chromophores based on highly conjugated molecules, composed by electron-donating (D) and electron-withdrawing (A) moieties linked by a π-conjugated bridge represent an important class of compounds in the field of organic materials. In this research area, pyrimidine derivatives have received intensive research with applications in various fields.[1] In this communication we report the synthesis, photophysical and electrochemical studies of novel type of push-pull pyrimidine derivatives, following a one-pot sequential selective palladium-catalyzed cross-coupling reactions of different organoindium reagents (R_3In) with 2,4,6-trichloropyrimidine in high yields.[2]



The electronic properties of pyrimidine derivatives have been analyzed by UV-visible absorption spectroscopy and cyclic voltammetry. The cyclic voltammogram of **2** exhibit a two-electron reversible oxidation process, whereas compound **1** exhibit only a one-electron reversible oxidation process, assigned to the diarylamine units. Further studies are in progress and will be present in the communication.

Acknowledgements: We are grateful to the Ministerio de Economía y Competitividad (CTQ2012-31200) for financial support.

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Au@pNIPAM SERRS TAGS FOR MULTIPLEX IMMUNOPHENOTYPING CELLULAR RECEPTORS AND IMAGING TUMOR CELLS

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Keywords: *bioimaging, SERRS, gold nanoparticles, microgels, multiplex*

Detection technologies employing optically encoded particles have gained much interest toward clinical diagnostics and drug discovery, but the portfolio of available systems is still limited. We report the fabrication and characterization of highly stable surface enhanced resonance Raman scattering (SERRS)-encoded colloids, for the identification and imaging of proteins expressed in cells. These plasmonic nanostructures are made of gold octahedra coated with poly(isopropylacrylamide) (Au@pNIPAM) microgels and can be readily encoded with different Raman active dyes (Astra blue, Nile blue and Malachite green) while retaining high colloidal stability in biofluids. A layer-by-layer polyelectrolyte coating was used to seal the outer surface of the encoded particles and to provide a reactive surface for covalent conjugation with antibodies. The targeted multiplexing capabilities of the SERRS tags was demonstrated by the simultaneous detection and imaging of three tumor-associated surface biomarkers EGFR, EpCAM and CD44 by Raman spectroscopy. The plasmonic microgels were able to discriminate tumor A431 (EGFR+/EpCAM+/CD44+) and non-tumor 3T3 2.2 (EGFR-/EpCAM-/CD44+) cells while co-cultured in vitro.

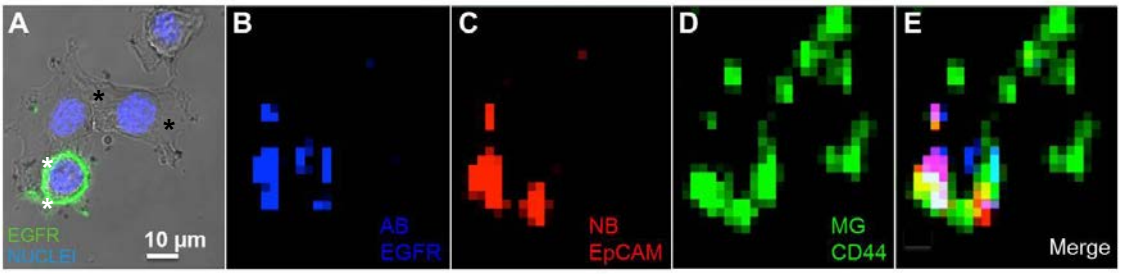

Figure 1. Multiplex detection and imaging of EGFR, EpCAM and CD44 by SERRS. (A) Bright field and confocal fluorescence microscopy image showing A431 (EGFR positive) and 3t3 2.2 (EGFR negative) cells. (B-E) SERRS mappings recorded in the same area using the 748 cm^{-1} peak of AB (B), 592 cm^{-1} peak of NB (C), 420 cm^{-1} peak of MGI (D), and merged image (E) of the three mappings.

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Au@Pd NANORODS: SYNTHESIS, OPTICAL PROPERTIES AND REFRACTIVE INDEX SENSITIVITY

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Keywords: *Pd, Plasmonic nanoparticles, refractive index sensitivity*

Commonly used plasmonic sensing materials such as Au and Ag usually display a shape and size-dependent susceptibility of the localized surface Plasmon resonance peak to medium refractive index changes. Recently, plasmonic Palladium has been proposed as a third plasmonic sensing material, showing.[1] The refractive index sensitivity it has been found to 2.5 times higher for Au@Pd spheres compared to Au spheres.

Elongated gold nanoparticles (nanorods and nanobipyramids) have been reported to exhibit the highest refractive index sensitivity. Therefore, analyzing the index sensitivity for elongated Pd nanoparticles should give rise to an improvement of the optical response. Unfortunately, the synthesis of Pd nanoparticles with size and shape control and with high monodispersity is not trivial. To overcome these limitations we proposed a novel method to synthetized Au@Pd nanorods based on the seed-mediated method where penta-twinned gold nanorods (PTW) are used as seeds. Palladium reduction will take place preferential at the tips of the nanorods leading to an increased in the aspect ratio of the particles and to a red-shift of localized surface Plasmon resonance (Fig.1).

The refractive index sensitivities for PTW and PTW@Pd nanoparticles were studied supported on glass slides which were immersed into water and ethanol-chloroform mixtures. The PTW@Pd particles are found to exhibit a higher index sensitivity compare to the PTW counterparts. These Au(core)/Pd(shell) nanoparticles exhibit a plasmonic response to hydrogen.

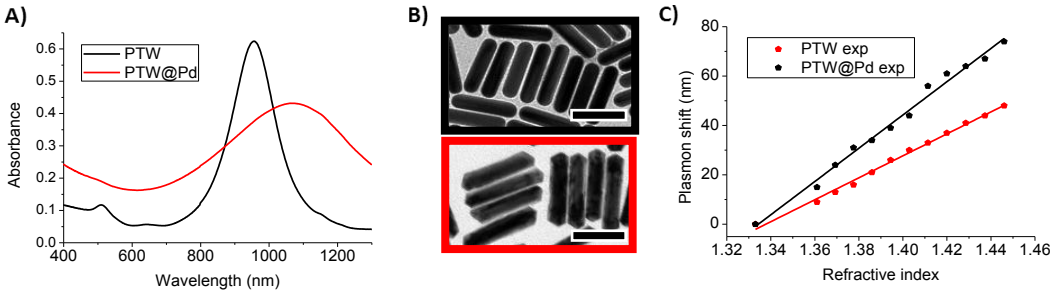

Fig 1. A) NIR-vis spectra of Au PTW nanorods (black line) Au PTW nanorods (red line)

B) TEM images of Au PTW nanorods (black line) Au PTW nanorods (red line) samples. Scale bar is 100nm.

C) Dependence of the longitudinal plasmon shift on the refractive index of the liquid mixture for PTW and PTW@Pd. The lines are linear fits.

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ESTUDIO DE LA ESTRUCTURA SECUNDARIA EN POLIFENILACETILENOS: LANGMUIR-SCHEAFER Y AFM

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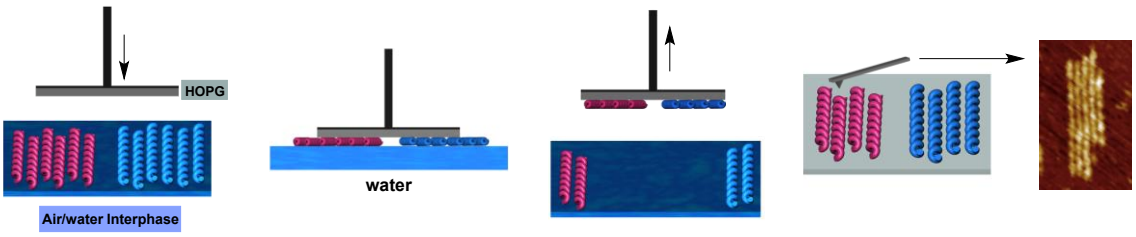
Palabras Clave: *Polifenilacetileno*, Estructura Secundaria, *AFM, Monocapas, Langmuir-Scheafer*

A lo largo de los últimos años uno de los grandes retos en el campo de polímeros helicoidales ha sido la elucidación de la estructura secundaria de estos mismos; para ello diversas técnicas complementarias como son el dicroísmo circular (CD), la calorimetría diferencial de barrido (DSC), RMN y Raman han sido usadas. Sin embargo el único modo de conocer los parámetros helicoidales como son el sentido de giro, el ángulo de empaquetamiento y la distancia de paso helicoidal, necesarios para elucidar la estructura secundaria que adopta el polímero es mediante la microscopía de fuerza atómica (AFM) [1,2]. Uno de los mayores retos consiste en la formación de dichos cristales [3,4], en esta comunicación presentamos una nueva aproximación para generar monocapas poliméricas mediante la técnica de Langmuir-Scheafer; que mediante un posterior análisis por AFM permite obtener los parámetros estructurales necesarios que nos permitan obtener la estructura 3D del polímero .



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S2: *Nanociencia y Materiales Moleculares*

SEGURIDAD Y SALUD EN EL TRABAJO CON NANOMATERIALES

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Palabras Clave: *nanomateriales, exposición, seguridad, salud, evaluación, prevención*

En España, como en otros países, el número de aplicaciones comerciales de los nanomateriales manufacturados está creciendo a un ritmo acelerado. Actualmente, la seguridad y salud en el trabajo con nanomateriales se enfrenta a una situación en la que casi todos los aspectos a tener en cuenta presentan lagunas de conocimiento debido a una limitada información en aspectos como los efectos para la salud, la eficacia real de los sistemas de ventilación y de los equipos de protección individual así como la falta de Límites de Exposición Profesional (LEP) y de definición de la métrica adecuada para determinar la exposición a los nanomateriales.

La legislación europea no contempla un marco específico para los nanomateriales, sin embargo tal y como ha expresado la Comisión Europea [1-3], en función de su peligrosidad y las condiciones de trabajo presentes, les será de aplicación la normativa de seguridad y salud existente. En este sentido, el INSHT elabora documentos para orientar a empresarios y responsables de prevención en el cumplimiento de sus obligaciones y garantizar una protección adecuada de los trabajadores expuestos a nanomateriales [4].

Por otra parte, teniendo en cuenta la información existente, el planteamiento propuesto por el INSHT para la evaluación de riesgos a nanomateriales es similar al empleado en la exposición a agentes químicos, siendo esencial recoger la máxima información posible sobre los materiales, los procesos implicados y los trabajadores potencialmente expuestos. Asimismo, las actuaciones preventivas deben orientarse a eliminar la exposición y, si no es posible, a reducirla al nivel más bajo técnicamente posible, todo ello siguiendo la legislación laboral y las orientaciones proporcionadas por instituciones u organizaciones de reconocido prestigio. Finalmente, la experiencia adquirida y la incertidumbre actual sobre los efectos de los nanomateriales en la salud indican la importancia de complementar y evaluar las medidas de control con una vigilancia periódica de la salud de los trabajadores que detecte precozmente cualquier efecto adverso, disfunción o síntoma que pudieran presentar.

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[4] Seguridad y salud en el trabajo con nanomateriales, INSHT, *en imprenta*.

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EMPLEO DE PELÍCULAS DE SÍLICE MESOPOROSA ORDENADA EN ANÁLISIS ELECTROQUÍMICO

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Palabras Clave: *Películas de sílice mesoporosa, Electroanalisis, Biosensores*

La modificación de la superficie de electrodos mediante nanomateriales mesoestructurados, los cuales poseen unas propiedades fácilmente controlables en cuanto a porosidad, espesor, funcionalidad química, permite el diseño de novedosas estrategias sin necesidad de recurrir a marcadores externos (label-free). En este sentido, la electrodeposición *in situ* de películas delgadas de sílice mesoporosa, con tamaño y orientación de los poros bien definidos [1], presenta la ventaja de formar estructuras rígidas, fáciles de modificar con numerosos grupos funcionales y con un crecimiento controlado.

En el presente trabajo se preparan este tipo de películas sobre la superficie de electrodos de oro. A continuación, se modifican químicamente las películas y se incorporan en el sistema biomacromoléculas selectivas como enzimas [2] o cadenas de ADN [3], que actúan como un elemento de biorreconocimiento de distintas especies químicas. Como resultado de dicha reacción se produce el bloqueo/desbloqueo de los poros, permitiendo o no el paso de una especie electroactiva hasta la superficie electródica, generándose una variación en la señal electroquímica relacionada con la concentración del analito (Fig. 1).

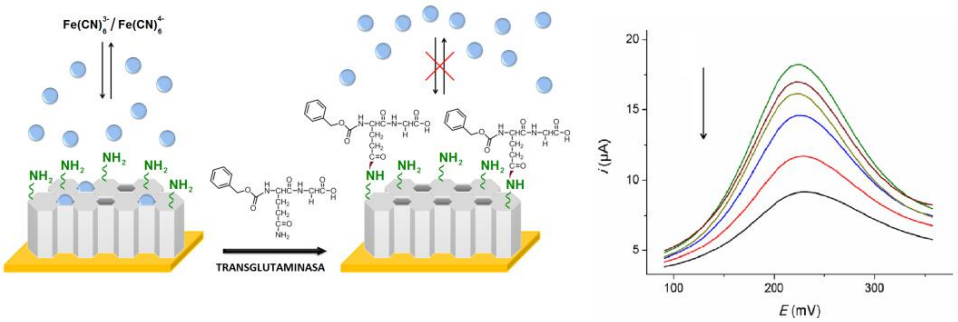

Figura 1. Esquema del funcionamiento y respuesta analítica del sensor electroquímico basado en las películas delgadas de sílice mesoporosa.

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A GENERAL APPROACH TOWARD POLYMER-COATED PLASMONIC NANOSTRUCTURES

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Keywords: *gold nanoparticles, self-assembly, polymers*

The combination of nanoparticles and polymers in a colloidal phase provides unique chemical tools toward the development of multifunctional platforms with properties that are characteristic of both components – e.g. a hard inorganic core and a soft polymer shell. We show a generic method for the preparation of polymer- coated plasmonic nanostructures with tunable thickness of the hydrophobic polymer spacer. By simply changing the order of addition of a block copolymer and water, encapsulation of either individual or assembled nanoparticles within copolymer micelles can be selected, thus providing wide versatility to the method.

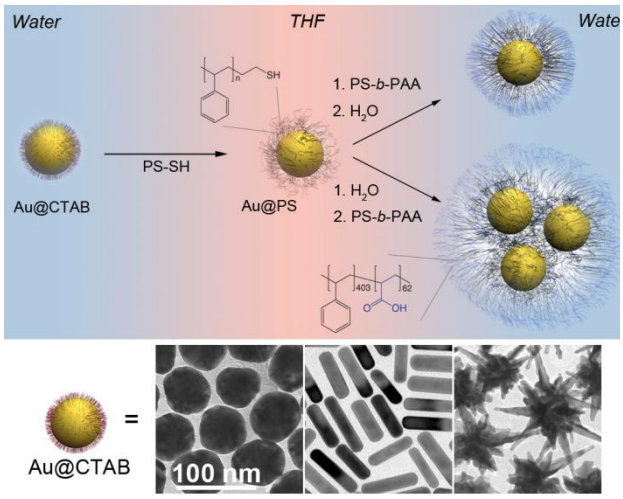

Figure 2 schematic representation of the strategy for polymer encapsulation of CTAB-stabilized plasmonic nanoparticles and assemblies. Representative TEM micrographs of the gold nanoparticles used in this study: nanospheres, nanorods and nanostars.

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S2: *Nanociencia y Materiales Moleculares*

DENDRÍMEROS RÍGIDOS DERIVADOS DE TETRAFENILMETANO. SÍNTESIS CONVERGENTE *VERSUS* DIVERGENTE.

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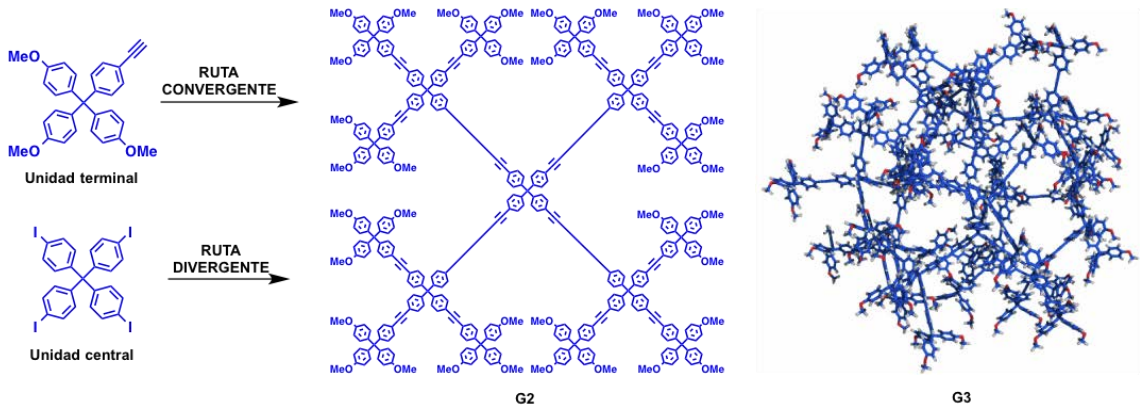
Palabras Clave: *dendrímero, tetrafenilmetano, reacción de Sonogashira, síntesis convergente, síntesis divergente.*

La precisión y regularidad estructural características de los dendrímeros y dendrones, junto con su alta ramificación, polivalencia y versatilidad estructural y funcional, los convierten en estructuras privilegiadas para numerosas aplicaciones en diversos campos [1].

Inspirándonos en las biomoléculas funcionales por excelencia, las proteínas, nos hemos planteado el reto de desarrollar dendrímeros en los cuales sea posible controlar de forma precisa la estructura tridimensional de las macromoléculas. Con este fin, hemos diseñado dendrímeros rígidos basados en tetrafenilmetano que poseen forma globular persistente para la segunda (G2) y tercera generación (G3), cavidades interiores bien definidas de tamaño y funcionalidad modificables, y grupos terminales que se mantienen en la periferia del dendrímero, minimizando el efecto conocido como *backfolding*.

En esta comunicación se describe la síntesis y caracterización de varios compuestos prototipo de esta nueva clase dendrítica, comparando la ruta convergente con la divergente y métodos mixtos.



Agradecimientos: Este trabajo ha sido financiado por el MEC y FEDER (MAT2013-42425-R y la Xunta de Galicia (PGIDT/PGIDIT, 08TMT002209PR).

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S2: *Nanociencia y Materiales Moleculares*

STUDY OF THE GELATION PROPERTIES OF THE ANTIASTHMATIC DRUG DISODIUM CROMOGLYCATE

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Keywords: *chromonics, cholesteric, alignment media.*

Disodium cromoglycate, an antiasthmathic drug commercially known as Intal gives its name to a family of lyotropic liquid crystals (LCs) called chromonics which has arisen interest in the last years.[1] Here we present our investigations on the aggregation properties of the cromolyn nematic LC phase in water by NMR, POM, X-Ray diffraction, and rheology. This LC phase was converted into its cholesteric counterpart upon the addition of different aminoacids[2] and analogous experiments were used to compare these chiral LC phases with the original one. Furthermore, we explored the applicability of both nematic and cholesteric LC phases as NMR alignment media for the structure elucidation and enantiomer discrimination[3] organic water-soluble molecules[4] through the use of residual dipolar couplings.[5]

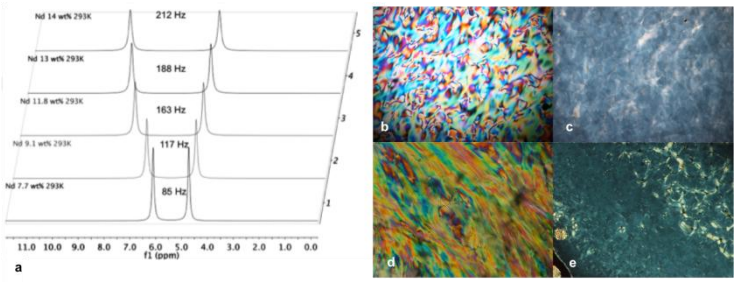

Figure 3 a) Deuterium splitting dependence with mesogen concentration in the cromolyn/NaCl doped phase and optical micrographs of the b) cromolyn nematic phase (x4); c) alanine (12 wt%) doped cromolyn cholesteric phase (x10); d) alanine (12 wt%) doped cromolyn cholesteric phase at 10ºC in the second annealing cycle between 4-27ºC (x20); e) proline (25 wt%) doped cromolyn cholesteric phase at 14ºC in the second annealing cycle between 4-27ºC (x20).

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S2: *Nanociencia y Materiales Moleculares*

SELF-ASSEMBLED METALLOPORPHYRINS

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Keywords: *porphyrin; magnetic properties*

Metalloporphyrins are very well known compounds in nature and as biomimetic models because of their roles in light-harvesting, oxygen transportation and catalysis. Recently, they are receiving a growing interest due to their possibilities to employ them as building blocks to synthesize more complex structures such as coordination polymers and metal-organic frameworks (MOFs).[1,2] Metalloporphyrins present some advantages such as their chemical stability, robustness and their great possibilities on chemical design. In addition, several metal ions can be placed on their cavities and different organic linkers can be inserted modulating the pores and the flexibility of the framework. Furthermore, heterobimetallic structures can be obtained tuning the nature of the metallic nodes and metalloporphyrins.

In this work, we will present preliminary results on the synthesis and characterization of new heterobimetallic frameworks using metalloporphyrines as building blocks.

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S2: *Nanociencia y Materiales Moleculares*

RELAJACIÓN DE LA MAGNETIZACIÓN A PARTIR DEL SEGUNDO DOBLETE EXCITADO EN UN COMPLEJO TRINUCLEAR Zn(II)-Dy(III)-Zn(II)

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Palabras Clave: *Propiedades magnéticas, SMM, disprosio, cálculos ab initio.*

En los últimos años el campo del Magnetismo Molecular basado en compuestos de coordinación ha experimentado un renacimiento debido al descubrimiento de que algunos complejos moleculares muestran relajación lenta de la magnetización e histéresis magnética. Este comportamiento viene provocado por el alto valor de espín del estado fundamental (S) y por la anisotropía magnética (D), que hacen que se genere una barrera que bloquea la magnetización molecular por debajo de una determinada temperatura (temperatura de bloqueo). Este tipo de moléculas se conocen como molécula imán (SMM) y presentan, entre otras cosas, potenciales aplicaciones en el procesamiento y almacenamiento de información a escala nanométrica.

La mayoría de estos nanoimanes son complejos paramagnéticos de metales de transición (3d) aunque en los últimos años, ha surgido una nueva generación de SMMs basados en compuestos de coordinación mixtos (3d-4f) o complejos mononucleares y polinucleares de Dy(III), Tb(III), Ho(III) y Er(III). Actualmente, los lantánidos juegan un papel importante en la obtención de los SMMs, ya que debido a la gran anisotropía magnética y a los grandes momentos magnéticos que generan es posible obtener moléculas con elevadas barreras térmicas para la inversión del sentido de la magnetización.

En esta comunicación presentamos la estructura, propiedades magnéticas y cálculos teóricos de un nuevo complejo trinuclear Zn(II)-Dy(III)-Zn(II) que presenta comportamiento de SMM, sintetizado a partir del ligando N,N'-dimetil-N,N'-etilendi(5-bromo-3-formil-2-hidroxibencil)amina. Éste es el segundo ejemplo que presenta un mecanismo de relajación desde el segundo doblete excitado,[1] con máximos entre 13 y 27 K en las gráficas χ"M vs. T y barreras de energía térmica de alrededor de 247 K.

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S2: *Nanociencia y Materiales Moleculares*

DESARROLLO DE POLIELECTROLITOS NANOESTRUCTURADOS PARA LA VEHICULIZACIÓN DE PRODUCTOS FARMACÉUTICOS

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Palabras Clave: *nanomateriales, polielectrolitos, nanofibras, fluorescencia, liberación sostenida, celdas de Franz.*

En general, el desarrollo de materiales nanoestructurados de naturaleza polimérica se ha debido en buena medida a la comparación que existe entre la respuesta nanoscópica y la macroscópica que permite en muchos casos aplicaciones únicas, y además empleando métodos de preparación sencillos. Los polímeros para la fabricación de nanomateriales terapéuticas o con fines diagnósticos, deben tener unos requerimientos mínimos, tales como: ser biodisponibles, no tóxicos, no carcinogénicos, apirógenos, no hemolíticos y esterilizables, teniendo en cuanta que las tres últimas características no son exigibles en todas las vías de administración [1].

El objeto es conseguir un polielectrolito o sistema polimérico capaz de agrupar todos estos requerimientos en una administración tópica. Para ello el sistema consta de : a) matriz biocompatible, empleando dos tipos de poliméros comerciales sintéticos; Poli-metil vinil éter-co-ácido maleico (PMVEMA-S) y Poli-metil vinil éter-co-ácido maleico monoetil ester (PMVEMA-ES), cuya funcion es transportadora, b) polilectrolitos conjugados basados en fluoreno (dos distintos, preparados en el laboratorio) cuya función es de señalización, y c) el fármaco o sustancia activa, estudiándose el ácido 5-aminolevulínico (5-ALA) y el péptido Dermicidina (DCD-1L). Como formas farmacéuticas nanoestructuradas, se han seleccionado las nanopartículas y las nanofibras formadas por la unión de polímeros de diferente naturaleza. El interés final del trabajo es comparar los resultados obtenidos en la liberación y visualización de los fármacos incorporados.

Los resultados obtenidos hasta el momento, datan de la baja toxicidad del polímero comerial, PMVEMA LD50 cerdos: 5-9g/Kg y del elaborado en el laboratorio con cepas de Echerichia Coli (Top 10 F´), CIM: 0.80µM y CI_{90}: 0.70µM. La preparación de nanopartículas por diferentes métodos y las nanofibras por electrohilatura nos dan unos resultados de tamaño inferiores a 450nm e inferiores a 100nm respectivamente.Las muestras que contienen el polielectrolito conjugado presentan una fluorescencia estudiada mediante espectrofotometria de fluorescencia característica en función de los componentes y del tipo de nanomaterial fabricado, en disolución o en estado sólido.El estudio de liberación del principio activo en las muestras nanoestrucutras, se realiza mediante protocolo establecido en las guias de la OECD [2] empleando celdas Franz y el seguimiento de este análisis se realiza mediante cromtografía líquida de alta resolución.

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S3. Catálisis Organometálica como Solución a Retos Sintéticos (CO) / Organometallic Catalysis as a Solution for Synthetic Challenges

El presente simposio pretende ser un foro donde presentar los avances más recientes en el campo de la catálisis organometálica. Se centra, principalmente, en el desarrollo de nuevas metodologías sintéticas y/o nuevos catalizadores, su aplicación a la síntesis de productos de interés y estudios mecanísticos.

This symposium attempts to be a forum to present the most recent advances in the field of organometallic catalysis. It is mainly centered in the development of new synthetic methodologies and / or new catalysts, their application to the synthesis of new products of interest and mechanistic studies.

Organizadores:

Javier Adrio Sevilla (UAM)

Ramón Gómez Arrayás (UAM)

e-mail de contacto: javier.adrio@uam.es / ramon.gomez@uam.es

Lunes 20 de Julio 2015

08:40 – 09:40	**PL-2**	***Conferencia Plenaria*** (Común a todos los simposios) **Tomás Torres Cebada** *"Phtalocyanines: Old Dyes, New Molecular Materials"*

Chairman: Ramón Gómez Arrayás

10:00 – 10:30	**S3-IL-01**	**Nuno Maulide** *"Catalytic Asymmetric Transformations of High-Energy Intermediates: from Palladium to Gold"*
10:30 – 10:45	**S3-OC-01**	**Diego J. Cárdenas** *"Alkyl-alkyl Cascade Cyclization and Cross-Couplings Catalyzed by First Row Transition Metals"*
10:45 – 11:00	**S3-OC-02**	**Salvatore Filippone** *"Chiral Metallo-fulerenes: Synthesis and Catalytic Activity"*
11:00 – 11:30		Pausa Café

Chairman: Pablo Mauleón

11:30 – 12:00	**S3-IL-02**	**Carlos Valdes** *"Sulfonylhydrazones: Versatile Reagents for Cross-Coupling Reactions and Cascade Processes"*
12:00 – 12:15	**S3-OC-03**	**Xavier Solans-Monfort** *"Influence of Reactant Nature on the Catalytic Efficiency of Schrock Type Alkene Metathesis Catalysts"*
12:15 – 12:30	**S3-OC-04**	**Monserrat Diéguez** *"Catalyst Design for Asymmetric Hydrogenation of Unfuntionalized Olefins. A Combined Experimental and Theoretical Study"*
12:30 – 12:40	**S3-FC-01**	**Nuria Rodríguez** *"Rh^{I}/Rh^{III} catalyst-controlled Divergent C□H Functionalization of Picolinamide Derivatives with Alkynes"*
12:40 – 12:50	**S3-FC-02**	**Iván Varela** *"Gold(I)-catalyzed multicomponent [2+2+2] cycloaddition of allenamides, alkenes and aldehydes"*
13:50 – 13:00	**S3-FC-03**	**Damián Padín** *"Ruthenium Catalyzed Cyclization of Aza-alkynals: An Afficient Entry to 1-vinylepoxypyrrolidines*
13:00 – 13:10	**S3-FC-04**	**Jesús González** *"Zinc-catalyzed synthesis of furan derivatives"*
13:10 – 13:20	**S3-FC-05**	**Miguel Paraja** *"Palladium-catalyzed Synthesis of Benzo-fused Carbo- and Heterocycles through Cascade Processes Based on N-*tosylhydrazones"
13:20 – 13:30	**S3-FC-06**	**Marta González** *"Estudio Computacional de la Reorganización de O-propargil Oximas Catalizadas por Cobre"*
13:30 – 15:30		Comida

Lunes 20 de Julio 2015

Chairman: Alfonso Cornejo

15:30 – 16:00	**S3-IL-03**	**John Bower** *"Directed Cycloadditions of Amino-Substituted Cyclopropanes: Scope and Mechanism"*
16:00 – 16:10	**S3-FC-07**	**Pablo Mauleón** *"Cu-catalyzed Silylation of Alkynes: A Traceless 2-pyridylsulfonyl Controller Allows Access to Either on Demand"*
16:10 – 16:20	**S3-FC-08**	**Marta Valencia** *"Dinuclear Iridium-carbene-Mediated Activation of Alcohols and Amines with High Catalytic Selectivity"*
16:20 – 16:30	**S3-FC-09**	**Gabriel Denis** *"Application of the 'One-Pot' Sonogashira–Heterocyclization–Heck Cascade to the Synthesis of Indolobenzazepinones"*
16:30 – 17:00		Pausa Café

Chairwoman: Nuria Rodríguez

17:00 – 17:30	**S3-IL-04**	**Lutz Ackermann** *"Ruthenium(Ii)-Catalyzed C–H Functionalizations by Carboxylate Assistance"*
17:30 – 17:45	**S3-OC-05**	**Moisés Gulías** *"Rh^{III}-Catalyzed Annulations Based on the C□H Bond Activation of 2-Alkenylphenols"*
17:45 – 18:00	**S3-OC-06**	**Antonio Urbano** *"Enantioselective Synthesis of Planar-chiral Ferrocenyl Helicenequinones and ortho-Condensed Aromatic Ferrocenes"*
18:00 – 18:10	**S3-FC-10**	**Alfonso Cornejo** *"Theoretical and Experimental Insights in the Behaviour of NHC-Ag Complexes in Solution"*
18:10 – 18:20	**S3-FC-11**	**Javier Iglesias-Sigüenza** *"Chiral N-heterocyclic Carbenes Fused into an Heterobiaryl System"*
18:20 – 18:30	**S3-FC-12**	**Carlos Jarava** *"Asymmetric synthesis of versatile benzylic boronic esters through a borylation-aromatization process"*

18:30	***Sesión de Pósteres (con entrega del premio al mejor póster)***

Comunicaciones Invitadas (IL)

S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

CATALYTIC ASYMMETRIC TRANFORMATIONS OF HIGH-ENERGY INTERMEDIATES: FROM PALLADIUM TO GOLD

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Keywords: *palladium, gold, allylic alkylation, cyclopropanation*

The turn of the century brought about a pressing need for new, efficient and clean strategies for the chemical synthesis of biorelevant compounds. Our group has studied the use of various molecular rearrangements and atom-economical transformations as particularly appealing means towards the streamlined synthesis of complex small molecule targets.[1,2,3]

In this lecture, we will present an overview of our research in these areas and how they provide efficient solutions for total synthesis as well as platforms for the discovery of unusual reactivity. In particular, we will focus on recent developments on asymmetric catalysis of the allylic alkylation reaction and new vistas on gold(I)-mediated cyclopropanation reactions.

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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

SULFONYLHYDRAZONES: VERSATILE REAGENTS FOR CROSS-COUPLING REACTIONS AND CASCADE PROCESSES

C. Valdés

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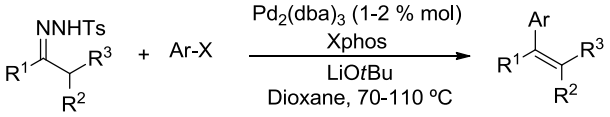
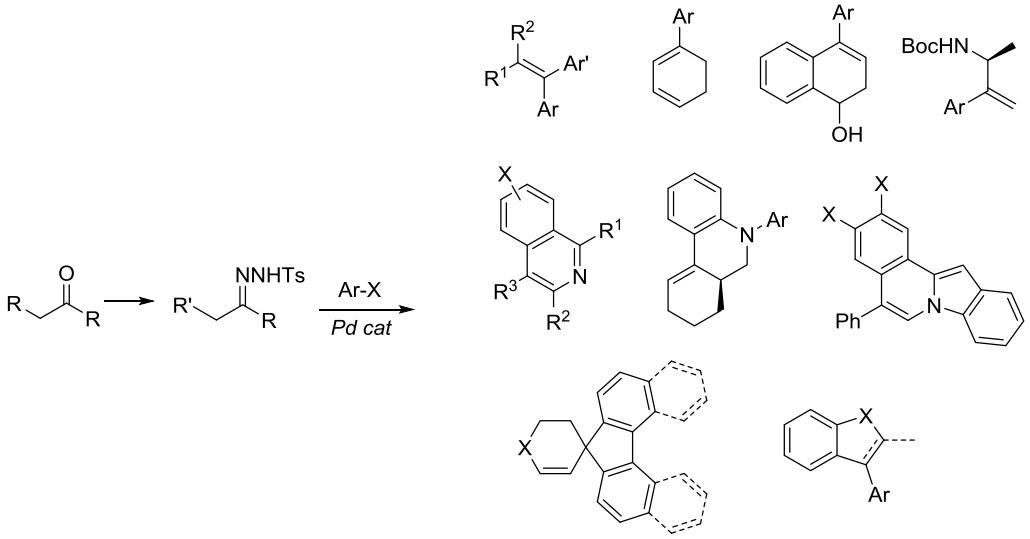
Keywords: *N-Tosylhydrazones, cross-coupling reactions, cascade processes*

Sulfonylhydrazones are classical reagents, that have been extensively used over the last sixty years as synthetic intermediates for the modification of carbonyl compounds. In 2007, we discovered a new Pd-catalyzed cross-coupling reaction that employs sulfonylhydrazones as the nucleophilic coupling partnert, and leads to the obtention of polisubstituted olefins.[1]



This reaction takes place through an original mechanism involving the formation of a Pd-carbene complex and a migratory insertion reaction. Moreover, the coupling reaction has been applied in a diversity of transformations including the synthesis of polisubstituted and functionalized olefins, dienes and heterocyclic compounds. As a result of the work of our group and others in this area, the chemistry of metal catalyzed reactions with sulfonylhydrazones has gained increasing popularity.[2] In this lecture, the contributions of our research group in this field will be discussed, with particular attention to our most recent advances, concerning the application of this methodologies in different classes of Pd-catalyzed cascade reactions.[3]



References

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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

DIRECTED CYCLOADDITIONS OF AMINO-SUBSTITUTED CYCLOPROPANES: SCOPE AND MECHANISM

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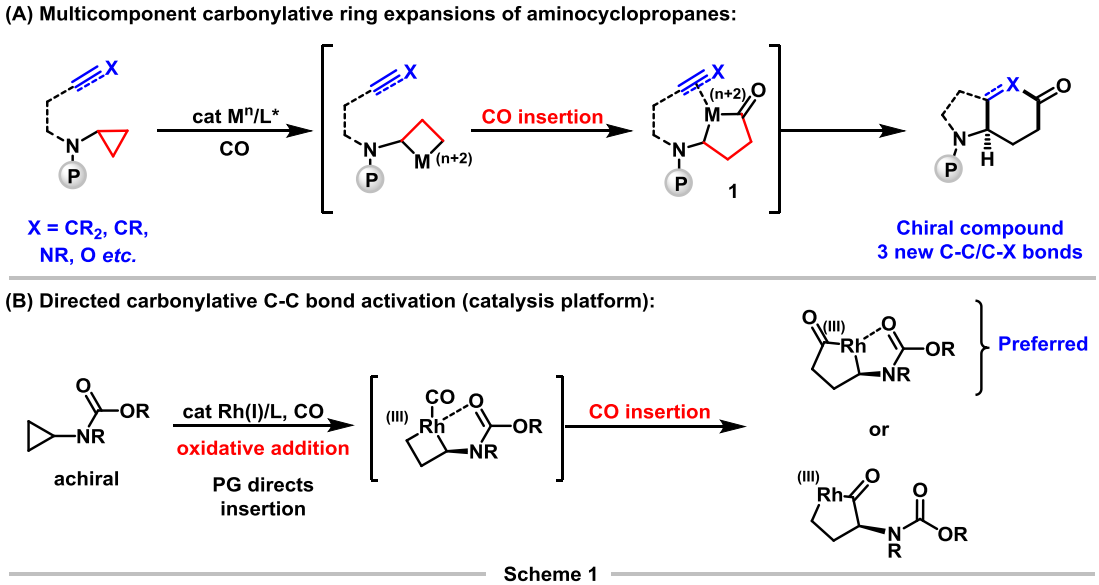
Keywords: *cycloaddition, heterocycle, rhodium catalysis, C-C activation*

Our research programme is focussed upon the development of new catalysis platforms that enable direct access to medicinally valuable chiral scaffolds. Recently, we outlined a metal-catalysed (3+1+2) carbonylative cycloaddition strategy for the synthesis of complex nitrogen containing scaffolds (Scheme 1A).[1,2] The key metallacyclic intermediates **1** are generated by Rh-catalysed carbonylative ring expansion of readily available amino-substituted cyclopropanes. To control the regioselectivity of this process we have developed a directing group based strategy, which takes advantage of the N-protecting group (Scheme 1B). This approach controls (a) the regioselectivity of oxidative addition (into the more hindered cyclopropane C-C bond) and (b) the regioselectivity of CO insertion. Mechanistic and synthetic aspects of this process will be discussed. A related cycloaddition-fragmentation strategy for accessing strained azocane ring systems will also be outlined.[3]



Scheme 1

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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

RUTHENIUM(II)-CATALYZED C–H FUNCTIONALIZATIONS BY CARBOXYLATE ASSISTANCE

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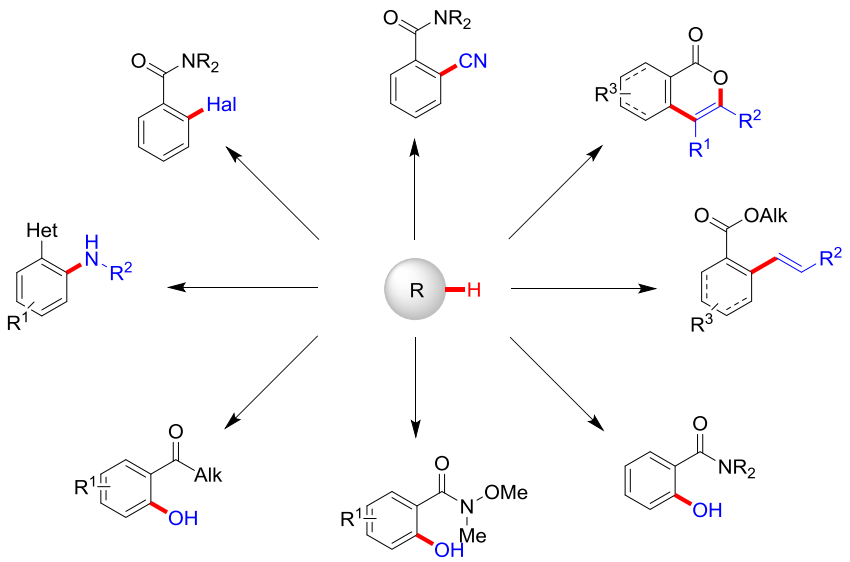
Keywords: *C–H Activation, Catalysis, Green Chemistry, Organic Synthesis, Reaction Mechanism*

Catalytic C–H functionalizations are attractive tools for streamlining organic synthesis, avoiding the preparation and use of prefunctionalized starting materials.[1] Recently, we have introduced carboxylates as additives for site-selective direct arylations and alkylations employing versatile ruthenium(II) complexes,[2] displayed complementary chemo- and site-selectivities as compared to palladium,[3a] nickel,[3b] cobalt[3c] or iron[3d] catalysts. Detailed mechanistic insight into the working mode of the C–H ruthenation step set the stage for ruthenium(II)-catalyzed twofold C–H bond functionalizations as well as step-economical oxidative annulations of alkynes.[4] The oxidative C–H bond functionalization strategy proved to be broadly applicable,[5] and enabled among others ruthenium(II)-catalyzed oxygenations, nitrogenations, cyanations and halogenations.



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Comunicaciones Orales (OC)

S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

ALKYL-ALKYL CASCADE CYCLIZATION AND CROSS-COUPLINGS CATALYZED BY FIRST ROW TRANSITION METALS

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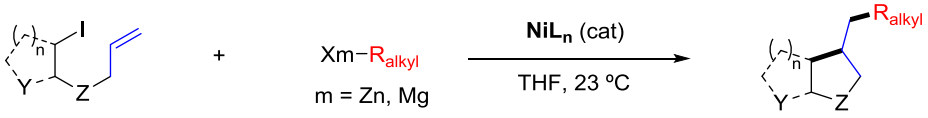
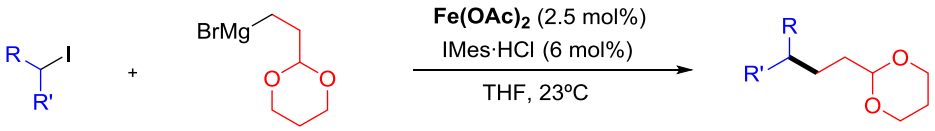
Keywords: *cross-coupling, nickel, iron, Grignard reagents, alkylzinc*

The use of first-row transition metal complexes, mainly Ni, Fe and Cu, as catalysts for cross-coupling reactions has experienced a renaissance during the last years, especially for the coupling of alkyl electrophiles. In addition to their convenience for economic and environmental reasons, these reactions allow expanding the reaction scope and have uncovered novel mechanisms. We have developed Ni-catalyzed cascade cyclization-coupling reactions of alkyl halides containing alkenes with alkylzinc or alkylmagnesium halides, which allow the formation of at least two C-C bonds in a single operation, taking advantage of the presence of an olefin within the electrophile. More recently, we have reported the first general Fe-catalyzed Kumada-type alkyl-alkyl cross coupling reaction in the presence of functional groups. Mechanistic evidence point to Fe(I) complexes as the catalytically active species.





We will present an overview of the scope and mechanism of Ni and Fe-catalyzed cascade and cross-coupling reactions for the formation of several $C(sp^3)$-$C(sp^3)$ bonds in a single operation. In addition, our results concerning the synthesis of modified NHC-type ligands in order to extend the scope of the Fe-catalyzed Kumada alkyl-alkyl cross-couplings will be discussed.

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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

CHIRAL METALLO-FULLERENES: SYNTHESIS AND CATALYTIC ACTIVITY

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Keywords: *Iridium Complexes; Chirality; Asymmetric synthesis.*

The discovery of fullerenes and the unique properties they exhibit, prompted a wide interest in the scientific community due to the potential applications in fields such as molecular electronics or nanoscience. However, the use of fullerenes in chemical transformations as catalysts still remains an open and intriguing question.

Recently, we have demonstrated that a full control in the stereoselective functionalization of fullerenes is possible. This has been accomplished by the use of different asymmetric metal-[1] and organo-[2] catalysed processes.[3]

In this communication, we report on the synthesis of chiral hybrids metallo-fullerenes where C_{60} is endowed with metals such as Ir, Ru, Rh. Interestingly, these unprecedented compounds exhibit a most efficient catalytic activity.

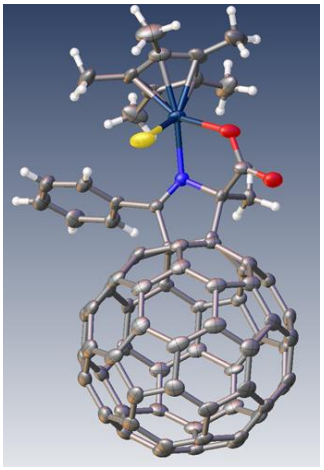

Figure 1. Representative example of a hybrid matallo-fullerene showing catalytic properties.

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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

INFLUENCE OF REACTANT NATURE ON THE CATALYTIC EFFICIENCY OF SCHROCK TYPE ALKENE METATHESIS CATALYSTS

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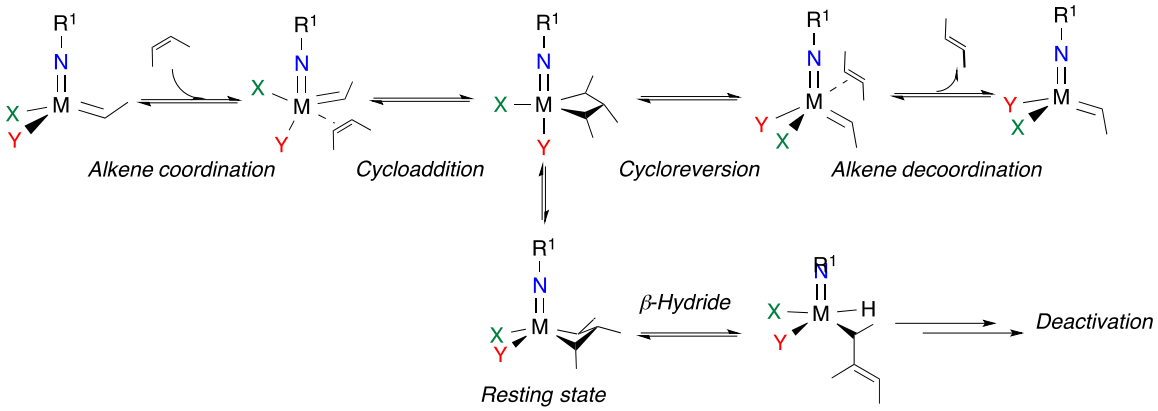
Keywords: *Olefin metathesis, DFT calculations, Schrock type carbenes, reaction kinetics*

Olefin metathesis implies the redistribution of alkene carbon ends through C=C double bond scission.[1] The reaction allows the formation of new C=C double bonds even in presence of other functional groups and thus, It is seen as one of the most efficient strategies for the synthesis of organic compounds. The reaction is catalysed by transition metal alkylidene complexes and the d^0 Mo and W-based Schrock type complexes M(NR^1)(CR^2)(X)(Y) are among the most efficient ones. Traditionally, X and Y were two alkoxy groups. Nevertheless, the synthesis of monoalkoxy pyrrolyl (MAP) imido alkyledene complexes (X =Me_2Pyr, Y = alkoxy) yielded to a new generation of catalysts that usually presents higher activities, selectivities and stabilities.[2] The higher catalytic activity of MAP complexes has been rationalized with DFT calculations with simplified models that do not include the full ligands.[3]

In this contribution, a computational kinetic study on the ethene and *cis*-2-butene metathesis reaction catalysed by M(NR^1)(CR^2)(X)(Y) is presented with the aim of analysing the role of reacting alkene. For this, we considered the full ligands of several existing catalysts and for the first time the full catalytic process: precursor activation, productive cycle and some catalyst deactivation pathways. Results show that the reaction energy profile is highly influenced by the nature of the reactants. The outcome is that the most active catalysts are different for ethene and *cis*-2-butene, suggesting that catalyst efficiency depends on the reacting alkene.



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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

CATALYST DESIGN FOR ASYMMETRIC HYDROGENATION OF UNFUNTIONALIZED OLEFINS. A COMBINED EXPERIMENTAL AND THEORETICAL STUDY

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Keywords: *Asymmetric catalysis*, *hydrogenation*, phosphite-containing ligands, *iridium*, *DFT study*

Asymmetric hydrogenation is an useful tool for preparing chiral compounds due to its high efficiency, low catalyst loadings, operational simplicity and perfect atom economy. Whereas today ligands for Ru/Rh-reduction of functionalized olefins are available, the reduction of unfunctionalized olefins is by far less developed.[1] Mixed phosphine/phosphinite-oxazoline have been the most used ligands.[1] Our group has contributed in this field with an improved generation of ligands. We have shown that phosphite groups into ligand is beneficial.[2] Mixed phosphite-N have emerged as extremely effective ligands, providing better substrate versatility than earlier Ir-phosphinite/phosphine-N systems.[2] Despite the advances with Ir-P,N catalysts, their selectivity for reducing some significant olefins still needs to be improved. In this respect, our research has more recently progressed to mixed P,X-ligands bearing more robust X-donor groups than oxazolines.[3] We described the first successful use of non-N-donor mixed ligand (P,S).[3b] We also carried out DFT that was crucial in the optimization of the ligand design. The asymmetric reduction were also performed using propylene carbonate as solvent, which allowed the Ir-catalyst to be reused [2,3]. In this communication I will present our progress in this field.

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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

Rh(III)-CATALYZED ANNULATIONS BASED ON THE C-H BOND ACTIVATION OF 2-ALKENYLPHENOLS

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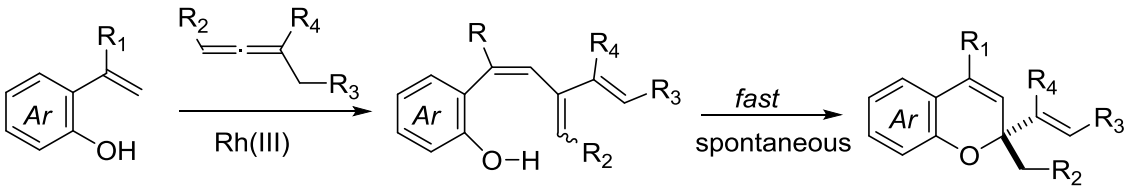
Keywords: *C-H activation, catalysis, Rhodium, annulation, allene*

In the last years, catalytic C-H bond activation is attracting a lot of attention because it provides new ways to create C-C and C-X bond through functionalization of "inert" C-H bonds [1]. In order to create new strategies leading to biologically relevant heterocyles, we recently initiated in our group a line of research based on associating the C-H activation with novel annulation processes. In particular we have developed a rapid access to isoquinolines, oxepines, coumarines or spirocyclic systems from simple starting materials through several annulations catalyzed by Rh(III) [2].

Herein, we describe mechanistic considerations of these Rh(III) catalyzed annulations and we also describe the scope and applications of the reactions between 2-alkenylphenols and allenes, a transformation that leads to highly valuable chromene systems in cascade process involving the cleavage of a sp^2 C-H bond and two pericyclic reactions [3].



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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

ENANTIOSELECTIVE SYNTHESIS OF PLANAR-CHIRAL FERROCENYL HELICENEQUINONES AND ORTHO-CONDENSED AROMATIC FERROCENES

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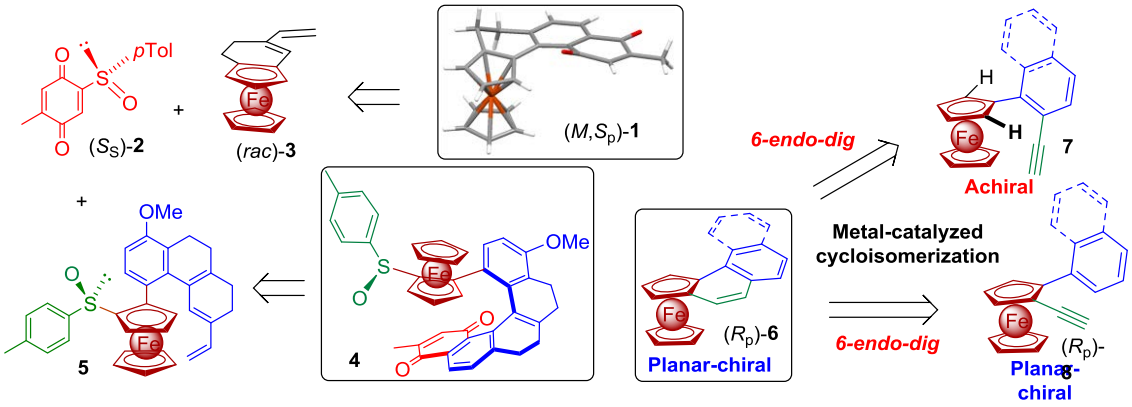
Keywords: *ferrocenes, helicenes, cycloisomerization, planar chirality*

Planar-chiral ferrocenes are important chiral scaffolds in organic and organometallic chemistry and have been utilized as chiral ligands, chiral catalysts, or chiral building blocks.[1] Other interesting structures used in these areas are chiral helicenes.[2] In spite of their usefulness in asymmetric synthesis, enantiomerically enriched forms of these compounds are not easy to synthesize. In 2011, we achieved a short asymmetric approach to a ferrocene-[4]-helicenequinone (M,S_p)-**1** based on the Diels-Alder reaction between an enantiopure sulfinylquinone (S_S)-**2** and a planar-chiral racemic ferrocene vinylcyclohexene **3**.[3]

In this presentation, we report the asymmetric synthesis of the four possible stereoisomers of enantiopure ferrocenyl helicenequinones **4**, bearing central, planar and helical chiralities, based on the asymmetric Diels-Alder reaction between sulfinylquinone (S_S)-**2** and diene **5**.



We also report a new approach to planar-chiral *ortho*-condensed aromatic ferrocenes (R_p)-**6** based on the metal-catalyzed cycloisomerization reaction, initially reported by Fürstner for the synthesis of phenanthrenes,[4] as the key step. Thus, both racemic and enantiopure tricyclic and tetracyclic derivatives (R_p)-**6** were prepared. The former were obtained from achiral 2-alkynylaryl ferrocenes **7**, through a *6-endo-dig* cyclization, whereas the enantiopure systems were available by enantioselective metal-catalyzed cycloisomerization in the presence of chiral ligands. The cycloisomerization of enantiopure planar-chiral 1-aryl-2-alkynyl ferrocenes (R_p)-**8** also afforded the enantioenriched *ortho*-condensed aromatic ferrocenes (R_p)-**6**.

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Comunicaciones Flash (FC)

S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

Rh(I)/Rh(III) CATALYST-CONTROLLED DIVERGENT C–H FUNCTIONALIZATION OF PICOLINAMIDE DERIVATIVES WITH ALKYNES

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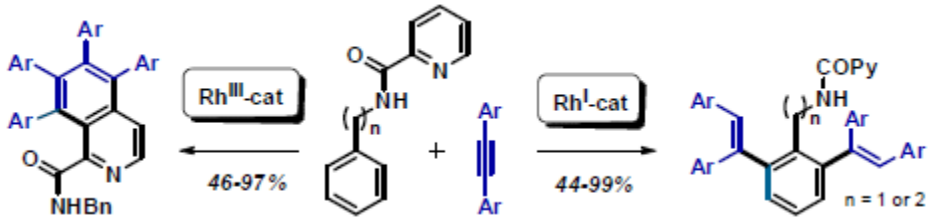
Recent progress on rhodium-catalyzed C-H bond functionalization has opened new possibilities for an ideal chemical synthesis enabling straightforward formation of new C-C bonds without previous functionalization steps.[1] However, investigations of catalyst controlled divergent C-H functionalizations of distinct C-H bonds are relatively uncommon, yet highly appealing.[2] The concept herein presented illustrates a divergent high site-selective control in the direct functionalization of both aryl and heteroaryl C-H bonds of *N*-substituted picolinamide substrates.[3] By simply switching the oxidation state of the Rh(I)/Rh(III) catalyst precursor, it is possible to access either isoquinoline derivatives or *ortho*-olefinated benzylamine and phenethylamine derivatives, respectively.[4]



Experimental mechanistic studies based on isolation and X-ray characterization of Rh(I) and Rh(III) picolinamide complexes and deuterium labeling studies, as well and DFT theoretical calculations have been performed to explain the factors that influence this switchable site- selectivity control for both Rh(I) and Rh(III) catalytic systems.

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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

GOLD(I)-CATALYZED MULTICOMPONENT [2+2+2] CYCLOADDITION OF ALLENAMIDES, ALKENES AND ALDEHYDES

I. Varela,[1] H. Faustino,[1] D. Cagiao,[1] J. Fernández-Casado,[1] R. Nelson,[1] J. L. Mascareñas[1,*] and F. López[1,2,*]

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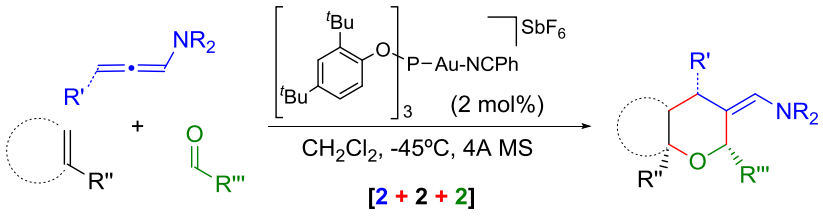
Keywords: *gold, catalysis, cycloaddition, tetrahydropyrans.*

During the last decade there have been extraordinary advances in the development of Au-catalyzed processes. Our group has demonstrated the possibility of using allenamides as two carbon-atom components in intermolecular Au-catalyzed [4 + 2] and [2 + 2] cycloadditions with dienes and alkenes, respectively.[1] We have also developed a simple and highly versatile cascade cycloaddition between allenamides and carbonyl-tethered alkenes that affords oxa-bridged seven-, eight- and even nine-membered carbocycles.[2]

More recently we have also demonstrated that it is possible to achieve annulations between allenamides, alkenes and carbonyl derivatives in a fully intermolecular way.[3] The three-component assembly is better carried out by using a phosphite-gold complex as catalyst, and takes place with high regioselectivity and, in many cases, with good diastereoselectivities. The reaction works with different types of allenes, alkenes and aldehydes and provides a straightforward entry to 2,6-disubstituted tetrahydropyrans. We will also disclose relevant mechanistic aspects and preliminary results of an enantioselective variant.



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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

RUTHENIUM CATALYZED CYCLIZATION OF AZA-ALKYNALS: AN EFFICIENT ENTRY TO 1-VINYLEPOXYPYRROLIDINES

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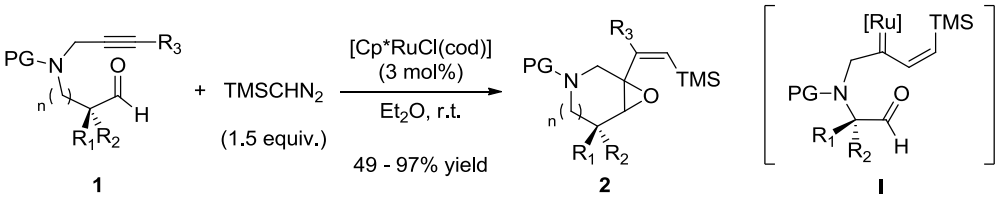
Key words: *carbenes, cyclization, heterocycles, ruthenium*

The development of new synthetic strategies from readily available starting materials continues to be a main goal in modern chemistry. Organometallic catalysis has emerged as a powerful tool for the synthesis of relevant heterocycles with biomedical applications.[1] Functionalized 1-vinylepoxypyrrolidines **2** (n=0), which combine the presence of a great value 6-oxa-3-azabicyclo[3.1.0]hexane nucleus and the versatile vinylepoxide group, are useful building blocks for the synthesis of biologically active products.[2]

Based on our studies on cyclization processes via *in situ* generation of catalytic ruthenium carbenes with diazocompounds,[3] herein we report the efficient synthesis of 1-vinylepoxypyrrolidines from aza-alkynals **1**. This cyclization reaction proceeds in high reaction yield, under very mild conditions and *cis* selectivity in the double bond geometry. By using this methodology 7-oxa-3-azabicyclo[4.1.0]heptanes **2** (n=1) were also synthesized. Such transformation most likely involves the formation of a key ruthenium vinyl carbene intermediate **I.**



PG = Protecting group
$R_1 = R_2$ = alkyl / R_1 = alkyl, R_2 = H
$R_3 = CH_3$ or H
n = 0, 1

Acknowledgements: MICINN (projects CTQ2011-28258 and ORFEO-CINQA CTQ2014-51912-REDC), Xunta de Galicia and European Regional Development Fund (projects GRC2014/032 and EM 2012/051). D. P. thanks Xunta de Galicia for a predoctoral contract. M. F.-M. thanks MINECO for a "Ramón y Cajal" contract.

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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

ZINC-CATALYZED SYNTHESIS OF FURAN DERIVATIVES

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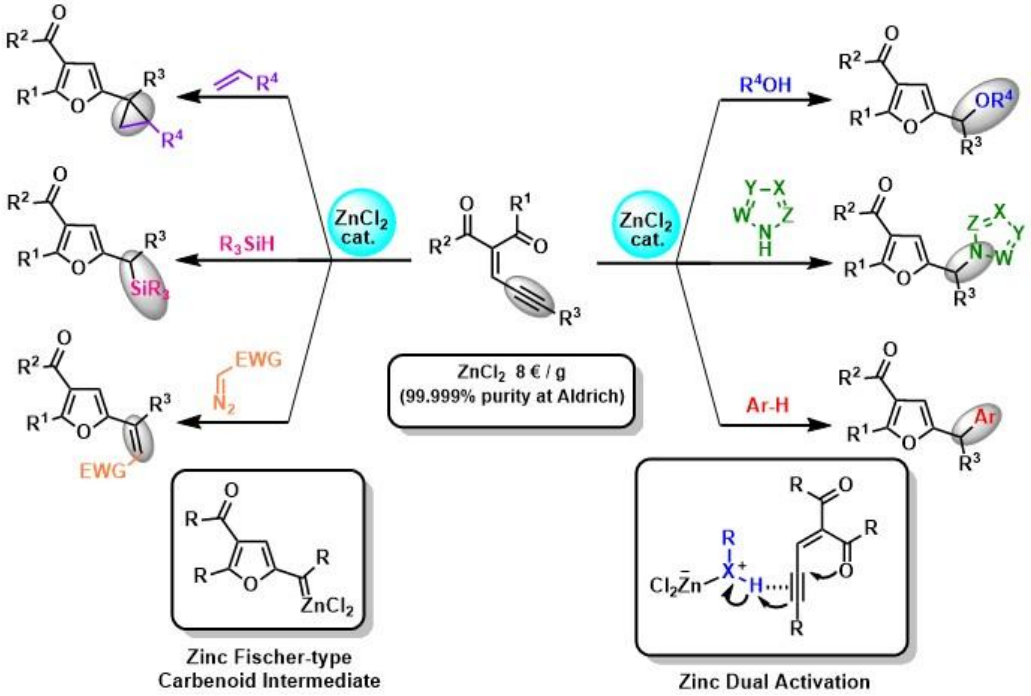
Key Words: *zinc, carbenes, heterocycles, dual activation, alkyne activation*

Catalysis by means of transition metals is currently one of the most powerful methodologies in organic synthesis as well as in the industry for the preparation of high valued chemicals. However, most of the catalysts employed in this field present some disadvantages such as high price, toxicity and restricted availability. For this reason, the development of new synthetic methods comprising the use of widely-available and environment-friendly metal catalysts is a highly desirable goal for both the academy and the industry. In this context, our research group has recently reported several zinc-catalyzed transformations of enynones through a furyl zinc-carbene intermediate. In these processes, the proposed carbene intermediate (supported by DFT calculations) is trapped by alkenes, silanes or diazo compounds leading to a diverse variety of furan derivatives.[1] Furthermore, in the presence of alcohols or azoles, the catalytic system allows the preparation of a different family of furan derivatives and triarylmethanes. In this case, DFT calculations indicate that the mechanism proceeds through a dual X-H activation of the alcohols or azoles by zinc.[2]



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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

PALLADIUM CATALYZED SYNTHESIS OF BENZO-FUSED CARBO- AND HETEROCYCLES THROUGH CASCADE PROCESSES BASED ON *N*-TOSYLHYDRAZONES

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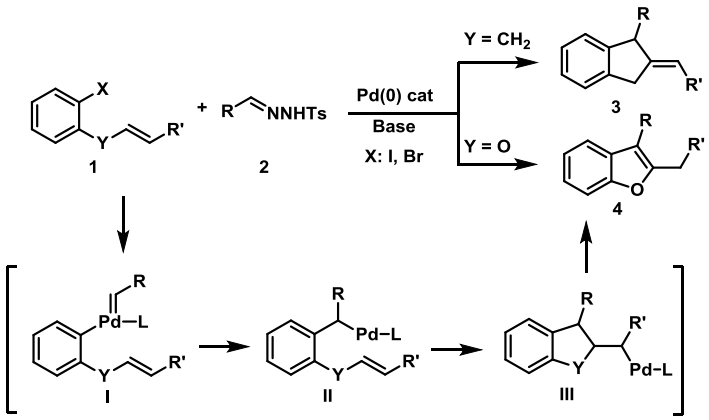
Keywords: *Palladium, N-Tosylhydrazone, cascade process.*

The cross-coupling reaction between sulfonylhydrazones and organic halides, first described in our research group in 2007,[1] has become since then a very useful transformation in organic synthesis, with applications in the preparation of polysubstituted alkenes, carbocycles and heterocycles.[2] [3]

We have recently turned our attention to processes that combine the migratory insertion typical of the reactions based on tosylhydrazones with an intramolecular Heck reaction. Indeed, *o*-haloallylbenzenes **1** are suitable substrates for this class of cascade reaction under proper catalytic conditions. Thus, after the migratory insertion of the carbene derived from the *N*-tosylhydrazone on intermediate **I**, the alkyl palladium complex generated **II** is intercepted through an intramolecular 5-*exo*-trig carbopalladation. After the final β-hydride elimination on complex **III**, indanes with an exocyclic bond **3**, and substituted benzofurans **4**, can be obtained in a process in which two C-C bonds are formed on the same carbon atom.



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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

ESTUDIO COMPUTACIONAL DE LA REORGANIZACIÓN DE *O*-PROPARGIL OXIMAS CATALIZADAS POR COBRE

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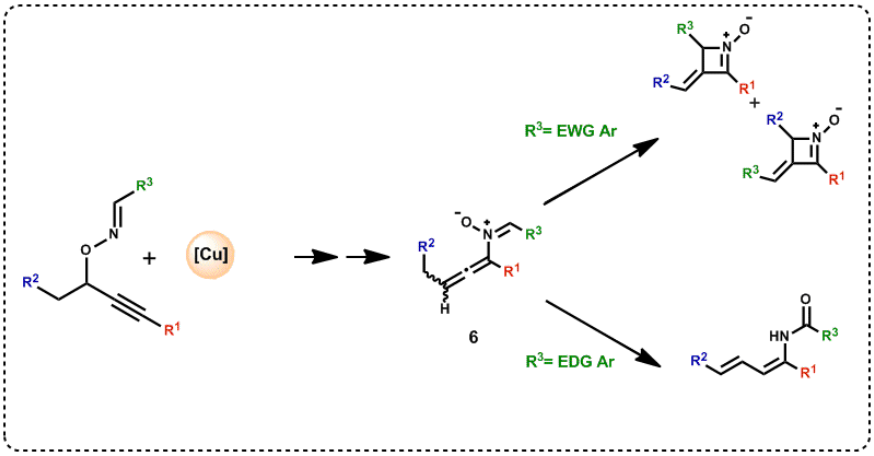
Palabras Clave: *cobre, reorganización, estudio computacional.*

Mediante la reorganización catalizada por cobre (I) de *O*-propargil oximas, Nakamura *et al.* consiguen obtener diferentes productos modificando el carácter electrónico del arilo (R^3), así, la presencia de sustituyentes electroatrayentes conduce a nitronas cíclicas de 4-miembros, [1] mientras que 1-amidodienos se obtienen cuando los sustituyentes son electrodonadores. [2]

Hemos decidido realizar un estudio computacional con el fin de establecer un mecanismo que pueda explicar: 1- la selectividad producida por los sustituyentes y 2- el papel que ejerce el cobre en esta peculiar reacción.

El mecanismo propuesto para este proceso presenta un intermedio común, la alenilnitrona 6, intermedio clave a partir del cual el mecanismo se bifurca en dos ramas dependiendo del carácter electrónico del arilo (R^3). La preferencia por un camino o el otro determinará el producto de la reacción.



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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

CU-CATALYZED SILYLATION OF ALKYNES: A TRACELESS 2-PYRIDYLSULFONYL CONTROLLER ALLOWS ACCESS TO EITHER REGIOISOMER ON DEMAND

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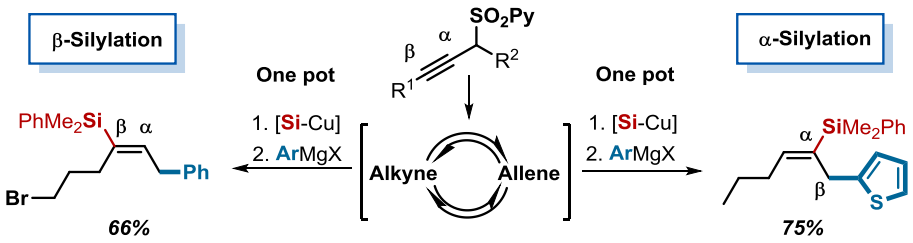
Keywords: *Cu catalysis • Sylilation • alkynes • vinyl silanes • regiochemistry control.*

The Cu-catalyzed silylation of terminal and internal alkynes bearing a 2-pyridyl sulfonyl group (SO_2Py) at the propargylic position affords a breadth of vinyl silanes in good yields and excellent regio- and stereocontrol under mild conditions. The directing SO_2Py group is essential in terms of reaction efficiency and chemoselectivity. Importantly, this group also provides the ability to reverse the regiochemical outcome of the reaction, opening the access to either regioisomer without modification of the starting substrate by virtue of an in situ base-promoted alkyne to allene equilibration which takes place prior to the silylcupration process.[1] Furthermore, removal of the directing SO_2Py allows for further elaboration of the silylation products. In particular, a one-pot tandem alkyne silylation/allylic substitution sequence, in which both steps are catalyzed by the same Cu species, opens up a new approach for the access to either formal hydrosilylation regioisomer of unsymmetrical aliphatic-substituted internal alkynes from propargyl sulfones.



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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

DINUCLEAR IRIDIUM-CARBENE-MEDIATED ACTIVATION OF ALCOHOLS AND AMINES WITH HIGH CATALYTIC SELECTIVITY

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Keywords: triazolylidene iridium catalyst

Iridium Cp* complexes containing mesoionic carbene ligands have shown a high activity in a variety of catalytic applications, including water oxidation.[1] In extension of this work, we have now synthesized a variety of mono- and bimetallic complexes featuring a functional pyridine-containing triazolylidene ligand, and have characterized the new complexes by NMR spectroscopy, microanalysis, and by X-ray diffraction. These complexes have been evaluated as potential catalysts for the oxidation of alcohols and amines, without the need of an oxidant or base as additive. In contrast to monometallic complexes, dinuclear iridium complexes show a remarkably high selectivity.

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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

APPLICATION OF THE 'ONE-POT' SONOGASHIRA–HETEROCYCLIZATION–HECK CASCADE TO THE SYNTHESIS OF INDOLOBENZAZEPINONES

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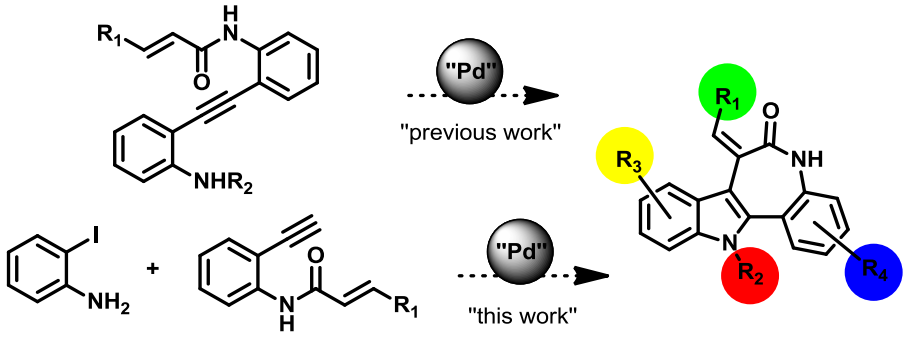
Keywords: one-pot, indolobenzazepinones*, Sonogashira, heterocyclization, Heck, palladium*

Indolobenzazepinones present promising antitumor properties, which might be related to their ability to inhibit cell-cycle cyclin-dependent kinases (CDKs) 1, 2, and 4 [1]. The synthesis of indolobenzazepinones and analogues has raised enormous interest over the last years, since these compounds have been found to also inhibit sirtuins, one of the deacetylase classes of epigenetic enzymes. Several methods for their synthesis have been published but we wanted to develop a new approach to their skeleton that in addition to versatility it could take place under milder reaction conditions. We have reported a new synthetic methodology [2] consisting on a complex sequence of palladium-catalyzed reactions that occur consecutively and include a heterocyclization and an oxidative Heck reaction.

In this work we have further increased the efficiency of the cascade reaction by incorporating a Sonogashira reaction prior to the heterocyclization–Heck. The one-pot sequence affords indolobenzazepinones starting from simple *o*-iodoanilines.



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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

THEORETICAL AND EXPERIMENTAL INSIGHTS IN THE BEHAVIOUR OF NHC-Ag COMPLEXES IN SOLUTION

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Keywords: *silver carbenes, conformational analysis, DFT, NMR, transmetalation*

Transmetalation of silver(I)-N-heterocyclic carbenes (NHC-Ag) to metal precursors is probably the most widely used synthetic method in the synthesis of NHC-metal complexes.[1] This method has gained increasing relevance because NHC-Ag can be synthesized in mild conditions from the corresponding imidazolium salt and silver oxide. Small modifications on the NHC ligand often leads to complex variations in the structure of NHC-Ag complexes in the solid state with a wide variety of dispositions around the silver centre.[1b, 2] For instance, NHC-AgBr, $(NHC)_2$-Ag^+ and $[Ag(\mu\text{-}Br)(NHC)]_2$ structures have been described in the solid state as a consequence of subtle variations of the NHC ligand.[3] Although physical and chemical properties of NHC-Ag complexes, neither the exact nature of NHC-Ag(I) halides in solution nor the carbene transfer mechanism have been clearly established yet.[4]

In this communication we present a thorough theoretical and experimental study on the interconnection ways of of silver(I) species in solution from NMR data and DFT calculations based in the bulk, limited conformations and concavity of the 3-mesityl-1-(2-pyridyl)imidazol-2-ylidene bidentate ligands. Starting from an adequate design of the NHC ligand, the delicate balance between meaningful species in solution that rules over their chemical reactivity will be stated by means of DFT calculations and confirmed by NMR experiments. This balance will be the key point to explain the easiness of most NHC transfer mechanism from NHC-Ag(I) halides to many metal sources. Particularly, transfer mechanism to $[RuCl_2(p\text{-cymene})]_2$ is thoroughly examined in this work

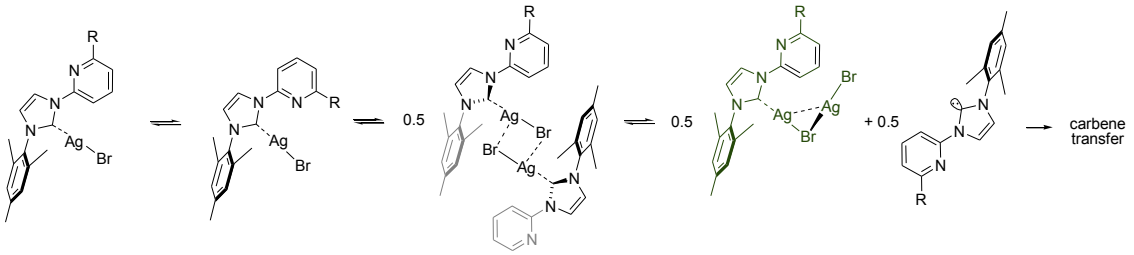

Figure 1. Some silver(I) species involved in solution equilibrium.

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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

CHIRAL *N*-HETEROCYCLIC CARBENES FUSED INTO AN HETEROBIARYL SYSTEM

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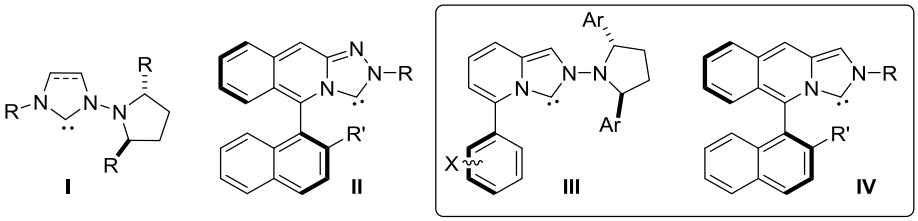
Keywords: *NHCs, Ligand design, Synthetic methods, Chirality*

N-Heterocyclic carbenes (NHCs) constitute a well established type of ligands in transition-metal catalysis. Characterized by strong σ-donor and variable π-acceptor properties, these ligands typically provide a high thermal and chemical stability to their complexes. These issues, with the convenient introduction of chiral elements, have made NHCs the ligand of choice for many metal-catalysed transformations.[1] In recent years, NHCs have also emerged as a useful class of Lewis bases with a plethora of applications in asymmetric organocatalysis.[2] We have been interested in the design and applications of new families of *N*-heterocyclic carbene ligands, with different chiral elements. For example, we have reported structures incorporating *N*-dialkylamino groups of type **I** [3] and more recently, triazol units embedded in a rigid axially chiral cyclic frame (type **II**).[4] We now wish to report the synthesis, resolution and coordination chemistry of new families of *N*-heterocyclic carbenes **III** [5] and **IV**. The first one incorporates a chiral *N*-dialkylamino moiety into an imidazo[1,5-*a*]pyridine system fused with a biaryl skeleton. On the other hand, new structures **IV** integrate a imidazo[1,5-*a*]isoquinolin-2-ylidene moiety into an axially chiral heterobiaryl structure.



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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

ASYMMETRIC SYNTHESIS OF VERSATIL BENZYLIC BORONIC ESTERS THROUGH A BORYLATION-AROMATIZATION PROCESS

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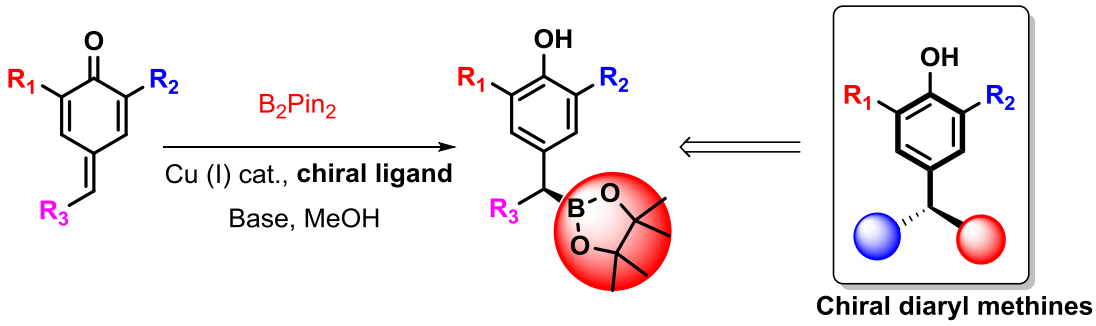
Key words: *para-Quinone methides, asymmetric catalysis, borylation, diaryl methines.*

para-Quinone methides (*p*-QMs)[1] have been known as reaction intermediates for more than a century. They consist of a cyclohexadiene moiety in *para*-conjugation with a carbonyl group and a*n* exo-methylene component. As a result of the intrinsic electrophilic reactivity *of p*-QMs, highly reactive transient *p*-QM species generated in situ are implicated in many chemical, medicinal, and biological processes. However, *p*-QMs have been scarcely used as starting materials in asymmetric catalysis.[2]

Recently, our group has been focused on the design of new copper-catalyzed borylation reactions.[3] In this context, we envisioned the synthesis of chiral diarylmethines through copper-catalyzed borylation-aromatization of *p*-quinone methides. The products are enantiomerically enriched dibenzylic boronates that can be transformed into important chiral diarylmethines derivatives (Scheme 1).



Acknowledgements: Financial support from Spanish Government (CTQ-2012-35957) and the European Research Council (ERC Starting Grant DAUBOR) is gratefully acknowledged.

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Presentaciones Póster (PP)

SEQUENTIAL ONE-POT INDIUM-CATALYZED INTRAMOLECULAR HYDROARYLATION /PALLADIUM-CATALYZED CROSS-COUPLING REACTIONS USING HALOPROPARGYL ARYL ETHERS AND ANILINES

L. Alonso-Marañón

THE CATALYSTS MATTER. RING-OPENING (ROP) VERSUS RING-EXPANSION (REP)

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Os-CATALYZED CYCLIZATION OF o-(ALKYNYL)PHENETHYLAMINES BY OSMACYCLOPROPENATION: AN EASY ENTRY TO DOPAMINERGIC 3-BENZAZEPINES

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GOLD (I) COMPLEXES AND SECONDARY AMINES WORK SYNERGISTICALLY

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MIZOROKI-HECK AND DIRECT ARYLATION REACTIONS IN THE CONSTRUCTION OF MEDIUM-SIZE RING SYSTEMS

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BENZOXAZINES VIA DUAL Ru-H / BRØNSTED ACID-CATALYZED CHAIN WALKING/ ENAMIDE ISOMERIZATION PROCESS

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RHODIUM-CATALYZED (5+1) ANNULATIONS BETWEEN 2-ALKENYLPHENOLS AND ALLENES

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GOLD CATALYZED β-ELIMINATION REACTION

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ENANTIOSELECTIVE ALKYNYLATION OF BENZO[e][1,2,3]-OXATHIAZINE 2,2-DIOXIDES CATALYZED BY COMPLEXES OF (R)-VAPOL-Zn(II): SYNTHESIS OF ASYMMETRIC PROPARGYLIC CYCLIC SULFAMIDATES

L. De Munck

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$Pd(OAc)_2$ CATALYZED C–H BOND FUNCTIONALIZATION OF ADAMANTANE DERIVATIVES

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FUNCIONALIZACIÓN DE METALOCENOS CATALIZADA POR COMPLEJOS DE ORO(I)

Enol López

SYNTHESIS OF ALKYLIDENE PYRROLO[3,4-b]PYRIDIN-7-ONE DERIVATIVES via Rh(III)-CATALYZED CASCADE OXIDATIVE ALKENYLATION/ANNULATION OF PICOLINAMIDES

Á. M. Martínez

METALACICLOS DE Pd(II) ESTABILIZADOS POR LIGANDOS DIALQUILTERFENIL FOSFINAS. APLICACIONES CATALÍTICAS EN LA REACCIÓN DE AMINACIÓN DE BUCHWALD-HARTWIG

Celia M. Maya

VINILARENOS COMO DIPOLARÓFILOS EN CICLOADICIONES [3+2] CATALÍTICAS ASIMÉTRICAS DE ILUROS DE AZOMETINO

A. Pascual-Escudero

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L.C de V. Poutás

ASYMMETRIC SYNTHESIS OF AXIALLY CHIRAL P,N-LIGANDS VIA DYNAMIC ASYMMETRIC C–P CROSS–COUPLING REACTION

A. Ros

RHODIUM (III)-CATALYZED ANNULATIONS BETWEEN 2-HETEROSUBSTITUTED STYRENES AND ALKYNES

A. Seoane

SALES DE IMIDAZOLIO FUNCIONALIZADAS: APLICACIÓN EN LA SÍNTESIS DE CARBENOS N-HETEROCÍCLICOS Y FORMACIÓN DE COMPLEJOS METÁLICOS

D. Sol

GROUP IV METALLOCENIUM CATALYSTS FOR THE CHEMO- AND STEREOSELECTIVE POLYMERIZATION OF POLAR DIVINYL MONOMERS

F. Vidal

MECHANISTIC STUDY ON THE BIMETALLIC COOPERATIVE CATALYSIS OF Au(I) AND Ag^{+} ON REARRANGEMENT OF ALKYNIL SUBSTITUTED SUBSTRATES

P. Villar Cruces

SÍNTESIS DE COMPLEJOS HETEROMETÁLICOS CONTENIENDO CARBENOS METALA-N-HETEROCÍCLICOS

M. Vivanco

S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

SEQUENTIAL ONE-POT INDIUM-CATALYZED INTRAMOLECULAR HYDROARYLATION/PALLADIUM-CATALYZED CROSS-COUPLING REACTIONS USING HALOPROPARGYL ARYL ETHERS AND ANILINES

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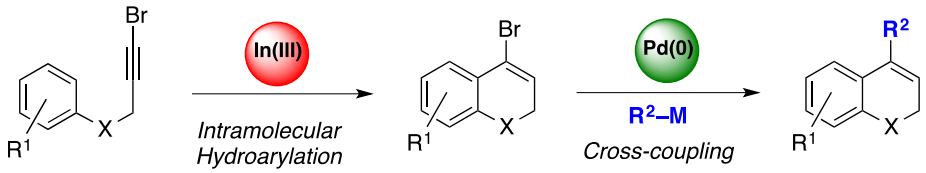
Keywords: *Hydroarylation, One-Pot reactions, Indium catalysis, Palladium catalysis, Cross-Coupling.*

Sequential one-pot reactions are attractive synthetic tools in modern organic chemistry.[1] The possibility to form several bonds in one vessel offers important synthetic advantages in terms of economy, sustainability and versatility. Although this methodology has been applied to some classical organic reactions, its development into sequential metal-catalyzed transformations is challenging due to the increasing level of complexity enabling redox-processes or ligand-exchange reactions.[2] In this communication we present the sequential one-pot indium-catalyzed intermolecular hydroarylation (IMHA)/palladium-catalyzed cross-coupling reaction using 3-bromopropargyl aryl ethers and anilines.



R^1 = H, OMe, Me, CO_2Me
X = O, NMe, NTs

R^2 = (Hetero)Aryl, alkyl, alkynyl
M = In, $B(OH)_2$, ZnCl, $SnBu_3$

Recently, we reported that In(III) halides efficiently catalyze the IMHA of functionalized propargyl aryl ethers to give the corresponding 4-substituted-*2H*-chromenes.[3] Now we found that the IMHA can be combined, in a sequential one-pot reaction, with Pd-catalyzed cross-coupling reactions using different organometallics. This methodology was also extended to 3-bromopropargyl anilines with good yields. Remarkably, best results are obtained when triorganoindium reagents (R_3In) are used as organometallics.

Acknowledgements: We are grateful to the Ministerio de Economía y Competitividad (CTQ2012-31200) for financial support.

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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

THE CATALYSTS MATTER. RING-OPENING (ROP) *VERSUS* RING-EXPANSION (REP)

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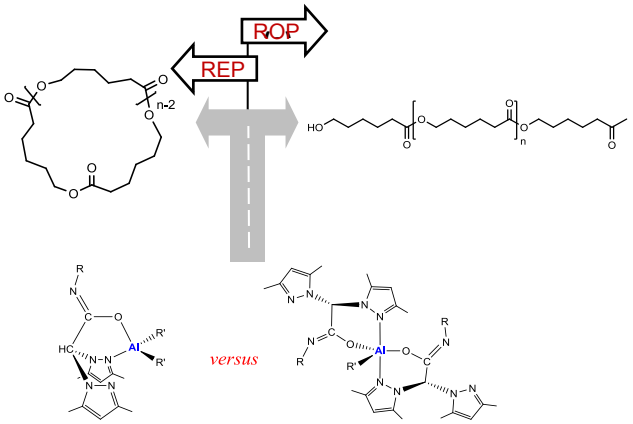
Keywords: *Ring-Opening Polymerization, Ring-Expansion Polymerization, Aluminiun catalysis, Heteroscorpionate Ligands.*

The last two decades of the twentieth century have witnessed a paradigm shift from biostable to biodegradable biomaterials for medical and related applications.[1] In fact, this current trend has promoted a spectacular advance in new polyester materials.[2] Although several elegant routes for the synthesis of cyclic polymers have been reported, there is still a need for a suitable method for the synthesis of high molecular weight cyclic polymers with narrow polydispersities.[3] Herein, we would like to report the first series of alkyl-organoaluminum catalysts for the well-controlled Ring-Expansion Polymerization of cyclic esters,[4] The designed alkyl-organoaluminum complexes show a very rare ability to generate controlled cyclic polylactones. [4c]

The synthesis of cyclic PCLs by polymerization with monoalkyl-organoaluminum compounds as initiators is particularly attractive because (1) it is well-controlled and efficient, (2) it is highly productive, (3) it does not generate linear intermediates, (4) it does not require time-consuming purification procedures, (5) only small quantities of initiator are required.



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S3: *Catálisis Organometálica como Solución a Retos Sintético*

Os-CATALYZED CYCLIZATION OF *o*-(ALKYNYL)PHENETHYLAMINES BY OSMACYCLOPROPENATION: AN EASY ENTRY TO DOPAMINERGIC 3-BENZAZEPINES

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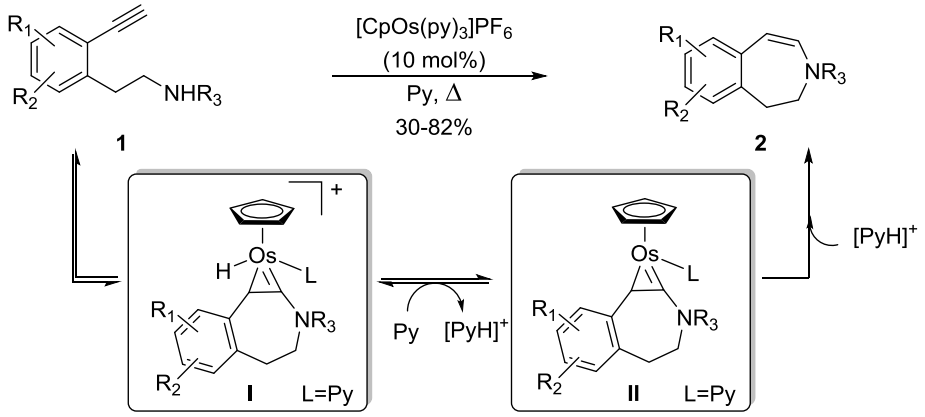
Key Words: *benzazepines, cyclization, osmium, osmacyclopropene*

Heterocyclic derivatives containing phenethylamine units have shown important dopaminergic properties.[1] In particular, seven-membered 3-benzazepines remain as one of the most reliable structural scaffold in terms of the affinity and selectivity against the D_1 receptor of mammalian brains.[2] Metal-mediated intramolecular hydroamin(d)ations of alkynylamin(d)es have been employed as one of the typical pathways for their preparation.[3] However, no *7-endo dig* cyclization of terminal *o*-(alkynyl)phenthylamines to 3-benzazepines has been described.

Based on our recently developed Os-catalyzed cyclization of terminal bis-homopropargylic alcohols,[4] we now report the novel Os-catalyzed *7-endo dig* cyclization of terminal *o*-(alkynyl)phenethylamines **1** to 3-benzazepines **2** via the formation of new osmacyclopropene intermediates **I** and **II**, which have been characterized by X-Ray analysis (L= P^iPr_3).



R_1, R_2 = H, Me, OMe, OCH_2O, CF_3, Cl
R_3 = Alk, Bn, Cy, $CH_2Ph(OMe)_2$, $CH_2CH_2Ph(OMe)_2$

Acknowledgements: This work was supported by MICINN (project CTQ2011-28258 and ORFEO-CINQA CTQ2014-51912-REDC), Xunta de Galicia and European Development Fund (projects GRC2014/032 and EM 2012/051). A.A-P. thanks MINECO (Spain) for a FPI fellowship (BES-2012-054798).

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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

GOLD (I) COMPLEXES AND SECONDARY AMINES WORK SYNERGISTICALLY

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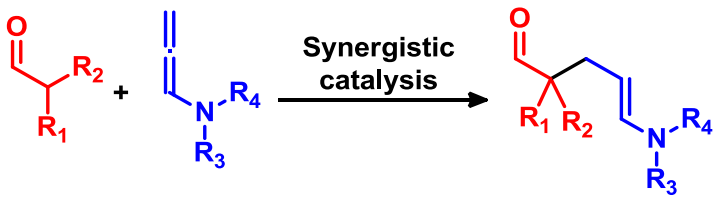
Keywords: *synergistic catalysis, allenamides, alehydes, gold, organocatalysis*

In the last few years asymmetric organocatalysis has proved to be a powerful tool to afford a variety of chemical transformations in good yield and enantioselectivity. Transition metal catalysis is well established as a method to activate different types of chemical bonds. The merging of these two methods allows new chemical transformations.[1] Synergistic catalysis consists on the simultaneous activation of the electrophile and the nucleophile by two separate and distinct catalysts to afford a single chemical transformation.[2] In this work a new synergistic catalytic system is tested.

Several Proline based organocatalysts work synergistically with cationic gold complexes to allow the intermolecular reaction between allenamides and aldehydes. The aldehyde is activated by the organocatalyst via an enamine intermediate, while the allenamide is activated by the gold complex. Specific additives are required to adjust the selectivity and avoid undesired side reactions. Thus, a new synergistic catalytic system that combines organocatalysis with cationic gold complexes allows the elusive reaction of aldehydes and allenamides to occur; as depicted in the scheme below.



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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

MIZOROKI-HECK AND DIRECT ARYLATION REACTIONS IN THE CONSTRUCTION OF MEDIUM-SIZE RING SYSTEMS

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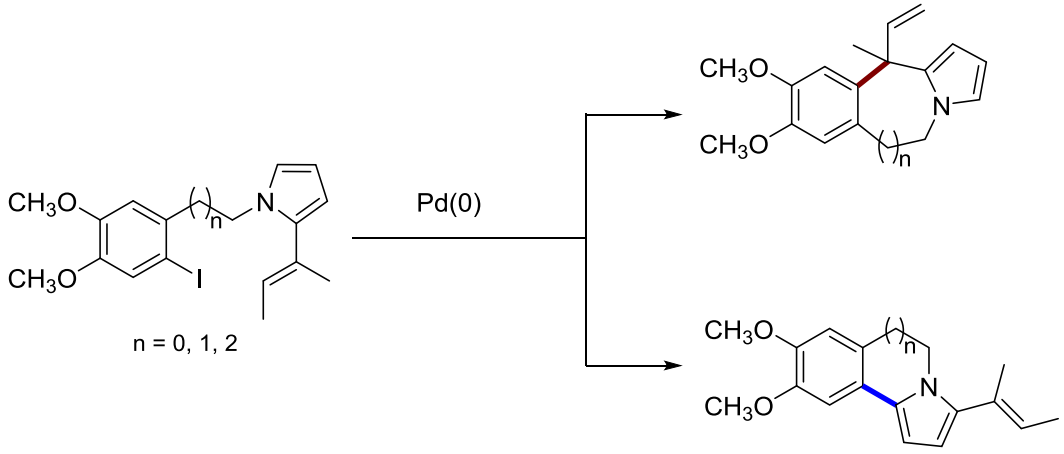
Keywords: *palladium, Heck reaction, direct arylation reaction, heterocycles*

The Mizoroki-Heck reaction of aryl and vinyl halides with alkenes has developed into one of the most important carbon-carbon bond-forming reactions in organic synthesis. The intramolecular variant represents an extremely powerful method for the construction of small and medium-size rings. Particularly in recent years, this procedure has become an effective method for the formation of tertiary and quaternary stereocenters, even in an asymmetric fashion. To achieve the formation of a quaternary centre, it is necessary to avoid the syn β-elimination of the hydride in the σ-alkylpalladium intermediate formed after the insertion of the arylpalladium to the alkene, so that the elimination takes place in another β' position and not on the carbon involved directly in bond formation. Thus, we have applied the Mizoroki-Heck cyclization on adequately functionalized pyrrole derivatives using different palladium catalysts and chiral bidentate phosphanes as ligands. In some cases, competition between Mizoroki-Heck reaction and C-H functionalization reaction on the pyrrole nucleus has been observed for this type of polyfunctionalized substrates. Moreover, a catalytic enantioselective Heck-type cascade reaction have led to the synthesis of lycorine class of *Amarillydaceae* alkaloids by the rational design of the substrates.



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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

Pd-CATALYZED AUTOTANDEM C-C/C-C BOND-FORMING REACTIONS WITH TOSYLHYDRAZONES: SYNTHESIS OF SPIROCYCLES WITH EXTENDED π-CONJUGATION

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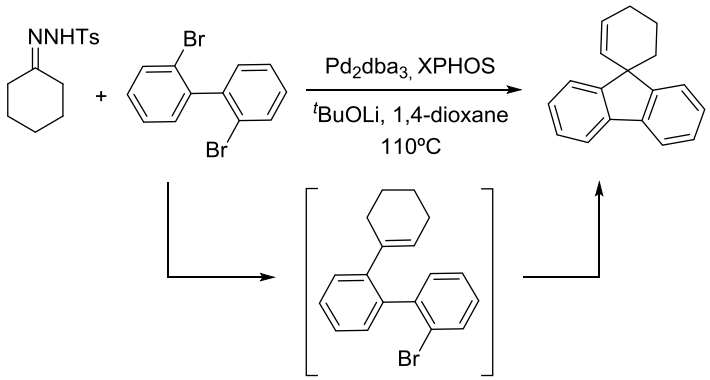
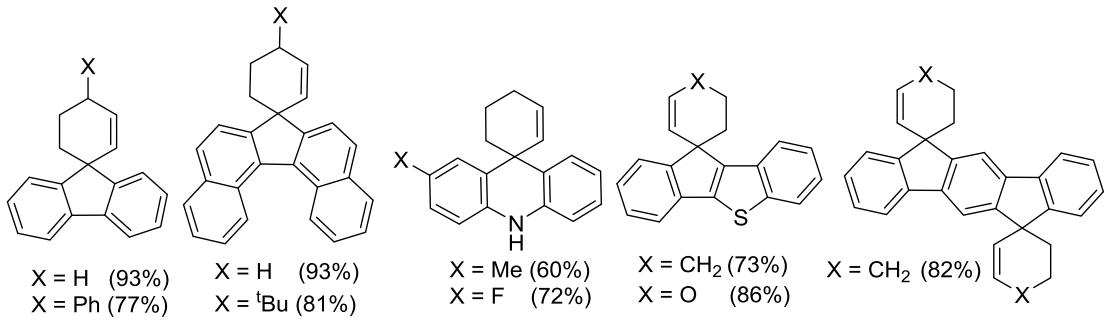
Keywords: *Tosylhydrazone / Autotandem / Spirocycles / Fluorescence*

According to our interest in the Pd-catalyzed cross-coupling reactions employing tosylhydrazones [1,2], we have reported the first autotandem process through a C-C/C-N sequence[3] and the first autotandem C-C/C-C process with participation of tosylhydrazones as a coupling partner[4]. We envisioned a different approach by designing a reaction cascade in which the funcionality generated in the first step would react again in a second step. In particular, considering the reaction of tosylhydrazones, the double bound formed in the first Pd-catalyzed cross-coupling might participate in an intramolecular Heck reaction to render spirocycles through a C-C/C-C autotandem sequence[5].



Some of these rigid spirocyclic structures with extended π-conjugation have shown fluorescent properties and would be employed in the development of electroluminiscent and optoelectronic materials[6].



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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

BENZOXAZINES VIA DUAL Ru-H / BRØNSTED ACID-CATALYZED CHAIN WALKING/ ENAMIDE ISOMERIZATION PROCESS

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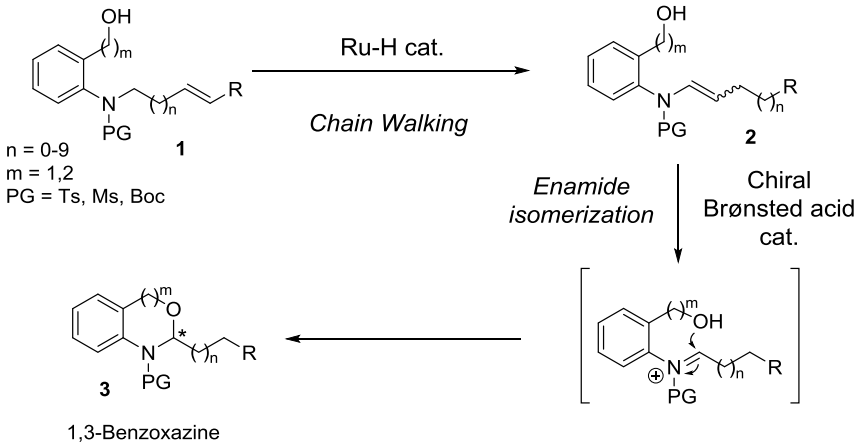
Key Words: *ruthenium, chain-walking, isomerization, cyclization, benzoxazines*

Tandem reactions have become important tools in organic synthesis since they allow the combination of different chemical transformations in *one-pot* reactions. [1]
Our research group has been working on a dual ruthenium hydride/ Brønsted acid-catalyzed in situ generation of highly electrophilic iminium ion intermediates, which can be trapped by a variety of nucleophiles in order to deliver cyclic products. The first step of the tandem reaction consists into the generation of the corresponding enamide through a long distance chain walking process of an alkene moiety, catalyzed by the ruthenium hydride complex. Then, a Brønsted acid catalyst enables the formation of the iminium species that reacts quickly with the nucleophile.[2]



Acknowledgements: This work is supported by MICINN (project CTQ2011-28258), Xunta de Galicia and European Regional Developement Fund (projects GRC2014/032 and EM 2012/051). R. B. thanks MEC for a predoctoral fellowship (FPU12/00941).

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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

HIGHLY ENANTIOSELECTIVE COPPER-CATALYZED ADDITION OF METHYL NITROBUTYRATE TO ISATIN KETIMINES. SYNTHESIS OF SPIROOXINDOLES

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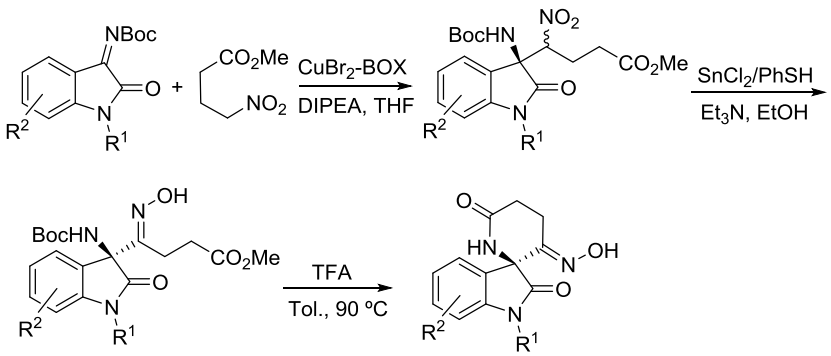
Keywords: *Asymmetric catalysis, Copper catalysis, Henry reaction, Ketimines, Oxindoles*

The 3,3'-spirooxindole framework constitutes a privileged pharmacophore and is present in a large number of natural alkaloids [1]. Among these, spiropiperidino-3,3'-oxindoles featuring a piperidine spiranic ring have raised much interest because of their biological and pharmacological activity. For instance, some spiropiperidino-3,3'-oxindoles show analgesic [2], anticonvulsive [3] or antimalarial [4] activities. They are also being investigated as type II β-turn peptide isosteres [5].

On the other hand, the asymmetric addition of carbon nucleophiles to isatin ketimines represents a straightforward procedure for the synthesis of 3-aminooxindoles bearing a stereogenic center at C3. Recently, we have reported the enantioselective aza-Henry reaction with *N*-Boc isatin ketimines using a copper(II)-BOX catalyst, which provided the corresponding 3-amino-3-nitroalkyloxindoles with high yields and excellent enantiomeric excesses [6]. In this communication, we will present an extension of this reaction using methyl 4-nitrobutyrate to give amino esters which can be cyclized to highly functionalized spiropiperidino-3,3'-oxindoles.



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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

RHODIUM-CATALYZED (5+1) ANNULATIONS BETWEEN 2-ALKENYLPHENOLS AND ALLENES

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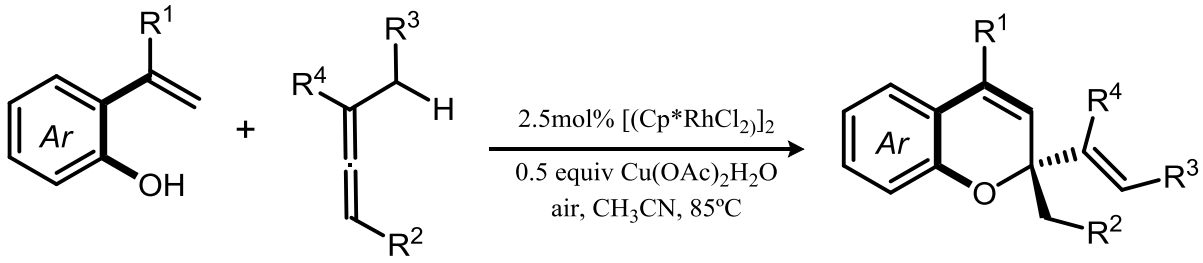
***Keywords**: C-H activation, allenes, Rhodium, Alkenylphenols*

Recent years have witnessed an impressive development of reactions involving the functionalization of C-H bonds. However, transformations in which the C-H activation is coupled to a formal cycloaddition have been much less studied [1]. We have recently reported several Rh-catalyzed oxidative annulations of 2-alkenylphenols with alkynes that allow to obtain interesting bicyclic products [2]. Interesting, while alkenes fail to participate in the annulations, allenes react with the alkenylphenols to give interesting 2,2-disubstituted chromenes [3]. Herein we present details of these annulations, including mechanistic aspects and synthetic scope.



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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

GOLD CATALYZED β-ELIMINATION REACTION

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Keywords: β- *elimination, gold catalysis*

Despite the impressive diversity and complexity of reactions catalyzed by gold, β-eliminations, a common process for other transition metals, are not usually considered for this metal. Recently Köppel and coworkers illustrated the mechanistic features that make the β-elimination unfeasible for Au(I) catalysts [1]. At the same time, Fernández *et. al.* employed a β-elimination of an oxetanyl substrate along the mechanism of the gold catalyzed allene cyclization reaction in the obtention of a highly tensed oxetene ring[2].

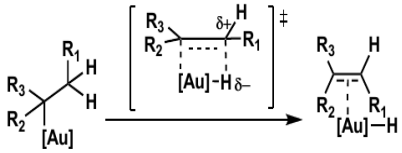

Figure 1. Gold catalyzed β-elimination reaction.

We have therefore carried out a detailed study exploring the possibility of finding β-eliminations on gold, taking particular attention to the effects of the metal oxidation state and coordination sphere.

Calculated reaction barriers are high, as previous results suggested, ranging from 67.5 kcal/mol to 27.6 kcal/mol, for the Au (III) and Au(I) unsubstituted substrates, respectively. Interestingly, we found how the alkyl substrate can modulate the reaction energetic profile. Thus, for Au(III) the incorporation of a phenyl substituent in β induces a significant drop of 5.7 kcal/mol in the computed reaction barriers. The elimination process also turns out to be sensitive to the electronic nature of substituents, and we find that with Au(III) the presence of a β substituent with high electron density (pNH$_2$(C$_6$H$_4$)), induces a lowering of the reaction barriers by 9.3 kcal/mol. For the Au(I) catalyzed reaction a different trend was identified, with an energy drop of 14.5 kcal/mol induced by an aromatic substituent at the α position. Despite electronic features being the most significant in the modulation of the reaction barriers, the energetic profile of this β-elimination reaction is also sensitive to sterical features.

As a result, an optimal combination of factors allowing for the gold-catalyzed β-elimination process to occur is provided.

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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

ENANTIOSELECTIVE ALKYNYLATION OF BENZO[*e*][1,2,3]-OXATHIAZINE 2,2-DIOXIDES CATALYZED BY COMPLEXES OF (*R*)-VAPOL-Zn(II): SYNTHESIS OF ASYMMETRIC PROPARGYLIC CYCLIC SULFAMIDATES

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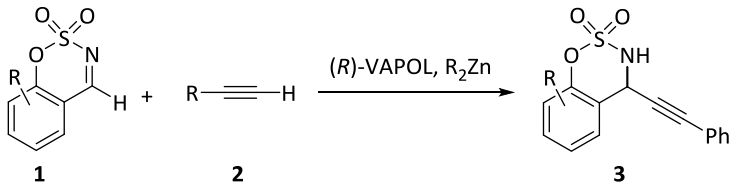
Keywords: *Enantioselective addition, alkynes, benzoxathiazine-2,2-dioxide, sulfamidate*

Optically active propargylic amines are efficiently obtained through asymmetric alkynylation of imines. [1] These propargylic amines are useful building blocks for the synthesis of nitrogen containing natural products and biologically active compounds. Typically, research concentrates on the asymmetric alkynylation of acyclic imines, while the asymmetric alkynylation of cyclic imines is less studied, although it is a powerful tool for the synthesis of optically active nitrogen containing heterocycles. [2] Therefore, our focus was drawn to the study of benzoxathiazine-2,2-dioxide, a molecule that has recently become an interesting electrophile in several transformations. [3] The Z geometry of the C=N bond and the lower conformational mobility of this imine make it an interesting electrophile for the asymmetric addition of alkynes.

In this communication we report the enantioselective addition of terminal alkynes **2** to benzoxathiazine-2,2-dioxides **1**, catalyzed by a complex of (*R*)-VAPOL-Zn(II), obtaining the corresponding sulfamidates **3** in good yields and enantioselectivities.



1 **2** **3**

Scheme 1

Acknowledgements

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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

SYNTHESIS AND CHIRALOPTICAL PROPERTIES OF ENANTIOPURE 5-(2-p-TOLYLSULFINYLFERROCENYL) SUBSTITUTED DITHIENYLETHENES

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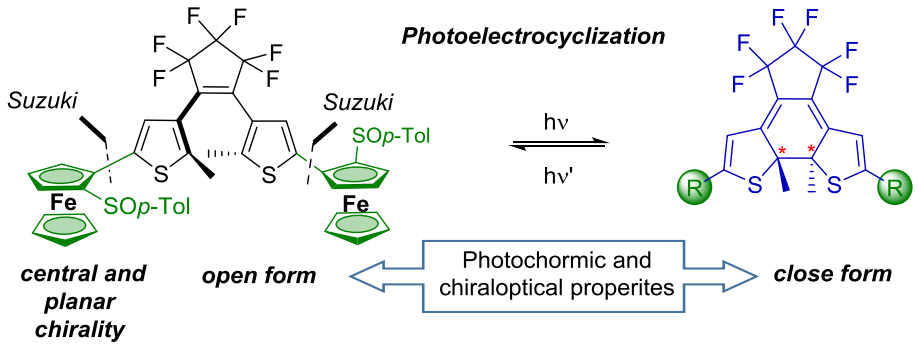
Keywords: *Ferrocene, Suzuki, chiral dithienylethenes, sulfoxide, enantiopure molecular photoswitches.*

The development of molecular photoswitches is an area of growing interest due to its possible applications in chemistry, biology, nanotechnology and information science.[1] A molecular photoswitch must be able to interconvert between two or more different species in a reversible manner, by means of an external light irradiation. Among the most widely used organic photoswitches[2] are azobenzenes and di(aryl)ethenes. Recently a ferrocene unit incorporated into a dithienylethene naphthalimide, has been reported to the design of a photo- and redox multi-addressable molecular switch, due to the reversible photoelectrocyclization of the dithienylethene system and the redox properties of ferrocene.[3] On the contrary, there are no precedents of introducing an enantiopure ferrocenyl unit into the dithienylethenes. In 2007, our research group uncovered a novel application of the sulfoxides as a conformational and configurational controller of enantiopure sulfinyl azobenzenes, modulating their chiraloptical properties.[4] We have now synthetized chiral dithienylethene derivatives bearing an enantiopure sulfinyl ferrocenyl group by means of a Suzuki cross-coupling reaction, and studied their behavior as enantiopure molecular photoswitches.



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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

RHODIUM (III)-CATALYZED INTRAMOLECULAR ANNULATIONS INVOLVING CARBOXILIC ACID-DIRECTED C-H ACTIVATIONS

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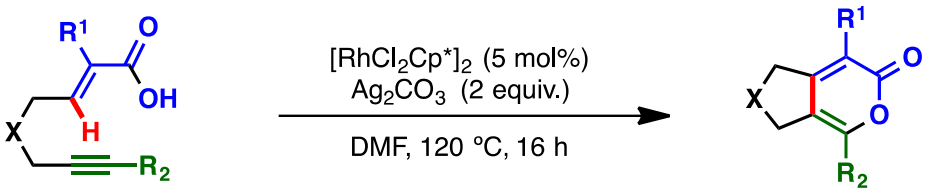
Keywords: *Annulations, Intramolecular, C-H activation, Rhodium.*

In recent years there has been a boost on the development of functionalization processes based on metal-promoted C-H activations. [1] There have been also many reports on processes that link the C-H activation with a formal cycloaddition, as they allow the assembly of different type of cycles in an atom economical manner. While most of these reports deal with intermolecular reactions the development of intramolecular versions is lagging behind.

Recently, our research group has demonstrated the viability of a Rhodium (III) catalyzed intramolecular formal [4+2] annulation between benzamides and N-tethered alkynes, reaction that provides interesting tricyclic isoquinoline derivatives in good yields. [2] We have now investigated other intramolecular reactions of substrates featuring different type of reacting partners, as well as different connecting tethers. Herein we present details of these annulations, including mechanistic aspects and synthetic scope.



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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

LIGANDOS PIRIDINO-HIDRAZONA EN CATÁLISIS ASIMÉTRICA

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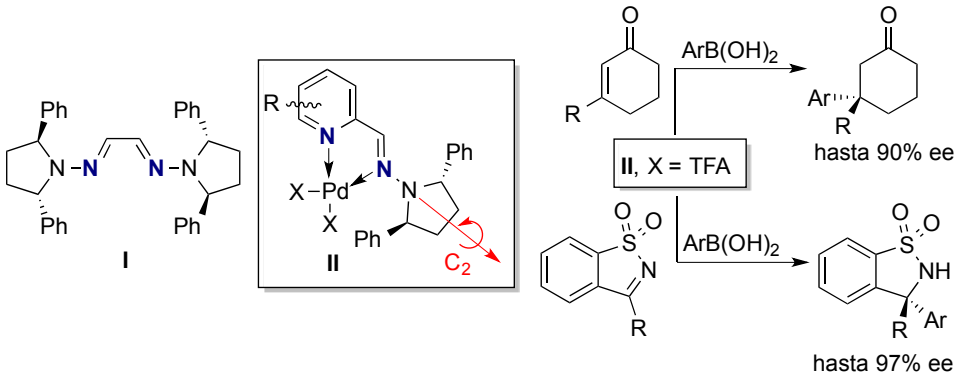
Palabras Clave: *Ligandos nitrogenados, catálisis organometálica, paladio, síntesis asimétrica*

El diseño y la síntesis de nuevas familias de ligandos quirales constituyen la base esencial para el desarrollo y evolución de la catálisis asimétrica. Actualmente, existe un interés creciente en ligandos nitrogenados [1], que ofrecen en general una superior variabilidad estructural y son más fáciles de manejar y reciclar que los universalmente extendidos ligandos fosforados. En particular, la agrupación C=N presente en bipiridinas, bisiminas, bisoxazolinas y piridino-bisoxazolinas ha permitido el desarrollo de un gran número de aplicaciones en síntesis asimétrica. En este contexto, en nuestro grupo de investigación hemos demostrado el potencial de ligandos basados en bishidrazonas quirales **I** (Esquema 1) en reacciones de Diels Alder catalizadas por Cu(II) y en reacciones de tipo Suzuki-Miyaura catalizadas por Pd(0) para la síntesis enantioselectiva de biarilos, alcanzándose en ambos casos elevados niveles de enantioselectividad.[2] La clave del diseño reside en el empleo del grupo (2*S*,5*S*)-2,5-difenilpirrolidina, que evita la pérdida del entorno quiral en las proximidades del centro metálico por rotaciones en torno al enlace N-N. En esta comunicación se presentan nuevos ligandos piridinohidrazona de segunda generación (**II**) y su aplicación en diversas reacciones de adición enantioselectiva de ácidos arilborónicos a enlaces C=C y C=N catalizadas por paladio.



Esquema 1.

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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

THEORETICAL STUDY OF METAL-CATALYZED CYCLIZATIONS

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Keywords: *Baldwin's rules, transition states, ring-closure, transition metals.*

Baldwin's rules [1,2] for ring closure are empirical descriptions of the relative easiness of ring formations (ring closure/cyclization). These rules were applied very effeciently in the last decades, but they have some limitations as well (*e.g.* do not apply to second row elements). An important question is the presence/absence of metals in the system. Are there any Baldwin-type rules for cyclization in the case of metal containing systems? To explore this issue, metal catalysed ring-closure reactions were studied computationally (Figure 1). The following four factors were investigated:

1) transition metals (9 late Transition Metals)
2) size of the formed rings (3-7)
3) geometry of the atom being attacked (dig and trig)
4) type of the ring closure (exo and endo).

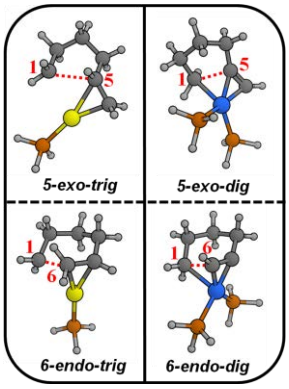

Figure 1 Calculated transition states: 5-exo- & 6-endo-trig with Au(I) and 5-exo- & 6-endo-dig with Co(I).

A total of 144 different possible model reactions were designed and finally 136 transition states were located. The barrier heights were computed and the feasibility of the different reactions were compared. Based on these calculations there is a clear preference favoring the exo process over the endo.

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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

HIDROSILILACIÓN REGIOSELECTIVA DE PROPARGIL 2-PIRIDILSULFONAS: SÍNTESIS DE VINIL SILANOS A DEMANDA

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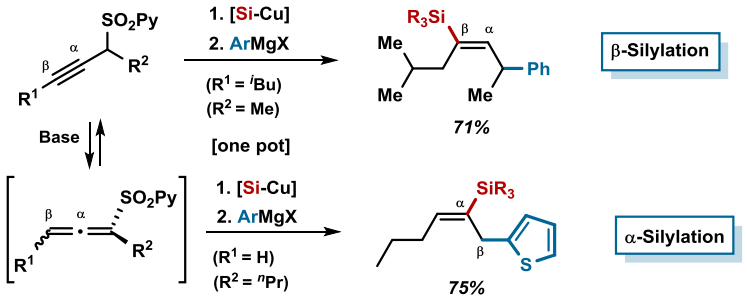
Palabras Clave: *sililcupración, hidrosililación, vinil silano, 2-piridilsulfona.*

Los compuestos vinil silanos son componentes básicos para la química sintética moderna. Por ello, los métodos para su producción siguen siendo un área de interés incuestionable [1]. La hidrosililación catalizada por metales es posiblemente la reacción más versatil y directa para la síntesis de estos reactivos ya que permite controlar por completo la regio- y estereoselectividad del proceso. La mayor parte de los ejemplos encontrados en la bibliografía se han centrado en la hidrosililación de alquinos terminales [2], debido fundamentalmente a que los alquinos internos poseen una reactividad inferior y presentan la dificultad inherente de poder llevar a cabo la hidrosililación con total regioselectividad, sobre todo cuando se utilizan alquinos internos no simétricos que poseen sustituyentes con propiedades electrónicas y/o estéricas muy parecidas. Recientemente, han aparecido las primeras metodologías en las que se ha conseguido una alta regioselectividad de la reacción de sililación, pero utilizando para ello sustratos con marcada diferencia electrónica en los sustituyentes acetilénicos [3].

En este trabajo se describe un método general y práctico para la síntesis regio- y estéreoselectiva de vinilsilanos di- y trisustituidos a partir de alquinos internos y terminales mediante hidrosililación catalizada por cobre. El empleo del grupo 2-piridilsulfonilo en la posición propargílica es clave en tres sentidos. En primer lugar, controla la reactividad del sistema. En segundo lugar, permite llevar a cabo el reordenamiento alquino/aleno, lo que conduce a un eficiente control en la regioselectividad del proceso de hidrosililación. Finalmente, su fácil eliminación permite nuevas transformaciones en los vinilsilanos obtenidos, aumentando por ello la versatilidad del sistema.



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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

REACTIVIDAD DE OXODERIVADOS DI- Y TRINUCLEARES DE TITANIO CON ^{i}PrNC: DE INSERCIONES A PROCESOS COOPERATIVOS

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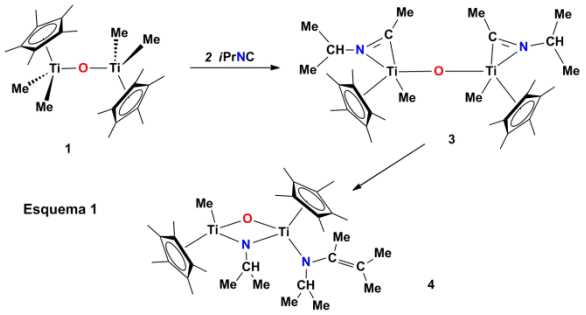
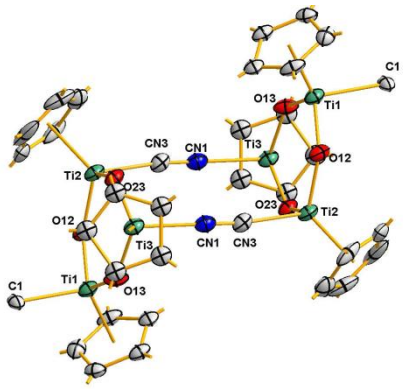
Palabras Clave: *inserción – titanio - isocianuros*

Los procesos de inserción con formación de complejos η^2-iminoacilo de metales de los primeros grupos de transición han sido ampliamente estudiados durante años.[1] En esta comunicación se describe la reactividad de los oxoderivados di- y trinucleares de titanio [{Ti(η^5-C_5Me_5)(μ-O)Me_2}$_2$] (**1**)[2] y [{Ti(η^5-C_5Me_5)(μ-O)Me}$_3$] (**2**)[3] con ^{i}PrNC .

Tal y como se observa en el Esquema 1, el tratamiento de **1** con dos equivalentes de ^{i}PrNC transcurre con inserción en ambos centros metálicos para dar [{Ti(η^5-C_5Me_5)(^{i}PrNCMe)Me}$_2$ (μ-O)] (**3**). Este derivado es inestable y evoluciona a temperatura ambiente al compuesto imido-vinilamido [{Ti(η^5-C_5Me_5)}$_2$(μ-O)(μ-N^{i}Pr)(^{i}PrNCMe=CMe_2)Me] (**4**) mediante un proceso de acomplamiento intramolecular.



Esquema 1



Por otro lado, la reacción análoga con el derivado trinuclear **2** e isopropilisocianuro transcurre con formación del complejo [{Ti(η^5-C_5Me_5)(μ-O)}$_3$ (^{i}PrNCMe)Me_2] (**5**), como resultado de la inserción en uno de los tres enlace titanio-carbono. El posterior tratamiento térmico del producto **5** conduce a la formación de la especie paramagnética [{Ti_3(η^5-C_5Me_5)$_3$(μ-O)$_3$Me}$_2$(μ-CN)$_2$] (**6**), cuya estructura molecular se muestra en la figura lateral.

Agradecimientos: M.C.T. (CTQ2013-44625-R) y Universidad de Alcalá (CCG2014/EXP-022). M. Gómez-Pantoja agradece a la Universidad de Alcalá la concesión de una beca predoctoral.

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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

$Pd(OAc)_2$ CATALYZED C–H BOND FUNCTIONALIZATION OF ADAMANTANE DERIVATIVES

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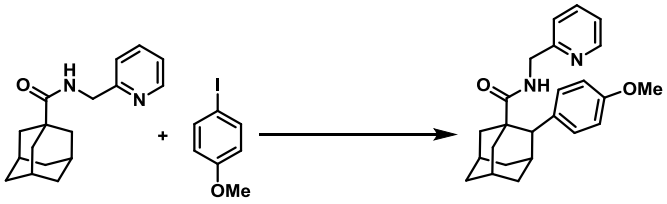
Keywords: *C(sp^3)-H functionalization, adamantane, palladium acetate, arylation*

The adamantane moiety has been used in number of bioactive compounds and comercial drugs.[1] There is a general need to develop new approaches for this class of derivatives.

In the last decades, palladium-catalyzed C-H activation/C-C bond-forming reactions have emerged as promising new catalytic transformations. The selective functionalization of secondary or tertiary C(sp^3)-H bond[2] in adamantane unit is challenging due to its rather inert character.

Herein we demonstrate that the C-H functionalization of adamantane derivatives is feasible using specific amides as directing groups and $Pd(OAc)_2$ as catalyst. We will present the screening of directing groups, the scope of the reaction and the mechanistic rationale.



Scheme 1

Acknowledgment: This work was supported by the LOEWE "SynChemBio" project, funded by the State of Hesse.

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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

FUNCIONALIZACIÓN DE METALOCENOS CATALIZADA POR COMPLEJOS DE ORO(I)

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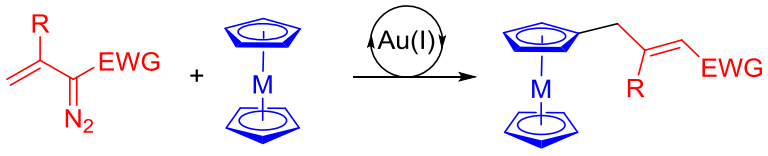
Palabras Clave: *ferroceno, catálisis, oro, funcionalización C-H, diazocompuestos.*

Debido a sus aplicaciones en catálisis, ciencia de materiales y medicina, los derivados funcionalizados de ferroceno constituyen una familia importante de compuestos organometálicos.[1] A pesar de esta importancia, el número de metodologías de funcionalización directa del ferroceno es muy limitado. En este sentido las rutas más comunes para la preparación de derivados sustituidos de ferroceno son la reacción de sustitución electrófila tipo Friedel-Crafts y la litiación del ligando Ciclopentadienilo (Cp) y posterior reacción con electrófilos. Sin embargo, estas metodologías requieren el empleo de cantidades estequiométricas de ácidos de Lewis o de reactivos organolíticos y muestran, por ello, una limitada compatibilidad con numerosos grupos funcionales.

En los últimos años nuestro grupo de investigación ha descrito nuevas aplicaciones sintéticas de diazoalquenos en procesos catalizados por complejos de oro.[1] Desde el punto de vista mecanístico estos procesos supondrían la generación de un vinilcarbenoide de oro intermedio con una elevada electrofilia en la posición vinílica y una acentuada tendencia a participar en procesos catiónicos. En esta comunicación se describe la extensión de este novedoso patrón de reactividad al ferroceno lo que ha permitido acceder a derivados funcionalizados de ferroceno de difícil preparación por metodologías tradicionales. Especificamente, la reacción de diazoalquenos **1** con ferroceno (**2**) en presencia de cantidades catalíticas de [Au(IPr)(CH_3CN)][SbF_6] (5 mol%) en diclorometano a temperatura ambiente conduce a los derivados funcionalizados de ferroceno **3** con rendimientos moderados (47-75%).[2] Este proceso se ha podido extender a la funcionalización del rutenoceno.



1 **2** (M = Fe) **4** (M = Ru) **3** (M = Fe) **5** (M = Ru)

Agradecimientos. E. L. agradece al Principado de Asturias la concesión de una beca predoctoral (Programa Severo Ochoa).

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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

SYNTHESIS OF ALKYLIDENE PYRROLO[3,4-b]PYRIDIN-7-ONE DERIVATIVES via Rh(III)-CATALYZED CASCADE OXIDATIVE ALKENYLATION/ANNULATION OF PICOLINAMIDES

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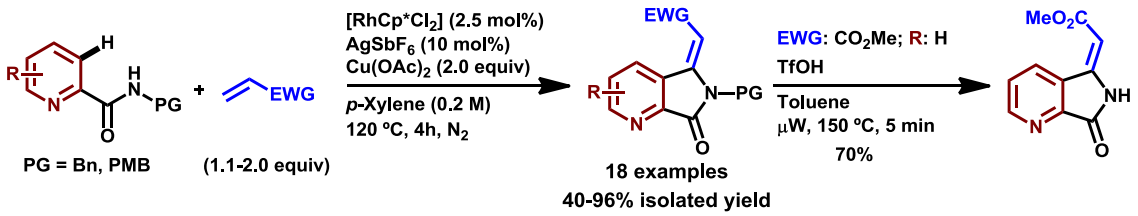
Key words: *Rh-catalysis, oxidative alkenylation/annulation, acrylates, picolinamides*

Metal-catalyzed C–H bond functionalization of nitrogen heteroarenes [1] is a highly appealing research as they are key functional units in drugs and functional materials.[2] However, its application to picolinamide substrates is challenging since the aminocarbonyl group at C2 might strengthen the interaction between the pyridinic nitrogen and the metal as a bidentate ligand, inhibiting thus the activity of the catalyst.[3] We herein described a Rh(III)-catalyzed oxidative olefination/annulation of picolinamide allowing a straightforward access to pyrrolo[3,4-*b*]pyridines.[4]



The catalyst features good structural versatility in both alkenes and heteroarene coupling components, complete regiocontrol and excellent stereocontrol. In addition, the benzylic nature of the *N*-substituent allows for an easy deprotection of the final products. These products have a special biological interest as they can be considered as conformationally constrained nicotinoids, thereby becoming attractive candidates for selective nicotinic acetylcholine receptor ligands.[5]

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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

METALACICLOS DE Pd(II) ESTABILIZADOS POR LIGANDOS DIALQUILTERFENIL FOSFINAS. APLICACIONES CATALÍTICAS EN LA REACCIÓN DE AMINACIÓN DE BUCHWALD-HARTWIG

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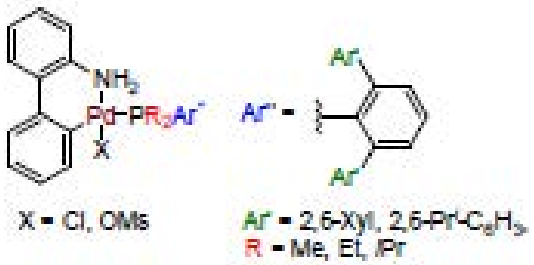
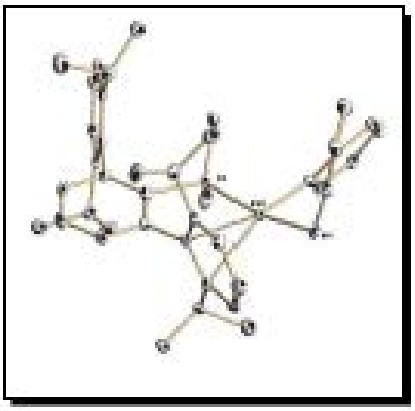
Palabras Clave: *complejos de Pd(II), fosfinas, acoplamiento cruzado.*

La química de acoplamiento cruzado basada en paladio constituye una herramienta fundamental en síntesis orgánica, para la formación de enlaces C-C y C-heteroátomo.[1]

En los últimos años, la investigación en este campo se ha centrado en el desarrollo de sistemas catalíticos de paladio, de composición bien definida, estabilizados por ligandos fosfinas muy voluminosos o ligandos carbeno N-heterocíclicos (NHCs).[2] Estos precatalizadores presentan la ventajas, sobre los sistemas preparados in situ, de generar de una manera más eficiente las especies monoligadas de Pd(0) responsables de la catálisis y de controlar de una manera más directa la influencia del ligando en el proceso de acoplamiento.

En nuestro grupo de investigación se han sintetizado recientemente una familia de ligandos dialquilterfenil fosfinas, relacionados estructuralmente con las biarildialquil fosfinas de Buchwald.[2a] En esta comunicación se discuten la síntesis, la caracterización estructural y el estudio de la actividad catalítica en reacciones de aminación de Buchwald-Hartwig de metalaciclos de Pd(II) estabilizados por ligandos dialquilterfenil fosfinas.





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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

VINILARENOS COMO DIPOLARÓFILOS EN CICLOADICIONES [3+2] CATALÍTICAS ASIMÉTRICAS DE ILUROS DE AZOMETINO

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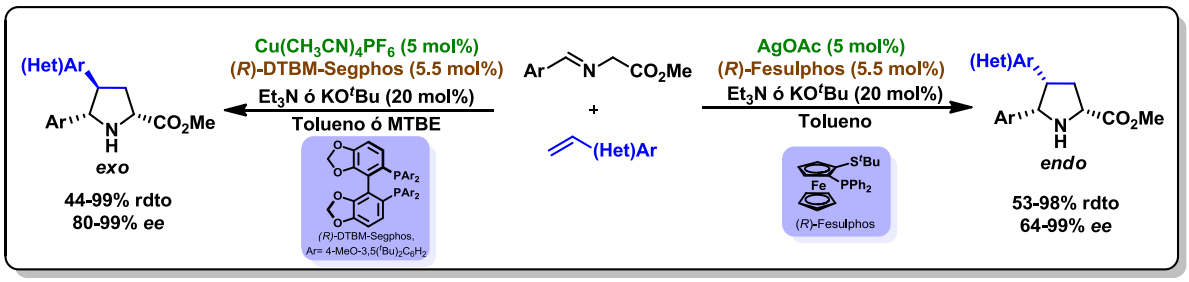
Palabras Clave: *cicloadición 1,3-dipolar, catálisis asimétrica*

La cicloadición 1,3-dipolar catalítica asimétrica entre iluros de azometino y alquenos activados es uno de los métodos más prácticos y convergentes para la síntesis de pirrolidinas enantioenriquecidas.[1] A pesar de los notables avances logrados en los últimos años, esta reacción sigue presentando importantes limitaciones estructurales tanto en el dipolo como en el dipolarófilo, lo cual restringe la aplicabilidad sintética de esta metodología.

En este contexto, nuestro grupo de investigación se ha centrado en los últimos años en la ampliación del alcance estructural de este proceso, consiguiendo desarrollar métodos que utilizan nuevos dipolos (α-iminonitrilos, α-iminopiridinas, α-iminoamidas y α-sililiminoésteres) y nuevos dipolarófilos (bisulfoniletilenos, sulfonilacrilatos, sulfonilenonas, borilacrilatos, azalactonas y 1,3-dienos).[2]

Hasta el momento únicamente alquenos activados con grupos fuertemente atractores de electrones han sido utilizados como dipolarófilos en este proceso. En esta comunicación se describen los primeros ejemplos de cicloadición 1,3-dipolar catalítica asimétrica con iluros de azometino y estirenos diferentemente sustituidos o vinilheterociclos. Este proceso permite el acceso a nuevas pirrolidinas enantioenriquecidas tanto con configuración *exo* como *endo*, en función del complejo metal-ligando quiral empleado.



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S3. *Catálisis Organometálica como Solución a Retos Sintéticos*

ESTUDIO COMPUTACIONAL DEL MECANISMO DE DEOXIDESHIDRATACIÓN DE GLICOLES CON UN CATALIZADOR DE VANADIO

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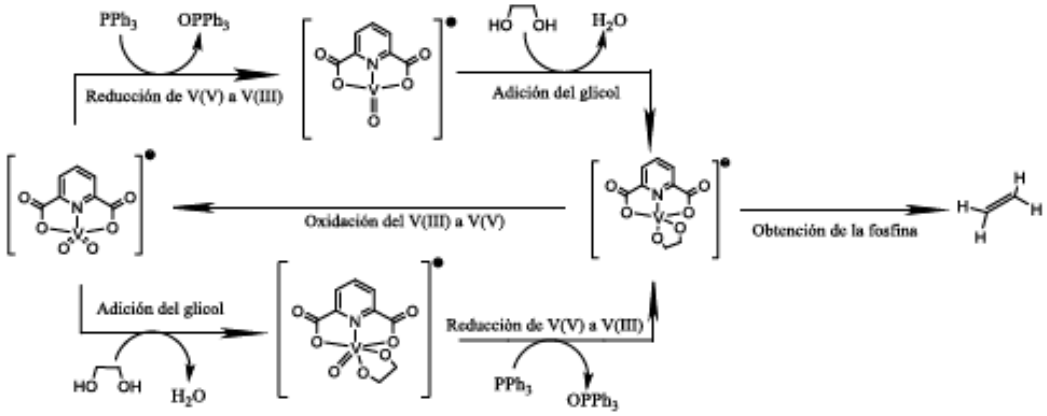
Palabras Clave: *deoxideshidratación, biomasa, catálisis homogénea, DFT, vanadio*

La valorización de residuos del procesado de la biomasa, como el glicerol obtenido como subproducto de la fabricación de biodiésel u otros polialcoholes obtenidos de la fermentación de residuos agroforestales, es un objetivo de interés tanto económico como ecológico. En nuestro grupo pretendemos establecer los mecanismos a través de los cuales catalizadores de vanadio y molibdeno en elevado estado de oxidación reducen estos polioles a compuestos pobres en oxígeno, más aptos para su uso como materias primas en la industria química, con el objetivo de mejorar estos procesos y diseñar nuevos catalizadores más eficientes y selectivos.
En este trabajo utilizamos DFT para estudiar la reacción de desoxideshidratación de glicoles con un complejo de vanadio (V) descrita por Chapman *et al.*[1] En esta reacción un núcleo de dioxovanadio estabilizado por un ligando tridentado rígido, transfiere oxígeno desde etilenglicol (el modelo de diol utilizado) a un reductor externo (fosfina), obteniéndose etileno como producto. Se han explorado varios caminos de reacción en los que las etapas de reducción del catalizador, coordinación del glicol y rotura de los enlaces C—O se suceden en distinto orden. Se observa que en estos mecanismos resulta esencial la participación de agua (u otras moléculas de alcohol) en el intercambio de protones entre distintas especies a lo largo de todo el ciclo catalítico.



Agradecimientos: Los autores agradecen al Centro de Supercomputación de Galicia los recursos computacionales asignados y a la Xunta de Galicia (Consellería de Cultura, Educación e Ordenación de Universidades) la financiación del proyecto EM2014/040.

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S3. *Catálisis Organometálica como Solución a Retos Sintéticos*

ASYMMETRIC SYNTHESIS OF AXIALLY CHIRAL *P,N*-LIGANDS *VIA* DYNAMIC ASYMMETRIC *C–P* CROSS–COUPLING REACTION

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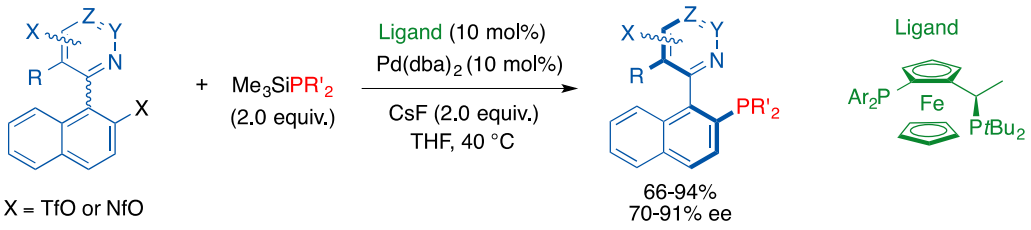
Keywords: *DYKAT, cross coupling, axial chirality, P,N-ligands*

Axially chiral *P,N*-ligands, such as Quinap, have had a considerable impact in asymmetric catalysis.[1] This type of ligands, however, are clearly underexploited for the lack of a general method for the synthesis of analogues, providing the structural variability required to the fine-tuning of their steric and electronic properties. The direct construction of the stereogenic axis by a cross–coupling reaction might appear as the most straightforward approach to these systems. In spite of the great progress achieved during the last years in asymmetric Suzuki-Miyaura cross-couplings, however, the reaction using heterocyclic substrates remains as an unsolved synthetic challenge, presumably due to the interferences caused by the coordination of the heteroatoms in the substrate, the limitations associated with the availability and poor stability of heteroaromatic organometallics and the low configurational stability of the products. Recently, we have developed an alternative methodology for the asymmetric synthesis of axially chiral heterobiaryls consisting of a dynamic asymmetric (DYKAT) Suzuki-Miyaura coupling between racemic triflates and arylboroxines.[2] On this basis, we decided to explore the applicability of this methodology to the asymmetric synthesis of *P,N*-ligands with axial chirality. The strategy is based on the assumption that the oxidative addition of Pd(0) catalysts generates cationic and configurationally stable intermediates incorporating the basic pyridine N atom as a ligand.



After an intense screening of ligands and phosphine sources, a Pd(0) complex containing a JOSIPHOS-type ligand was identified as the most selective/active catalyst for the dynamic asymmetric (DYKAT) *C-P* coupling between racemic triflates/nonaflates and diaryl/dialkyl trimethylsilylphosphines, leading to axially chiral *P,N*-ligands in high yields and ee´s up to 91%.

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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

RHODIUM (III)-CATALYZED ANNULATIONS BETWEEN *2*-HETEROSUBSTITUTED STYRENES AND ALKYNES

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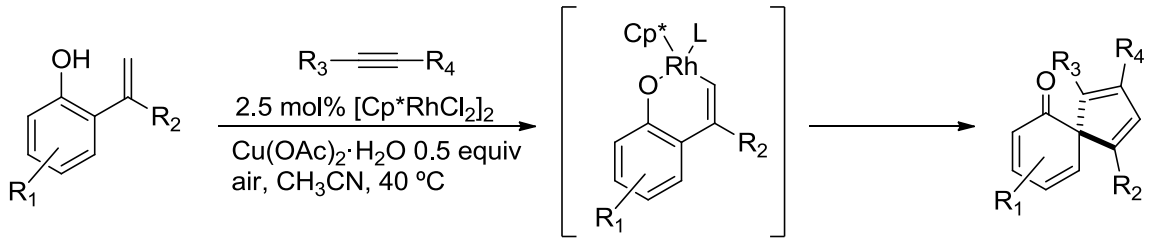
Keywords: *Annulations, C-H activation, Rhodium, Alkynes, Styrenes*

In the past decade C-H functionalization processes have emerged as powerful tools to increase molecular complexity [1]. Combining C-H activations with cycloaddition processes allows to obtain relevant cyclic structures while minimizing the generation of waste.

Recently, we have demonstrated that catalytic amounts of $[Cp^*RhCl_2]_2$ and $Cu(OAc)_2$ can promote formal (5+2) cycloadditions between *ortho*-vinylphenols and alkynes to give highly valuable benzoxepines, in a reaction involving the cleavage of an O-H and a sp2 C-H bond [2]. The presence of a substituent in the internal position of the alkene changes the reaction outcome, which now provides spirocyclic molecules through a formal (3+2) cycloaddition [3]. We recently found that replacing the hydroxyl substituent by amine or amide groups also promotes a dramatic change in the reactivity.



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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

SALES DE IMIDAZOLIO FUNCIONALIZADAS: APLICACIÓN EN LA SÍNTESIS DE CARBENOS N-HETEROCÍCLICOS Y FORMACIÓN DE COMPLEJOS METÁLICOS

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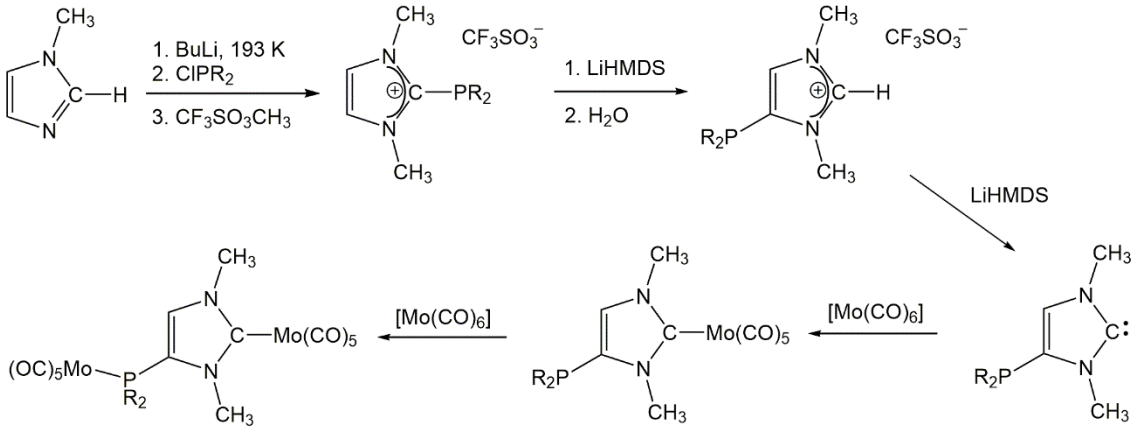
Palabras Clave: *NHC, sal de imidazolio, funcionalización, fosfinas, complejos metálicos.*

Los carbenos N-heterocíclicos (NHCs) así como sus principales precursores, las sales de imidazolio, son ampliamente conocidos por su gran importancia en la Química Organometálica actual debido a su alta capacidad de estabilizar una gran diversidad de complejos de metales de transición y a sus aplicaciones catalíticas. Muy recientemente, en nuestro grupo de investigación se han preparado sales de imidazolio doblemente funcionalizadas con grupos fosfino en las posiciones 4 y 5 del anillo heterocíclico estudiando así su diversa reactividad,[1] una línea de investigación muy poco explorada, ya que hasta el comienzo de nuestros trabajos únicamente se conocían dos ejemplos en la bibliografía.[2]

En la presente comunicación se describe la síntesis de sales de imidazolio funcionalizadas con grupos fosfino de distinta naturaleza situados sobre el carbono en posición 4 del anillo heterocíclico y el estudio de su reactividad orientada a la formación de complejos metálicos, singularmente aquellos que contienen el carbeno N-heterocíclico derivado de la desprotonación del catión imidazolio. Alguno de los compuestos obtenidos, solubles en líquidos iónicos, son potencialmente aplicables en catálisis homogénea y bifásica.



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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

GROUP IV METALLOCENIUM CATALYSTS FOR THE CHEMO- AND STEREOSELECTIVE POLYMERIZATION OF POLAR DIVINYL MONOMERS

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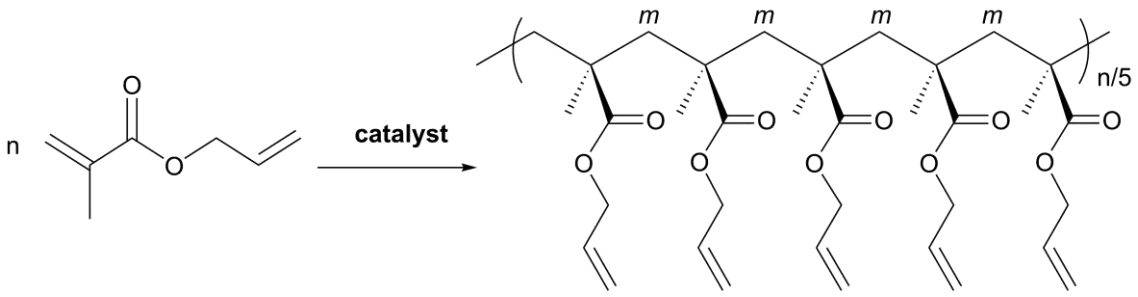
Keywords: *metallocenium enolate catalysts, bifunctional vinyl monomers, chemoselectivity, stereoselectivity, functional polymers*

Linear polymers that carry accessible vinyl groups in every repeating unit are of great interest since they can be photo-, thermal-, and chemically modified or crosslinked to obtain new functional materials with specific properties. A leading strategy to produce such materials is to develop chemoselesctive polymerization of divinyl monomers, such as allyl methacrylate, in which the methacrylic double bond is selectively polymerized while the unconjugated double bond remains intact. However, only a few cases of chemoselective polymerization of polar divinyl monomers have been described, while a simultaneous control over both chemoselectivity *and* stereoselectivity remains a challenge. In this presentation, we will describe the use of chiral, single-site *ansa*-metallocenium catalysts to achieve the chemo- and stereoselective polymerization of methacrylate-based bifunctional divinyl monomers. The conjugate-addition coordination, living, and stereospecific polymerization by such chiral metallocenium catalysts is responsible for the observed high degree of control over the polymerization characteristics and stereochemistry. The resulting highly stereoregular polymers bearing the reactive side-chain double bonds have been post-functionalized through thio-ene click reactions and photocuring thin-film formation.



S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

MECHANISTIC STUDY ON THE BIMETALLIC COOPERATIVE CATALYSIS OF Au(I) AND Ag^+ ON REARRANGEMENT OF ALKYNIL SUBSTITUTED SUBSTRATES

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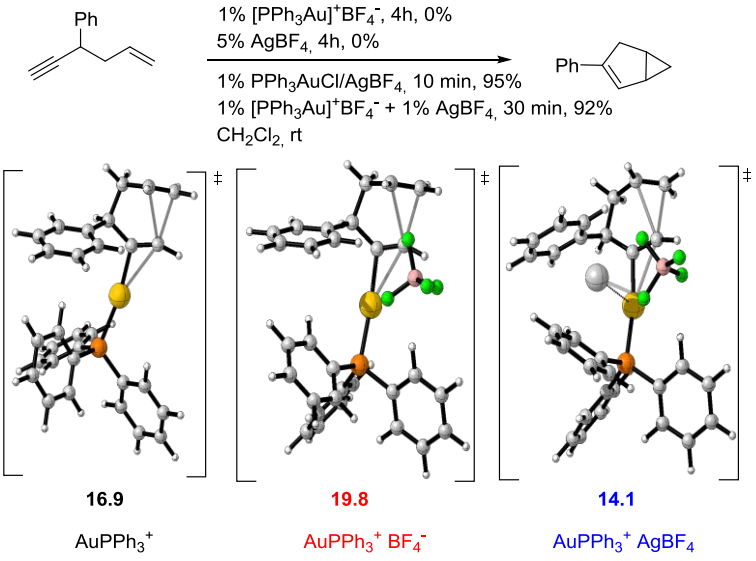
Keywords: *organometal, catalysis, Au(I), Ag salts, bimetallic, rearrangement*

Gold catalyzed reactions have been studied for decades resulting in an incredible, still growing, development of the organic Au catalyzed transformations [1]. Catalyst active species has been demonstrated to be $[L\text{-}Au(I)]^+$, the actual π- acid coordinating alkynes and alkenes. Its most common preparation method goes through the treatment of the L-AuCl with Ag salts. Traditionally, it is believed that the Ag forms AgCl and has no effect on the reaction mechanism, Wang et al. shown that it is not completely true there are some cases where the Ag it is not necessary at all, but there are some that not take place without Ag presence [2].

We have studied computationally some of the addressed revisited Au(I) catalyzed reactions in order to shed light into the Ag role on the overall catalytic cycle.



For example, calculations on the Au(I) promoted rearrangement of the hex-5-en-1-yn-3-ylbenzene to the 3-phenylbicyclo[3.1.0]hex-2-ene have shown that the asynchronous concerted transition state of the bicycle formation after activation of the alkyne moiety by the $AuPPh_3^+$ complex has an activation barrier of 16.9 kcal/mol, but the presence of the BF_4^- contraanion hindered the process increasing the activation barrier of this TS up to 19.8 kcal/mol. When a Ag atom is coordinated to the Au metallic center the barrier lowered to 14.1 kcal/mol. Thus, Ag^+ is mandatory along the transformation acting as a BF_4^- coordinating agent, stablishing effective charge interchange to the Au(I) center and stabilizing the TS by phenyl interactions.

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S3: *Catálisis Organometálica como Solución a Retos Sintéticos*

SÍNTESIS DE COMPLEJOS HETEROMETÁLICOS CONTENIENDO CARBENOS METALA-N-HETEROCÍCLICOS

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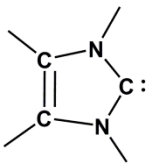
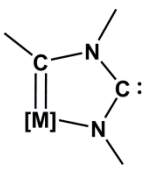
Palabras Clave: *NHC, carbenos metala-N-heterocíclicos, MNHC, complejos metálicos.*

Teniendo en cuenta las importantes aplicaciones que encuentran los carbenos N-heterocíclicos (NHC) y sus complejos metálicos en multitud de procesos catalíticos, recientemente se están desarrollando diversas variaciones sobre la arquitectura básica de estos ligandos que permitan modificar de forma controlada sus propiedades electrónicas. Una de estas variaciones implica la sustitución de algún átomo de carbono del ciclo imidazol por heteroelementos, tales como fósforo y boro. En este sentido, en nuestro grupo hemos accedido a la síntesis de complejos de Mn(I) y Fe(II) que poseen ligandos carbeno fuertemente dadores, que derivan formalmente de la sustitución de un átomo de carbono por un fragmento metálico en el ciclo imidazol-2-ilideno, y que por tanto pueden considerarse como carbenos metala-N-heterocíclicos (MNHC).[1]

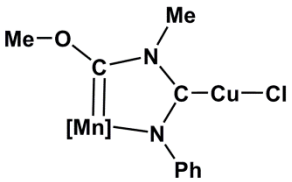
Ahora hemos encontrado que es posible generar y atrapar dichos carbenos MNHC, sintetizando previamente sus sales de metala-imidazolio precursoras, que a su vez pueden ser preparadas mediante una isomerización de diaminocarbenos a formamidinas, catalizada por Ag_2O.[2] Se ha comprobado también que los MNHCs son más fuertemente dadores que muchos de los NHCs convencionales, y que adicionalmente pueden experimentar procesos de transmetalación, lo que abre un camino hacia la síntesis de una gran variedad de complejos metálicos con dichos ligandos.



NHC



MNHC



[Mn] = $Mn(CO)_2(bipy)$

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S4. Enseñanza, Historia y Divulgación de la Química (EHDQ) / Teaching, History and Popularization of Chemistry

Se trata de un simposio conjunto entre los Grupos Especializados de "Historia de la Ciencia" (RSEQ) y "Didáctica e Historia de la Física y de la Química" (RSEF). Además de las comunicaciones orales y pósteres, se prevén cuatro conferencias invitadas, dos sobre Historia de la Química y dos sobre Enseñanza y Divulgación de la Química. Sin duda, será un buen momento para conocernos y discutir sobre temas comunes.

This is a joint symposium between the specialized groups of "Hystory of Science" (RSEQ) and "Didactics and History of Physics and Chemistry" (RSEF). Besides oral and poster communications , there will be four invited conferences, two on the History of Chemistry and another two on Teaching and Divulgation of Chemistry. It will certainly be a good opportunity to meet and discuss common issues.

Organizadores:

Manuela Martín Sánchez (UCM)

Pascual Román Polo (UPV-EHU)

e-mail de contacto: mmartins@edu.ucm.es

Lunes 20 de Julio 2015

08:40 – 09:40	**PL-2**	***Conferencia Plenaria*** (Común a todos los simposios) **Tomás Torres Cebada** *"Phtalocyanines: Old Dyes, New Molecular Materials"*

Chairman: Pascual Román

10:00 – 10:30	**S4-IL-01**	**Mario Redondo Ciércoles** *"La Química en la Nueva Ley de Educación"*
10:30 – 10:45	**S4-OC-01**	**Jesús M. Arsuaga** *"Nomenclatura Química: ¿Qué y Cómo Enseñar?"*
10:45 – 11:00	**S4-OC-02**	**L. Moreno** *"El Kernel de la Química: Configuraciones Electrónicas. Análisis Didáctico e Histórico"*
11:00 – 11:30		Pausa Café

Chairman: Gabriel Pinto

11:30 – 12:00	**S4-IL-02**	**Marcos Martinón-Torres** *"La Ciencia del Arte: Una Aproximación Química y Microscópica a la Orfebrería Prehispánica de Colombia"*
12:00 – 12:15	**S4-OC-03**	**Pascual Román** *"La Tabla Periódica de los Elementos Químicos para Niños y Abogados"*
12:15 – 12:30	**S4-OC-04**	**Santiago García-Granda** *"Experimentos Ejemplares en la Historia de la Química"*
12:30 – 12:45	**S4-OC-05**	**Rosario Torralba** *"Los Laboratorios Virtuales: Una Herramienta Didáctica de Apoyo, Sostenible y de Bajo Coste"*
12:45 – 13:00	**S4-OC-06**	**Rosa Domínguez** *"La Química en la Ingeniería Civil"*
13:00 – 13:30	**S4-IL-03**	**Manuel Bermejo Patiño** *"Marie Anne Paulze: Una Científica Moderna"*
13:30 – 15:30		Comida

Lunes 20 de Julio 2015

Chairwoman: Manuela Martín Sánchez

15:30 – 16:00	**S4-IL-04**	**Fina Guitart** *"Una visión General de Proyectos Europeos para Enseñanza de las Ciencias basada en la Indagación (IBSE), o en la Visión Interdisciplinar STEM y las Aportaciones de la Química en Concreto"*
16:00 – 16:15	**S4-OC-07**	**J. Quilez** *"Enseñando a Argumentar Científicamente en Inglés: El Caso de los 'Sentence Connectors' "*
16:15 – 16:30	**S4-OC-08**	**Elisa Jiménez** *"La Extraordinaria Química de las Cosas Ordinarias"*
16:30 – 17:00		Pausa Café
17:00 – 17:15	**S4-OC-09**	**A. Marchal** *"Jornadas Nobel de la Universidad de Jaen"*
17:15 – 17:30	**S4-OC-10**	**Ana Elduque** *"Divulgando la Esencia de la Química: Su Utilidad Social"*

Chairman: Manuel R. Bermejo

17:30 – 17:40	**S4-FC-01**	**J. M. Hernández** *"El Reactivo de Tollens, Historia y Aplicaciones Didácticas: de la identificación de aldehídos al uso en nanotecnología"*
17:40 – 17:50	**S4-FC-02**	**Gabriel Pinto** *"La Colección de Pinturas de los Calendarios de Maxam como Recurso para la Difusión y Enseñanza de la Química"*
17:50 – 18:00	**S4-FC-03**	**Manuela Martín Sánchez** *"Los Problemas de la Química como Recursos para la Adquisición de Competencias Básicas en Ciencia y Tecnología y para Promover el Pensamiento Crítico"*
18:00 – 18:05	**S4-FC-04**	**Araceli Calvo** *"Recursos Didácticos en la Web para el Aprendizaje de la Interrelación Luz-Química"*
18:05 – 18:10	**S4-FC-05**	**J. Klett** *"La Química en 3D: Talleres de Visualización Molecular en Distintos Niveles Educativos"*
18:10 – 18:15	**S4-FC-06**	**M. Jiménez** *"Metodología de la Investigación Científica"*
18:15 – 18:20	**S4-FC-07**	**Laura Roces** *"Literatura Infantil como Herramienta para Fomentar Vocaciones Científicas: El Monstruo Curioso"*
18:20 – 18:25	**S4-FC-08**	**Miquel Seco** *"Técnicas avanzadas en el laboratorio de Química (TALQ) : una nueva herramienta "on-line"*

18:30	***Sesión de Pósteres***

Comunicaciones Invitadas (IL)

S4: *Enseñanza, Historia y Divulgación de la Química*

LA QUÍMICA EN LA NUEVA LEY DE EDUCACIÓN

M. Redondo Ciércoles

Presidente de la sección de Enseñanza del ANQUE , Inspector d Madrid, mario.redondo@madrid.org

Keywords: *Chemistry teaching, Spanish Education Laws*

Una vez más nos encontramos ante una nueva reforma educativa, con sentimientos encontrados entre las expectativas que podrían suponer un avance en la enseñanza de las Ciencias y el escepticismo de la inestabilidad y corta duración de las leyes educativas.

El currículo que define la LOMCE introduce algunas novedades respecto a la LOE, siendo la principal los estándares de aprendizaje, que son las especificaciones de los criterios de evaluación, y que pudiendo facilitar la labor docente a la hora de evaluar a los alumnos, así como facilitar la evaluación final en la ESO y Bachillerato, tienen una serie de inconvenientes respecto al principal déficit del aprendizaje de los alumnos, las competencias. Desde que se introdujeron con la LOE, las competencias no han sido capaces de estar presentes en el proceso de enseñanza, ha faltado información y formación, cuestión que parece que con la LOMCE tampoco se va a resolver.

La organización de la ESO beneficiaría a la Química, al tener una mayor presencia explícita en los cursos 2º y 3º, además de 4º ESO. Este hecho podrá facilitar el aprendizaje de contenidos con una mayor profundidad que lo que se ha hecho hasta el momento.

En Bachillerato no hay ningún cambio, lo más significativo es que siguen unidas las dos disciplinas de Física y Química en primero de Bachillerato, a pesar de los continuos mensajes que se hacen llegar a los responsables legislativos, el currículo es inabordable, perjudicando seriamente la base de conocimientos de los alumnos al terminar Bachillerato.

En lo que respecta a los contenidos, no se han introducidos avances e innovaciones que se consideran imprescindibles para mostrar a los alumnos de secundaria una Química moderna y cercana, que permita hacerla más comprensiva.

La declaración de intenciones sobre el interés y el fomento del uso de las TIC, del laboratorio, de la realización de proyectos, etc., se recogen con cierto escepticismo ante la escasa disponibilidad de recursos y la poca autonomía de los centros que no pueden incluir aquellas estrategias innovadoras y metodológicas en el proceso de enseñanza. mario.redondo@madrid.org

Como conclusión final, decir que es necesaria una seria reflexión sobre los contenidos y competencias que nuestros estudiantes de secundaria deben aprender. Hay muchas experiencias en España que sirven de ejemplo y ponen en valor la necesidad de cambios en el currículo.

S4: *Enseñanza, Historia y Divulgación de la Química*

LA CIENCIA DEL ARTE: UNA APROXIMACIÓN QUÍMICA Y MICROSCÓPICA A LA ORFEBRERÍA PREHISPÁNICA DE COLOMBIA

M. Martinón-Torres, M. A. Uribe-Villegas

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Museo del Oro, Banco de La República, Bogotá, Colombia (muribevi@banrep.gov.co)

Palabras clave*: Química analítica, microscopía electrónica, arqueología, oro,*

El ojo público no es ajeno a la belleza y sofisticación de la orfebrería prehispánica de Colombia. Cientos de adornos corporales para rituales chamánicos, híbridos entre hombres y animales, accesorios para el consumo de drogas, máscaras funerarias o figuras de guerreros son testamento de la complejidad simbólica y cultural, así como de la sensibilidad artística y destreza técnica de los anónimos artesanos que llevaban milenios trabajando el oro de Colombia cuando llegaron los europeos.

La química analítica y las ciencias de los materiales nos permiten asomarnos a este patrimonio desde una perspectiva nueva, ayudándonos a entender la selección de materiales y las técnicas empleadas con grados de resolución excepcionales. Lo que es más, las técnicas analíticas nos revelan rasgos característicos de estas obras de arte, tales como gestos, trucos técnicos y materias primas que nos permiten atribuirlas a artistas específicos. De esta forma podemos identificar artistas individuales y reconstruir escuelas de un modo similar al que lo hacen los historiadores del arte europeo.

En esta conferencia se hará una presentación general de los estudios técnicos de la orfebrería prehispánica de Colombia, para después centrarnos en la tradición muisca. Combinando química y microscopía electrónica con observaciones históricas y arqueológicas, trataremos de sacar del anonimato a los orfebres que crearon figuras de guerreros, madres con bebés, escenas de sacrificios humanos… o incluso la famosa Balsa Muisca, un icono del patrimonio colombiano particularmente famoso en todo el mundo por su vinculación a la leyenda de El Dorado.

Historias de ofrendas muiscas. Museo del Oro, Banco de la República, Bogotá, 2013

http://www.banrepcultural.org/sites/default/files/historias-de-ofrendas-muiscas.pdf

S4: *Enseñanza, Historia y Divulgación de la Química*

MARIE ANNE PAULZE: UNA CIENTÍFICA MODERNA

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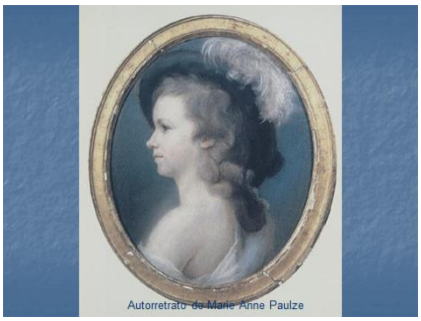
Palabras Clave: *ciencia, química, género*



Marie Anne Paulze se encuentra en la literatura científica hoy por ser la esposa de Antoine Lavoisier. Por esta razón fue denominada la madre de la química, pero ¿ha sido sólo eso?. ¿Será que, como ha sucedido con muchas otras científicas a lo largo de la historia en otras ocasiones, su nombre ha sido obscurecido por la sombra de un gran hombre?. ¿Ha perjudicado a Marie Anne, científicamente hablando, el haber estado trabajando siempre con su esposo?.

En esta conferencia quiero presentar, brevemente, la vida y la obra de Marie Anne Paulze resaltando preferentemente sus contribuciones científicas; tratando de ver si estas contribuciones se pueden considerar dignas de una científica moderna. Para conocer su obra indicaremos:

1º Sus investigaciones en las hoy denominadas ciencias sociales.

2º Su correspondencia con científicos de la época; las diversas traducciones por ella realizadas, así como sus desinteresadas contribuciones en el mundo de la química.

3º Sus trabajos concretos en el campo de la química, entre los que destacaremos: la traducción del libro de Kirwan “Essay on Phlogiston”; sus didácticas acuarelas sobre la respiración animal; sus trabajos de compilación, traducción y edición de la revista “Annales de Chimie”; las traducciones de otras publicaciones de Kirwan para esta revista; el prólogo, parte de la redacción y la edición de la obra póstuma de Lavoisier “Memoires de Chimie”; …etc.

4º Especial consideración debemos dar a las representaciones gráficas, realizadas en forma de las famosas XIII láminas para el libro de Lavoisier “Tratado Elemental de Química”. Algunas de ellas sirvieron como auténticos prototipos -el gasómetro- y, todas ellas, contribuyeron a comprender y realizar la química que contenía el libro denominado la “biblia” de los químicos.

Finalicemos señalando que Marie Anne acompañó a Lavoisier en todos los grandes descubrimientos de la historia inicial de la Química: el desarrollo de las teorías de la combustión y de la respiración; el descubrimiento de la composición del aire y los experimentos de la descomposición y síntesis del agua; la fijación del lenguaje químico, con el establecimiento de las “Normas de Nomenclatura Química”; la redacción y edición del “Tratado Elemental de Química”;…etc. Durante 25 años Marie Anne construyó, de la mano de Lavoisier, la química moderna….y, de repente, un silencio enorme de más de 30 años, hasta su muerte en 1836.

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UNA VISIÓN GENERAL DE PROYECTOS EUROPEOS PARA ENSEÑANZA DE LAS CIENCIAS BASADA EN LA INDAGACIÓN (IBSE), O EN LA VISIÓN INTERDISCIPLINAR STEM Y LAS APORTACIONES DE LA QUÍMICA EN CONCRETO

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La finalidad de la enseñanza de las ciencias, las estrategias y metodologías utilizadas han sido un constante motivo de reflexión de los docentes del ámbito científico. El informe Rocard (2007) [1]. analizó la situación de la educación en ciencias en Europa y puso de manifiesto una actitud poco positiva hacia las ciencias y poca satisfacción y utilidad de las clases de ciencias. Entre las recomendaciones que propone se incluyen: la de usar metodologías con un enfoque basado en la indagación (ECBI), acciones de formación para el profesorado, la promoción de redes de docentes, la colaboración con instituciones de investigación, universidades, museos, etc. y el desarrollo de proyectos europeos para generar materiales didácticos y de formación. El informe *Science Education in Europe: Critical Reflections* [2]. una propuesta didáctica y metodológica basada en resultados de la investigación, concreta las recomendaciones anteriores y destaca la importancia de la indagación o participación del alumnado en prácticas científicas.

La investigación educativa muestra que una estrategia para desvelar el interés de los alumnos por los estudios y profesiones del ámbito científico-tecnológico es promover la conexión entre las disciplinas de ciencias, tecnologías, ingeniería y matemáticas en el ámbito interdisciplinar llamado STEM (Science Technology, Engineering and Maths). STEM ofrece la oportunidad de dar sentido al mundo de manera integral, en lugar de en pequeñas parcelas. Es un enfoque interdisciplinar en el cual los estudiantes aplican la ciencia, la tecnología, la ingeniería y las matemáticas, en contextos que conectan la escuela, la comunidad, el trabajo y la empresa, con el objetivo de formar ciudadanos alfabetizados y competentes para actuar y competir en la sociedad del futuro.

Se presentaran proyectos europeos que han generado materiales de enseñanza de las ciencias basada en la indagación (ICBE) y del ámbito de educación en ciencias, tecnologías, ingeniería y matemáticas (STEM). Se discutirán las características de los materiales y los retos de su implementación en nuestro sistema educativo desde el punto de vista de la enseñanza de la química, diferencias y similitudes de estas propuestas con los proyectos CTS (Ciencia, Técnica y Sociedad), los proyectos de ciencia en contexto, y con la enseñanza de las ciencias con enfoque competencial.

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Comunicaciones Orales (OC)

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NOMENCLATURA QUÍMICA: ¿QUÉ Y CÓMO ENSEÑAR?

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Palabras Clave: *Nomenclatura química, IUPAC, Currículo de Química*

La docencia de Nomenclatura Química (y Formulación) constituye uno de los caballos de batalla de todo profesor de Física y Química. Esto es así por múltiples razones enlazadas entre sí. En primer lugar, está comprobada la aversión que produce en la mayoría de los alumnos, incluidos los estudiantes considerados "de ciencias"; sin embargo, este rechazo contrasta con la importancia que los especialistas le conceden. Además, como profesores, editoriales y responsables académicos se esfuerzan por "estar a la última", se busca un grado extremo de actualización buscando el paradigma de la "última versión", supuestamente definitiva, de Formulación y Nomenclatura. En este contexto surge "la pregunta del millón": ¿Pero, qué dice la IUPAC de …?

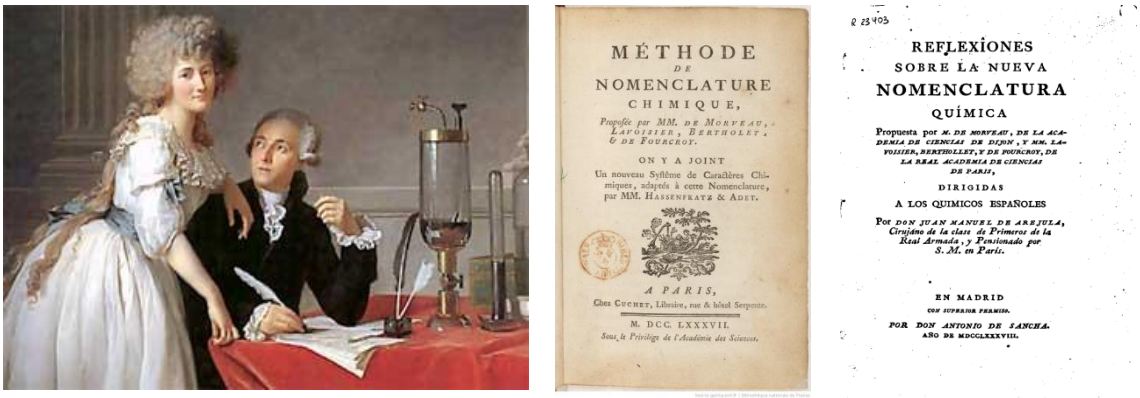

Figura 1. Lavoisier (izda.), el "padre de la química" fue también uno de los impulsores de la moderna Nomenclatura (centro). Las *Reflexiones* de Aréjula (dcha.) se publicaron casi inmediatamente después.

En esta comunicación, dividida en tres secciones, se aborda la problemática de la Nomenclatura. Primero, se hace una breve incursión histórica sobre la sistematización de la nomenclatura química (Fig. 1). Seguidamente, se plantean reflexiones personales sobre su didáctica desde la experiencia personal como profesor y autor [1]. Por último, se revisará brevemente qué se recoge al respecto en la LOMCE, tanto en el currículo de la ESO como en el de Bachillerato [2].

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EL *KERNEL* DE LA QUÍMICA: CONFIGURACIONES ELECTRÓNICAS. ANÁLISIS DIDÁCTICO E HISTÓRICO

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Palabras Clave: *Configuraciones electrónicas, diagrama de Moeller, Sistema Periódico, Charles R. Bury, Educación Secundaria.*

La determinación de las configuraciones electrónicas de los átomos de los elementos químicos que integran el Sistema Periódico constituye uno de los aspectos fundamentales en Química[1], ya que la estructura electrónica de los átomos determina las propiedades químicas y muchas de las propiedades físicas de los elementos así como su situación en el Sistema Periódico.

En Educación Secundaria, las configuraciones electrónicas comienzan a estar presentes en el currículo desde la materia de Física y Química de tercer curso de ESO (estructura atómica[2]) hasta la materia de Química de segundo curso de Bachillerato (estructura electrónica[3]). Dada su presencia en el currículo escolar, se hace fundamental abordar un análisis didáctico de cómo suele llevarse a cabo el aprendizaje de las configuraciones electrónicas a lo largo de los distintos cursos, así como de su tratamiento en los libros de texto.

La utilidad del modelo atómico de Niels Bohr[4] (1885-1962) como marco conceptual para el inicio del aprendizaje de la estructura electrónica[5], las limitaciones del diagrama de Moeller[6] (habitualmente empleado para obtener la configuración electrónica de los átomos de los elementos a partir de su número atómico) y sus consecuencias para la estructura del Sistema Periódico[7] son algunos de los aspectos a tratar en la presente comunicación que pretende también abordar la contextualización histórica del estudio de las configuraciones electrónicas, generalmente ausente en los libros de texto, con científicos como Erwin Madelung (1881-1972), Charles R. Bury[8] (1890-1968) o Therald Moeller (1913-1997), entre otros.

Referencias

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LA TABLA PERIÓDICA DE LOS ELEMENTOS QUÍMICOS PARA NIÑOS Y ABOGADOS

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Palabras Clave: *tabla periódica, Moseley, Mendeléiev, Lavoisier, niños, abogados, juego, reglas mnemotécnicas*

Con ocasión de conmemorarse en 2015 el centenario de la muerte de Henry Moseley (1887-1915), quien junto con Dimitri Mendeléiev (1834-1907) está considerado el otro padre de la moderna tabla periódica de los elementos químicos, en el presente trabajo se pretende rendirle un emocionado tributo de gratitud por su gran aportación al acervo científico y cultural de la humanidad al haber encontrado la clave que permite ordenar los elementos químicos de manera científica y racional, es decir, según el orden creciente de su número atómico. Esta es sin duda alguna, la propiedad más importante de la materia. Con esta clave los niños nos guiarán en el aprendizaje de la tabla periódica A este juego se invita también a los abogados, quienes colaborarán con sus reglas mnemotécnicas para aprender grupos o familias de elementos que nos ayudarán en esta tarea. Una de las primeras tablas de elementos químicos se debe al abogado y padre de la química moderna el francés Antoine Laurent de Lavoisier (1743-1794), que fue publicada en su obra *Traité élémentarie de chimie.*

El uso de los juegos infantiles junto con la habilidad que han adquirido los niños de contar con soltura la serie de los números naturales, que coincide con el orden creciente del número atómico, les permite completar la tabla periódica de los elementos químicos. La identificación del número atómico con el nombre del elemento y su símbolo, permitirá al profesor reforzar la idea de que la propiedad esencial de la materia es el número atómico. Se establecen las pautas para que cada estudiante pueda generar su propia tabla periódica. Los abogados mediante el empleo de reglas mnemotécnicas pueden ayudar a recordar familias y grupos de elementos para memorizar los nombres y símbolos de los elementos químicos. Los profesores pueden estimular a sus alumnos implicándoles en la creación de nuevas reglas mnemotécnicas y sugerirles que entre los elementos de cada grupo hay propiedades físicas y químicas comunes, como las hay en literatura entre distintos escritores que pertenecen a un mismo movimiento literario. La tabla periódica, además de icono científico, es un juguete cultural donde se pueden aprender nociones de arte, filología, geografía, gramática, historia, lenguas –sobre todo, el inglés–, mitología, y otras habilidades y destrezas –como el manejo de los paquetes de programas del MS Office u OpenOffice, Adobe Acrobat, PowerPoint y otros–, así como la navegación a través de Internet [1,2].

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EXPERIMENTOS EJEMPLARES EN LA HISTORIA DE LA QUÍMICA

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Palabras Clave: *experimento, historia, ingenio*

Es casi imposible hablar de Química sin mencionar alguna ley, y es también muy complicado enunciar alguna ley sin describir uno o varios experimentos. Pero ¿cuáles de todos esos experimentos se pueden considerar como "ejemplares"?, entendiendo por ejemplares aquellos que sobresalen sobre los demás por su trascendencia, por el ingenio de su diseño, por su sencillez, o por la cantidad de trabajo requeridos, por mencionar algunos aspectos destacados.

Desde el descubrimiento del fuego (que no es otra cosa que una "simple" reacción química, y de hecho Faraday usaba como modelo la llama de una vela para sus lecciones de química [1]), hasta la reciente obtención de grafeno empleando cinta adhesiva, en la historia de la química se han llevado a cabo multitud de experimentos que seguramente deben aparecer bajo la denominación de "ejemplares": la obtención de la pólvora, el fuego griego, la comprobación de la ley de la conservación de la masa [2], la síntesis de Miller y Urey de materia orgánica a partir de componentes inorgánicos [3], o la ya mencionada obtención del grafeno [4], por poner algunos ejemplos.

Se pretende con este trabajo determinar los 10 experimentos más destacados de la historia de la química, y para ello se presenta de forma resumida, y a modo de propuesta, una breve descripción de varios de ellos, señalando los aspectos más destacados de cada uno. La idea es que cada uno de los asistentes al congreso vote por los 3 experimentos que considere "ejemplares" (pueden ser de los presentados en este trabajo u otros propuestos por ellos), indicando su elección en la urna virtual dispuesta a tal efecto. Con los resultados obtenidos se pretende preparar un artículo de divulgación que se publicará en una revista especializada y se distribuirá en los centros de enseñanza y en las redes sociales.

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LOS LABORATORIOS VIRTUALES: UNA HERRAMIENTA DIDÁCTICA DE APOYO, SOSTENIBLE Y DE BAJO COSTE

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Palabras Clave: *laboratorio virtual, Química, metales, suelos contaminados, estudiantes de Ingeniería Civil.*

Los laboratorios virtuales suponen una buena herramienta didáctica que permite la realización de prácticas de laboratorio que, por el tiempo requerido para su ejecución, su elevado coste o por el posible riesgo que supondría para los estudiantes, no serían viables.

La experiencia de la Universidad Politécnica de Madrid (UPM) con los laboratorios virtuales se remonta al año 2011, en el que se llevaron a cabo una serie de Proyectos de Innovación Educativa que permitieron el desarrollo de los primeros laboratorios (Plataforma de Experimentación para los Estudios de Ingeniería y Arquitectura – UPM). La UPM ha dado continuidad a estos laboratorios mediante un servicio gestionado por el Gabinete de Tele-Educación (GATE), lo que está permitiendo ampliar la oferta virtual.

En concreto, el Laboratorio de Experimentación Química estaba formado inicialmente por un único edificio, en el que los estudiantes pueden acceder a diversos materiales audiovisuales (videos y juegos), y en él hay un laboratorio donde se pueden realizar operaciones básicas y experiencias sencillas. Puesto que los entornos virtuales permiten ampliar fácilmente los espacios a los requerimientos específicos de las prácticas, a este primer edificio se le han añadido dos más, en los que se alojan las salas donde los alumnos de la asignatura de Ciencia Medioambiental (tercer curso/segundo semestre), del Grado en Ingeniería Civil de la UPM, realizan la práctica "Determinación de metales en suelos contaminados mediante digestión en horno de microondas y análisis por ICP-AES", de manera que uno de los edificios está dedicado a la preparación de muestras y otro a la realización de los análisis mediante ICP-AES, que es una técnica que requiere personal especializado y cuyo coste es elevado. En cada una de las salas, los estudiantes pueden encontrar el material de laboratoiro y los instrumentos necesarios para realizar la práctica, los cuales han sido diseñados con tal cantidad de detalles que les proporcionan un aspecto muy real. Aunque un Ingeniero Civil no va a realizar este tipo de análisis en el ejercicio de su profesión, consideramos que es interesante incluir una práctica de estas características en su formación universitaria, ya que les proporciona unos conocimientos y una visión real de este tipo de análisis, lo que confiamos favorezca el interés y la concienciación medioambiental de los futuros ingenieros.

Durante el desarrollo técnico de esta práctica virtual, se han realizado dos pruebas piloto con estudiantes voluntarios, lo que ha permitido corregir fallos y añadir mejoras que facilitan el seguimiento del procedimiento experimental. Esta práctica de laboratorio se ha incluido en la programación de la asignatura prevista para el curso académico 2014-15 (135 alumnos).

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LA QUÍMICA EN LA INGENIERIA CIVIL

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Palabras Clave: *Material didáctico, Innovación, Universidad, Enseñanzas Medias*

Desde hace ya bastante tiempo, existe entre los profesionales y docentes de las carreras científicas y tecnológicas, una preocupación por la falta de vocaciones para este tipo de estudios. Esto ha motivado una inquietud por tratar de subsanar este problema por lo que, desde hace varios años, la UPM y los Grupos de Innovación Educativa (GIE) en concreto los formados por profesores que imparten asignaturas de Química, organizan jornadas de puertas abiertas, cursos y distintas actividades para promover la relación entre los docentes de los distintos niveles educativos (Universidad – Enseñanzas Medias), como por ejemplo las jornadas de Enseñanza y divulgación de la Química y la Física [1]

Nuestro Grupo de Innovación Educativa ATANI (Acción Tutorial para los Alumnos de las Nuevas Ingenierías) ha participado desde el inicio en estas actividades, así como en la generación de material para Punto de Inicio, OCW [3], Videos de Prácticas [2], Quimitrivial [4] (Castellano/Inglés) y Laboratorios Virtuales …., todos ellos disponibles en abierto

Por otra parte en este curso, estamos participando en un proyecto transversal denominado *UPM PARA JOVENES: UNA MIRADA HACIA EL FUTURO,* constituido por un conjunto de proyectos de diferentes áreas de las Titulaciones de Grado ofertadas por nuestra Universidad y en el que se encuentran involucrados diferentes GIEs de distintos centros de la UPM. Este proyecto transversal pretende poner en contacto a los jóvenes, antes de iniciar sus estudios universitarios, con actividades que les permitan conocer sus capacidades para enfrentarse y resolver problemas relacionados con el ámbito científico y tecnológico de la Ingeniería Civil y que por ser tan cotidiano no se reflexiona sobre ello.

En concreto el proyecto de nuestro GIE[5] "UPM para jóvenes otra visión de la Ingeniería Civil". Para ello se han organizado dos jornadas para alumnos con edades comprendidas entre 10 y 18 años:

- Ingeniería Civil en Edificación
- Ingeniería Civil en Infraestructuras

que incluyen varios talleres con actividades tanto de Química como de destrezas en el campo de la Ingeniería Civil.

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S4: *Enseñanza, Historia y Divulgación de la Química*

ENSEÑANDO A ARGUMENTAR CIENTÍFICAMENTE EN INGLÉS: EL CASO DE LOS 'SENTENCE CONNECTORS'

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Palabras Clave: *CLIL, ciencia en inglés, argumentación científica, conectores*

El presente estudio se enmarca en un trabajo previo [1] de integración de un modelo contrastado de enseñanza/aprendizaje de las ciencias con una metodología de aprendizaje del inglés, denominada *CLIL* (*Content and Language Integrated Learning*) [2]. El trabajo referido ha permitido el diseño y la puesta en práctica de una unidad didáctica de Física y Química de primero de bachillerato en donde los contenidos se desarrollan completamente en inglés. En concreto, los alumnos trabajan durante diez sesiones el tema titulado *Atomic Structure: From Dalton to Bohr*. Entre otras cuestiones lingüísticas, en el mismo se trabajan explícitamente aspectos de comprensión lectora, de vocabulario y de comunicación tanto oral como escrita. De esta forma, se propician situaciones que suponen que los alumnos argumenten en inglés dentro del contexto científico del estudio histórico y epistemológico de la estructura del átomo.

Los 'sentence connectors' (*however, therefore, moreover, instead, etc.*) son términos no técnicos que desempeñan un papel esencial a la hora de argumentar científicamente [3], ya que son elementos necesarios en la realización de explicaciones y justificaciones científicas fundamentadas. Si los alumnos no entienden o no dominan estas palabras, su capacidad para comprender y producir razonamientos científicos se ve seriamente limitada. A pesar de su importancia, no existen muchos estudios que hayan analizado las dificultades de los alumnos a la hora de entender y utilizar los conectores en el ámbito científico [4].

En este trabajo se comparan los resultados correspondientes a la capacidad de identificar y de utilizar en inglés esta clase de términos por parte de dos grupos de primero de bachillerato del mismo centro educativo. El grupo experimental desarrolló el tema elegido empleando la metodología CLIL, y el grupo control lo estudió en castellano. Se han obtenido notables diferencias entre ambos grupos, no sólo a la hora de reconocer los distintos conectores y su función dentro de la frase, sino que además, los alumnos del grupo experimental superan ampliamente a los del grupo control en la comprensión su significado, así como cuando tienen que ordenar frases y unirlas con los mismos, concluyéndose que esta metodología contribuye a mejorar el aprendizaje del inglés y de forma paralela el de la ciencia, al propiciar el desarrollo capacidades de razonamiento científico.

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S4: *Enseñanza, Historia y Divulgación de la Química*

LA EXTRAORDINARIA QUÍMICA DE LAS COSAS ORDINARIAS

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Palabras Clave: *Divulgación científica, aportaciones de la Química, ciencia-sociedad, cultura científica.*

¿La transmisión de conocimientos de las Universidades debe ceñirse exclusivamente a nuestras aulas o debe entenderse de una forma más amplia y considerar que somos un servicio público comprometido con toda la sociedad y la cultura? Si atendemos a la legislación vigente, comprenderemos que es esta última consideración la que debemos aplicar en nuestro deber como profesores universitarios. La Ley Orgánica de Universidades actualmente en vigor recoge que "… específicamente las universidades promoverán el acercamiento de las culturas humanística y científica y se esforzarán por transmitir el conocimiento a la sociedad mediante la divulgación de la ciencia".

Si tenemos en cuenta que la cultura es el conjunto de conocimientos que nos permite desarrollar un juicio crítico, es primordial que los ciudadanos tengan suficientes conocimientos de Ciencia y Tecnología porque la vida diaria está llena de ellas y los seres humanos hacemos uso y nos aprovechamos favorablemente de sus resultados.

La transmisión de conocimientos en la divulgación es más complicada que en la enseñanza reglada porque tenemos que dirigirnos a un público heterogéneo de diferente edad, formación y, sobre todo, diferentes expectativas. Hay que tener muy claro lo que queremos transmitir y la forma de trasmitirlo para cubrir el amplio abanico del público. La frase "*no entiendes realmente algo a menos que seas capaz de explicárselo a tu abuela*", atribuida a un premio Nobel de Física, pone claramente de manifiesto la dificultad de abordar este tipo de comunicación.

En base a estas consideraciones, hemos desarrollado una serie de conferencias donde se realizan un conjunto de entre 5 a 10 experimentos con resultados aparentemente extraordinarios o inesperados (de ahí "*La extraordinaria Química...*"), a continuación se explica con rigor científico, con mayor o menor profundidad dependiendo del auditorio, se relaciona con procesos o productos de nuestra vida diaria (por ello "*... de las cosas ordinarias*") y, por último, se les muestra la repercusión social y su aportación al desarrollo y bienestar de la Humanidad.

En resumen pretendemos ayudar a consolidar la cultura científica, estableciendo una comunicación y un diálogo entre los químicos y la sociedad, concienciando a las personas que cuando se actúa con ética, la Química sólo beneficia a los pueblos, ya que el saber científico se utiliza para aumentar el bienestar de la humanida y de la paz y el desarrollo sostenible.

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Palabras Clave: *Divulgación, Premios, Nobel*

En la presente comunicación se describe una de las multiples actividades que desde la Unidad de Cultura Cientifica e Innovación de la Universidad de Jaén se llevan a cabo para dar a conocer entre el alumnado y la ciudadania en general las diferentes lineas de investigación que se desarrollan en las institución universitaria, las JORNADAS NOBEL DE LA UNIVERSIDAD DE JAÉN –UJA- [1-3]. Estas Jornadas surgen en el año 2012 tras conocerse la posibilidad de asistir en directo via *on line* al veredicto de los jurados encargados de decidir cada uno de los Premios Nobel (economía, paz, física, química, medicina y literatura) durante el mes de octubre de cada año y, darse la circunstancia de que algunos investigadores de la UJA, han tenido la oportunidad de llevar a cabo estancias de investigación con Premiados, conocen a Premiados o trabajan en lineas premiadas. Así, estas Jornadas se ha configurado como un conjunto de conferencias en las que las que los investigadores invitados comentan las lineas de investigación que desarrollan y que los vinculan de alguna manera con los Premios, comentando de camino anécdotas, curiosidades, y vivencias personales para finalemente, conectar en directo con Estocolmo para conocer a los premiados del año en curso y establecer posteriormente un breve debate.

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DIVULGANDO LA ESENCIA DE LA QUÍMICA: SU UTILIDAD SOCIAL

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Palabras Clave: *divulgación-química, comunicación-sociedad, utilidad-social*

La Química es una Ciencia que nació básicamente con un objetivo: proporcionar al hombre las sustancias y los materiales que precisa para mejorar sus condiciones de vida. La Química, sin su esencia utilitarista y su carácter social, no existiría. No hay productos nuevos que resistan el paso del tiempo sin convertirse en útiles para algo y alguien. Divulgar nuestra Ciencia es, simplemente, imprescindible.

Divulgar no es informar. No es dar detalle de nuestros descubrimientos. Divulgar es comunicar la Ciencia y la Tecnología al gran público.

Las formas de divulgar la Química son tan variadas como el público al que está destinada. Cuando el mensaje debe direccionarse a un receptor variado, el emisor debe usar todos los vehículos que le permitan alcanzar el objetivo de forma eficiente. Para divulgar con eficacia hay que usar medios periódicos, como son publicaciones, conferencias, talleres, colaboraciones permanentes… que permiten que la imagen de marca creada sea conocida. Tiene una finalidad, además de la propiamente divulgadora, de recordatorio. Junto a la anterior, se precisan acciones puntuales, como son la publicación de libros, la celebración de años temáticos, exposiciones… que permiten dar énfasis a aspectos concretos. Además de este objetivo, las celebraciones específicas deben tener un componente de atracción de nuevo público a las actividades de divulgación. Cada acción debe tener su propia finalidad.

Todo esto no puede hacerse a través de un meritorio, pero poco efectivo, ejercicio de voluntariado. Se precisa crear estructuras estables en las que la divulgación sea el *leit motiv* de las mismas. Son necesarios departamentos de proyección social en muchas de nuestras instituciones científicas, hay que buscar patronazgos para cátedras de divulgación científica, unidades culturales, museos científicos, páginas web... Y junto a ello, estabilizar los recursos humanos que se precisan para alcanzar los objetivos de calidad. También es importante reconocer las acciones y trayectorias de muchos profesionales que desarrollan labores de difusión. Además del reconocimiento al trabajo, estos galardones sirven para crear redes de personas, equipos e instituciones que fortalezcan la labor divulgativa.

Desde nuestra Facultad, nuestro grupo de trabajo quiere presentar lo que estamos haciendo siguiendo las líneas anteriormente expuestas. Nuestra revista (*conCIENCIAS,* https://ciencias.unizar.es/web/conCIENCIAS.do, las exposiciones realizadas (*INSTRUMENTA*, *Botánica*), los talleres (*PequeZiencias*), el *Premio de Divulgación Científica José Mª Savirón* y el resto de nuestras actividades es lo que persiguen.

Comunicaciones Flash (FC)

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EL REACTIVO DE TOLLENS, HISTORIA Y APLICACIONES DIDÁCTICAS: DE LA IDENTIFICACIÓN DE ALDEHÍDOS AL USO EN NANOTECNOLOGÍA

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Palabras Clave: *Historia de la Química, Didáctica de la Química, Nanotecnología, Nanopartículas de plata, Reactivo de Tollens*

Nuestro trabajo consta, por una parte, de un resumen de la biografía del químico alemán Bernhard Tollens (1841-1918) que puede ser un ejemplo de profesor por su dedicación y apoyo a los estudiantes [1] y, por otra, del "reactivo de Tollens". En este último aspecto, se describen su historia y sus aplicaciones didácticas, destacándose su empleo en la obtención de nanopartículas.

El reactivos de Tollens [2] es uno de los utilizados para reconocer los aldehídos, concretamente la glucosa. Es importante desde el punto de vista didáctico porque para que se produzca la reacción del nitrato de plata en medio básico es necesario formar el complejo amoniacal y que, de esa forma, el ión plata se mantenga en disolución y se pueda realizar la oxidación de la glucosa. Además, si se hace en un recipiente muy limpio se puede conseguir que la plata formada se pegue a las paredes originando el "espejo de plata" que le resulta muy llamativo a los estudiantes desde hace generaciones. Por ejemplo, se les puede hacer pensar a los alumnos sobre la diferencia entre la plata metálica que aparece en suspensión, que es un polvo gris, y cuando esas partículas se unen formando el enlace metálico que da lugar al espejo de plata. [3]

El reactivo de Tollens se utiliza también actualmente en la obtención de nanopartículas. [4-6] Por ello, presentamos trabajos encontrados en bibliografía actual con propuestas de posibilidades para trabajar con los estudiantes temas variados, utilizando técnicas analíticas de última generación, y que sirven para introducirlos en el ámbito de la nanotecnología.

Agradecimiento: Se agradece el apoyo de la Universidad Politécnica de Madrid (proyecto de innovación educativa PT14_15-03002).

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LA COLECCIÓN DE PINTURAS DE LOS CALENDARIOS DE MAXAM COMO RECURSO PARA LA DIFUSIÓN Y ENSEÑANZA DE LA QUÍMICA

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Palabras Clave: *Divulgación de la Química, Enfoques Ciencia-Tecnología-Sociedad, Explosivos, Historia de la Quimica, Química y arte, Publicidad.*

Se propone el empleo de la colección pictórica de la empresa MAXAM (antes *Unión Española de Explosivos*) como recurso para la enseñanza y difusión de la química en general, y del sector de explosivos en particular. La colección se ha gestado con motivo de la publicación, desde 1900, de un calendario donde pintores de prestigio han ido realizando un cuadro por encargo para cada año. Las pinturas siempre aluden a alguna actividad de esta empresa de explosivos, fundada por Alfred Nobel en 1872. A través de los popularmente conocidos como "calendarios de Explosivos", se pretende abarcar distintos objetivos: (a) divulgar entre los profesionales de la química la existencia de esta colección, dado que los cuadros se refieren a actividades de la industria química; (b) proponer el uso de alguna de las obras como recurso educativo para ilustrar y analizar cuestiones de química; (c) sugerir algunos cuadros como posible punto de partida para la discusión de aspectos de ética y ciencia (por ejemplo, el uso de explosivos) y para divulgar la Química; (d) plantear ejemplos que puedan servir, en distintos niveles educativos, para articular enfoques de enseñanza contextualizada.

En cuanto a aspectos educativos referidos a la química, abarcan temas de: historia de esta ciencia (desarrollo de explosivos, evolución de la industria química española, etc.); química aplicada (descubrimiento de la dinamita, obtención de explosivos, pirotecnia, química de la explosión, entre otros); y relaciones de esta ciencia con la ingeniería (fabricación de explosivos, industria química, ingeniería civil, etc.). Sobre los aspectos divulgativos y para posible aplicación en otras materias distintas de la Química, estos cuadros pueden servir para estudiar aspectos como: la biografía de Alfred Nobel, el origen de los premios que llevan su nombre, la historia de la pintura española contemporánea, o el desarrollo de la publicidad, entre otros.

Se plantea el área de fabricación de explosivos como una de las grandes aportaciones de la industria química al desarrollo y progreso de la humanidad en los últimos dos siglos. Aparte de su uso para el ocio (caza y pirotecnia), han sido y son esenciales para minería y construcción (carreteras, autopistas, edificios, túneles, canales, presas, etc.). Por ejemplo, su uso en minería y obras públicas permite reducir significativamente el consumo de hidrocarburos, las emisiones de gases de efecto invernadero y la duración de los trabajos.

Agradecimiento: Se agradece el apoyo de la Universidad Politécnica de Madrid (proyecto de innovación educativa PT14_15-03002).

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LOS PROBLEMAS DE QUÍMICA COMO RECURSOS PARA LA ADQUISICIÓN DE COMPETENCIAS BÁSICAS EN CIENCIA Y TECNOLOGÍA Y PARA PROMOVER EL PENSAMIENTO CRÍTICO

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Palabras Clave: *Aprendizaje Basado en Problemas, Aprendizaje por Indagación, Competencias educativas, Pensamiento Crítico*

El profesorado de química, especialmente en niveles previos a la Universidad, está acostumbrado a la utilización con sus alumnos de ejercicios-tipo, donde se ofrecen los datos de partida necesarios y se demanda una única solución. Son complementarios y adecuados para el proceso de aprendizaje, pero se hace necesario plantear también problemas más complejos, que fomenten el aprendizaje activo por indagación, el pensamiento crítico y la adquisición de competencias en ciencia y tecnología.

Recientemente (enero de 2015) se publicaron los Reales Decretos que establecen el currículo básico de E.S.O. y de Bachillerato, así como las relaciones entre competencias, contenidos y criterios de evaluación. Esta legislación señala que para potenciar la motivación por el aprendizaje de competencias se requieren metodologías activas y contextualizadas, es decir, las que facilitan la participación e implicación del alumnado y la adquisición y uso de conocimientos en situaciones reales. Además, algunas de las competencias clave en el Sistema Educativo Español son las "básicas en ciencia y tecnología" y "aprender a aprender". Se considera que la resolución de problemas facilita la adquisición de estas competencias en aspectos como: "capacitar para identificar, plantear y resolver situaciones de la vida cotidiana", "abordar los saberes o conocimientos científicos, los cuales se derivan de conceptos, procesos y situaciones interconectadas", y "utilizar datos y procesos científicos para alcanzar un objetivo; es decir, identificar preguntas, resolver problemas, llegar a una conclusión o tomar decisiones basadas en pruebas y argumentos." Aspectos similares se dan en la enseñanza universitaria desde la creación del *Espacio Europeo de Educación Superior*. Se analizan propuestas de problemas que se han abordado con metodologías de trabajo en equipo, caracterizados por tener un resultado abierto y requerir la búsqueda de datos (*data mining*). Además, se discuten resultados y dificultades de alumnos (y profesores) con este tipo de problemas. Algunos ejemplos propuestos ser refieren a: información comercial de productos (aguas minerales, medicamentos, dentífricos, productos antipolilla…), emisión de CO_2 por automóviles, seguridad en la cocina (interacción agua/aceite a alta temperatura), envases inteligentes (bebidas autocalentables), uso de calderas de condensación, etc.

Agradecimiento: Se agradece el apoyo de la Universidad Politécnica de Madrid (proyecto de innovación educativa PT14_15-03002).

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RECURSOS DIDÁCTICOS EN LA WEB PARA EL APRENDIZAJE DE LA INTERRELACIÓN LUZ-QUÍMICA

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Palabras Clave: *Didáctica de la Química/ Luminiscencia/Espectros/Páginas web*

El 20 de diciembre de 2013, la *Organización de las Naciones Unidas* (ONU), en su 68ª Asamblea Anual, proclamó 2015 como el *Año Internacional de la Luz y las Tecnologías basadas en la Luz*[1]. En España el testigo lo ha recogido la *Sociedad Española de Óptica*. La página web informativa es http://www.luz2015.es/. La inauguración ha sido el 16 de febrero de 2015, en el teatro Poliorama de Barcelona, con la intervención de Ignacio Cirac.

De la decisión de la ONU se desprende que fundamentalmente se trata de potenciar el tema de la luz desde el punto de vista tecnológico, y quizás por eso en la mayoría de los países el testigo lo han tomado las sociedades de Física o de Óptica y sin embargo no se habla para nada de las sociedades de Química.

Puede que sea la explicación por la que, rastreando páginas web, nos encontramos muy pocas que traten el tema de la química y la luz, a pesar de la relación existente entre ambas. Únicamente la *Royal Society of Chemistry* tiene tres apartados con vídeos muy cortos para alumnos de secundaria dedicados a fenómenos químicos en los que interviene la luz [2].

Nuestro trabajo ha consistido en buscar recursos en la web (páginas, vídeos, simulaciones…) que permitan a estudiantes de distintas etapas educativas entender la relación que la luz tiene con la química.

Agrupamos los temas en varios bloques, diferenciando los recursos por su aplicación en Primaria, ESO, Bachillerato y Universidad:

- ¿Cómo se producen las ondas electromagnéticas desde ultravioleta a infrarrojas?
- Reacciones químicas que producen luz
- Reacciones químicas que se activan con la luz
- Color y estructura de los pigmentos
- Polímeros electroluminiscentes[3]
- Premio Nobel de Química de 2014[4,5]

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LA QUIMICA EN 3D: TALLERES DE VISUALIZACIÓN MOLECULAR EN DISTINTOS NIVELES EDUCATIVOS

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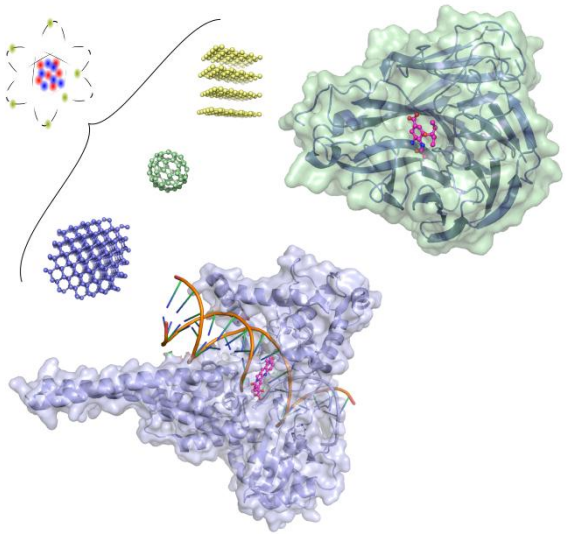
Palabras Clave: química, *visualización molecular, divulgación*



En este trabajo se presentan varias experiencias divulgativas dirigidas a estudiantes de educación primaria y secundaria, que tratan de mostrar uno de los múltiples aspectos de la química: la estructura tridimensional de los átomos y de las moléculas. También se muestran algunos talleres empleados en docencia de grado.

En estos talleres se emplean algunas herramientas computacionales capaces de representar de forma virtual sistemas moleculares formados por conjuntos de átomos. Los talleres muestran distintos ejemplos prácticos que abarcan los distintos niveles de complejidad química, desde la estructura de materiales formados sólo por átomos de carbono, como el carbón y el diamante, la estructura de pequeñas moléculas como algunos fármacos conocidos (agentes antitumorales, antigripales, analgésicos, etc.) interaccionando con sus dianas farmacológicas, hasta la configuración tridimensional de estructuras moleculares complejas como son las proteínas o el ADN. El objetivo principal de estos talleres es despertar el interés hacia la química a través de herramientas modernas complementarias a la enseñanza tradicional de la química que resulten atractivas para los estudiantes. Con esta aproximación los estudiantes son capaces de apreciar otro aspecto importante y esencial de la química: la estructura tridimensional, necesaria para entender las propiedades de las moléculas que nos rodean. Los contenidos de los talleres se han adaptado a los niveles de conocimiento de cada nivel educativo.

Agradecimientos: Estas actividades de diseminación y de compromiso con la sociedad se han llevado a cabo dentro de la organización de la Semana de la Ciencia de la Comunidad Autónoma de Madrid y dentro de los proyectos financiados por la Comunidad Europea (programas Marie Curie GLYCOPHARM FP7-PITN-GA-2012-317297 y TOLLerant H2020-MSC-ETN-642157).

S4: *Enseñanza, Historia y Divulgación de la Química*

METODOLOGÍA DE LA INVESTIGACIÓN CIENTÍFICA

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Palabras Clave: *metodología, investigación, ciencia.*

La investigación científica es por su naturaleza un conocimiento de tipo instrumental para producir nuevas ideas, modelos teóricos, procesos de innovación y en definitiva evidencias teórica y empírica que contribuyan a una mejor comprensión de la realidad y que facilite la detección y la resolución de problema concretos. La asignatura optativa "Metodología de la Investigación Científica" (Grado de Nutrición y Dietética) es una contribución didáctica al conocimiento de la investigación científica donde se enseñan los criterios conceptuales y metodológicos del proceso de investigación.

La impartición de estos conocimientos comenzó hace unos veinte años con un curso de doctorado sobre el método científico transformado en dos asignaturas de libre configuración (Licenciatura Farmacia) "Metodología Científica" (estudio de la ciencia clásica o paradigma newtoniano-cartesiano) e "Historia y Filosofía de la Mecánica Cuántica" (estudio del nuevo paradigma cuántico-relativista) que se han reunificado en la actual asignatura. Nuestra materia consta de un primer bloque donde se estudia la génesis e historia del pensamiento científico, los tipos precientíficos de conocimiento y se define el concepto de ciencia moderna. Un segundo bloque trata del método científico (observación, modelos y representación de hechos, medidas, hipótesis, experimentos, la explicación científica, leyes y teoría). En un tercer bloque se abordan los valores científicos-humanísticos, la ética y la bioética. Las clases teóricas se complementan con las prácticas que consisten en el diseño de un trabajo de investigación científica: búsqueda de información, procedimiento metodológicos, interpretación de resultados, redacción de informes y trabajos científicos, diseño de tablas, figuras, gráficas, póster y exposición de trabajos.

Las competencias que se pretenden impartir son el conocimiento del método científico y de la actividad investigadora las cuales se podrán aplicar en la realización del trabajo Fin de Grado y tal vez en posteriores estudios de Doctorado. Por todo lo expuesto y dada la importancia instrumental de esta materia sugerimos la necesidad de que este tipo de conocimientos se incluyan en todos los Grados científicos.

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S4: *Enseñanza, Historia y Divulgación de la Química*

LITERATURA INFANTIL COMO HERRAMIENTA PARA FOMENTAR VOCACIONES CIENTÍFICAS: EL MONSTRUO CURIOSO

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Palabras Clave: *vocaciones científicas, enseñanza ciencia, cristalografía*

El fomento de las vocaciones científicas es fundamental para el desarrollo de nuestra sociedad. La elección de una carrera profesional es un proceso dinámico, que se desarrolla a lo largo de la infancia. Durante los primeros 14 años de vida, las personas desarrollan la percepción de su propio ser, a la vez que se va formando una percepción de su entorno familiar, social y laboral [1]. Así, la observación, desde una edad temprana, de científicos/as desarrollando su trabajo y el entendimiento de la ciencia como algo cotidiano y familiar, tendrá un claro efecto en el desarrollo de las vocaciones científicas [2]. En este sentido, la literatura infantil es una gran herramienta para acercar la ciencia a los niños y niñas; De de vida acceden a libros a través de los cuales conocen hechos y conceptos sobre su entorno. Es por ello que, a través de la literatura infantil es posible hacer llegar al alumnado una imagen amplia y, a la vez, cotidiana de la ciencia, su importancia y aplicaciones y el desarrollo profesional en este ámbito. Este es el objetivo de El Monstruo Curioso, un proyecto didáctico-divulgativo que pretende acercar la ciencia y la tecnología al alumnado de educación infantil y primaria a través de la literatura infantil. Esta actividad se encuadra dentro de un proyecto de divulgación científica más amplio titulado "Programa de actividades para el desarrollo de la cultura y las vocaciones científicas en el marco del IYCr2014", cofinanciado por MINECO-FECYT. Como primera etapa en este proyecto, hemos creado un personaje y un entorno que atraiga a niños y niñas, y con el que puedan sentirse identificados: El Monstruo Curioso. El protagonista se llama Mati y es un monstruo, pero, ante todo, es un niño, y como niño que es, tiene un mundo interior lleno de curiosidad y color. Mati le hace muchas preguntas a su mamá, que es científica, y ella le responde utilizando un lenguaje claro, sencillo y adaptado, ilustrando los conceptos que van tratando, en la medida de lo posible, con objetos cotidianos. Dentro del proyecto, hemos definido tres líneas de actuación fundamentales que se complementan entre sí: Creación, edición e impresión de libros y láminas; Elaboración de material didáctico de apoyo; Realización de talleres presenciales. En esta comunicación presentaremos el proyecto de El Monstruo Curioso en general y la primera de las obras creadas: *El Monstruo Curioso y las Estrellas de Carbón*, que es un cuento que habla sobre el polimorfismo de los cristales de carbono, tema estrella en cristalografía.

Agradecimientos: *Ministerio de Economía y Competitividad* (MINECO-13-MAT2013-40950-R, FECYT-FCT-14-8647), Gobierno del Principado de Asturias (GRUPIN14-060) y FEDER.

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TÉCNICAS AVANZADAS EN EL LABORATORIO DE QUÍMICA (TALQ) : UNA NUEVA HERRAMIENTA *"on-line"*

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Palabras Clave: *laboratorio, química, experimental, operaciones, prácticas.*

En estos últimos años, un grupo de profesores de la Universidad de Barcelona, *grupo GIDOLQUIM*, hemos desarrollado un proyecto de innovación docente para su utilización en el aprendizaje de las técnicas avanzadas en el laboratorio de química (**TALQ**) (www.ub.edu/talq). Consideramos el proyecto como la segunda parte del ya desarrollado Operaciones Básicas en el Laboratorio Químico (www.ub.edu/oblq). El objetivo del proyecto es dar a conocer al alumno, de forma sencilla y gráfica, las operaciones que podríamos definir como "avanzadas" que se llevan a término en un laboratorio de química. Por otro lado se pretende proporcionar al profesor una herramienta de apoyo efectiva en el trabajo de descripción de estas operaciones que se pueda llevar a cabo en el aula, previamente a introducir al alumno en el laboratorio. Se trata por tanto de una herramienta dirigida tanto al estudiante como al profesor. El contenido se ha distribuido en 5 amplios apartados :

Tema 1. Disolventes y reactivos. Conceptos y tratamiento previo; **Tema 2**. Trabajar con gases. Generación de gases. Reacciones con gases a presión; **Tema 3**; Activación de reacciones químicas por métodos físicos: agitación, temperatura, microondas, ultrasonidos, fotoquímica; **Tema 4**. El proceso de la liofilización. Conceptos y procedimientos; **Tema 5**. Reacciones en atmósfera inerte. Técnicas de creación, materiales y procedimientos.

Creemos que el material desarrollado puede ser muy interesante para toda la comunidad educativa involucrada en el aprendizaje práctico del trabajo en Química Organometálica y es por ello que nuestra intención es que sea un material libre en su utilización, dentro de los términos habituales de registro de autor de material electrónico.

Presentaciones Póster (PP)

Listado de presentaciones póster

UN SOFTWARE QUE APLICA LA ESTRUCTURA DE LOS SISTEMAS DE COMPARTIMENTOS A LA QUÍMICA ORGÁNICA

F. García-Sevilla

DIGITALIZACIÓN DE CONTENIDOS EN CIENCIAS POR ALUMNOS DE BACHILLERATO

M.C. Guillén Miró

DETERMINATION OF TRIAZINIC HERBICIDES IN SEAWATER SAMPLES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

N. Rodríguez

S4: *Enseñanza, Historia y Divulgación de la Química*

UN SOFTWARE QUE APLICA LA ESTRUCTURA DE LOS SISTEMAS DE COMPARTIMENTOS A LA QUÍMICA ORGÁNICA

F. García-Sevilla[1], M.D. Masiá[2], M. García-Moreno[2], M.Ll. Amo-Saus[2], J. Masiá-Pérez[2], M. Molina-Alarcón[3] y R. Varón[2]

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Palabras Clave: *Compartimentos, software, compuesto, química orgánica, obtención.*

Los modelos lineales multicompartimentales se aplican a muchos aspectos de la ciencia y la Ingeniería [1]. Los estudios estructurales de estos modelos requieren establecer previamente el diagrama de conexión entre compartimentos para, a partir de él, obtener los trayectos entre dos compartimentos y sus longitudes, los ciclos, los compartimentos sucesores y precursores de otro y las matrices de conectividad. En esta comunicación asimilamos los diferentes tipos de compuestos orgánicos a compartimentos y los métodos de obtener un tipo de compuesto a partir de otro tipo a una conexión entre compartimentos.

Una vez estructurado el sistema de compartimentos indicado anteriormente, se propone un software, de carácter fundamentalmente educativo, que permita, de una manera cómoda y rápida, establecer los diferentes caminos de síntesis para cualquier tipo de compuesto orgánico a partir de cualquier otro. Así mismo, este software proporciona el conjunto de todos los tipos de compuestos orgánicos tales que, a partir de cualquiera de ellos, se puede obtener el tipo de compuesto especificado y las correspondientes vías de síntesis. También el software proporciona el conjunto de tipos de compuestos que se pueden obtener a partir de un tipo específico y las correspondientes vías de síntesis.

El algoritmo empleado en la implementación del presente software está basado en el análisis de los sistemas lineales de compartimentos desarrollado previamente por nuestro grupo [2]. La aplicación, que no necesita ser instalada en el sistema, se ha compilado para los sistemas operativos Windows (8.1 y anteriores) empleando el entorno de desarrollo Microsoft Visual C# 2010 y no tiene ningún otro requerimiento de CPU o memoria más allá de los exigidos por el sistema operativo instalado en el equipo. Este software ofrece la posibilidad de interacción con él, introduciendo o eliminando tipos de compuestos y/o de reacción entre ellos, lo que facilita la adaptación del mismo a las necesidades de los estudiantes, profesores o cualquier otra persona interesada.

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S4: *Enseñanza, Historia y Divulgación de la Química*

DIGITALIZACIÓN DE CONTENIDOS EN CIENCIAS POR ALUMNOS DE BACHILLERATO

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Palabras Clave: *exelearning, digitalización, idevices*

Introducción: Teniendo en cuenta la evolución de la Ciencia y la Tecnología, y su impacto en el desarrollo social, es necesario preparar a nuestros alumnos para vivir en la sociedad del conocimiento, garantizando el acceso de todos a las nuevas tecnologías y como recomienda la LOMCE, propiciando el oportuno cambio metodológico para que el alumnado sea un elemento activo en el proceso de aprendizaje. En este sentido, los alumnos de 1º de Bachillerato del IES El Carmen de Murcia, han llevado a cabo durante el curso 2014/2015 un trabajo consistente en la elaboración de su propio material de estudio, mediante la realización de un libro electrónico, con el diseño de sus unidades didácticas.

Contenidos: Para la realización de este libro electrónico, que lleva por título " Ciencias para el Mundo Contemporáneo ", basado en textos de Gil y col [1], se ha utilizado el programa exelearning que permite incluir idevices, o instrumentos que proveen un marco de trabajo adecuado para insertar contenidos, tales como textos, fotos, videos, power points, artículos de la Wikipedia etc. El libro se ha estructurado en capítulos denominados: El Universo, El Evolucionismo, Las Plagas del siglo XXI, Las Catástrofes, El Genoma Humano, El Cambio Climático etc. En cada capítulo se han incluido preguntas tales como: el origen de la Luna, la teoría de Darwin, los medicamentos, el DNA, naturaleza de los volcanes, causas del cambio climático. Estos idevices se completaban con fotos, videos o power points .

Conclusiones: La experiencia, no exenta de ciertas dificultades de tipo técnico en su mayoría, resulta interesante ya que permite considerar al ordenador, como la herramienta más provechosa en el proceso de enseñanza-aprendizaje, potencia además la autonomía del alumnado a la hora de seleccionar contenidos e incrementa su autoestima, permite la integración de contenidos digitales y ofrece una formación complementaria para integrar dichos contenidos

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DETERMINATION OF TRIAZINIC HERBICIDES IN SEAWATER SAMPLES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

N. Rodríguez, M.J. González and E. Beceiro

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Keywords: *Undergraduate Laboratory Instruction, Analytical Chemistry, HPLC, Hands-On Learning/Manipulatives, Environmental Science, Triazines*

A student activity that focuses on the determination of four chloro-*s*-triazines (atrazine, propazine, simazine and terbuthylazine) in sea water samples by using High Performance Liquid Chromatography with Ultraviolet Detection (HPLC-UV) is presented. During the laboratory sessions, students learn both the use of the instrument and the principles of chromatographic measurements by testing several mobile phases and applying the optimized method to the analysis of surface waters. Additionally, this project has students practicing and developing a number of skills including solution preparation, solid phase extraction (SPE) and sample concentration procedures.

Before performing the laboratory period, students are required to complete a prelab exercise that assesses their preparedness to perform the experiment. They need to be able to describe the configuration of a HPLC system and what experimental parameters are expected to be important. The prelab exercise must be shown to the instructor at the beginning of the laboratory sessions.

The experiment is divided into two 3 h lab periods and one 2 h classroom period. In the laboratory sessions, the students work in small groups which let to generate stimulant discussions between the members of the group. In the first lab period, students acquaint with HPLC technique (components of HPLC system and development of HPLC-UV methods). In the second lab period, they prepare the seawater samples by SPE and the standard solutions for calibration; then run the equipment to measure the concentration of triazines. After completing the experiment, the students are required to pool their results in a report, which helps the students to develop the scientific writing skills they will need later in their careers. Finally, a classroom session with all groups of students is carried out for a postlab discussion about the overall procedure.

This project allows students to participate actively in learning concepts through practical experience. It increases the student motivation and makes teaching the principles involved in chromatographic techniques easier.

Acknowledgements: This work has been supported by Program of Consolidation and Structuring of Units of Competitive Investigation of the University System of Galicia (Xunta de Galicia) potentially cofounded by European Regional Development Fund (ERDF) (reference: GRC2013-047).

S5. Derivados de Metales Representativos: Estructura, Reactividad y Propiedades Únicas (DMR) / Derivatives of Representative Metals: Structure, Reactivity and Singular Properties

El simposio está dedicado a la química de los derivados de metales de los grupos principales. Esta área ha resurgido con fuerza en las últimas décadas debido a su gran diversidad estructural y a los novedosos comportamientos químicos que presentan, que han abierto nuevas rutas dentro de la química sintética. Los ponentes invitados nos darán una perspectiva de los últimos avances tanto en especies moleculares como estructuras extendidas.

The symposium is devoted to the chemistry of the derivatives of main group metals. This area has generated a lot of interest in the last decades due to the large structural diversity generated and to the new and interesting chemical behaviour these metals show, that have allowed to open new routes in synthetic chemistry. Invited speakers will give a perspective of the last breakthroughs both in molecular species and in extended structures.

Organizadores:

Marta E. G. Mosquera (UAH)

Antonio Rodríguez Delgado (US)

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Simposio patrocinado por la Universidad de Alcalá de Henares

Miércoles 22 de Julio 2015

08:40 – 09:40	**PL-4**	***Conferencia Plenaria*** (Común a todos los simposios) **Luis Liz-Marzán** *"Chemical Growth of Metal Nanoparticles: Why and How?"*

Chairman: Marta E. G. Mosquera

10:00 – 10:30	**S5-IL-01**	**Eva Hevia** *"Main Group Mixed-Metal Chemistry: New Perceptions and Practices"*
10:30 – 11:00	**S5-IL-02**	**Elena Fernández** *"Versatile Boranes for Synthetic Board Games"*
11:00 – 11:30		Pausa Café

Chairman: Antonio Rodríguez

11:30 – 12:00	**S5-IL-03**	**Ángeles Monge** *"Preparation and Properties of New Group 13 Based Metal-Organic Frameworks"*
12:00 – 12:15	**S5-OC-01**	**Sonia Pérez-Yáñez** *"Developing Porous Heterometallic Scandium(III)/Alkaline/ Pyrimidine-4,6-dicarboxylate Frameworks as Ionic Conductors"*
12:15 – 12:30	**S5-OC-02**	**Agustín Lara-Sánchez** *"Synthesis od Cyclic Carbonates Catalyzed by Aluminium Heteroscorpionate Complexes"*
12:30 – 13:00	**S5-IL-04**	**Jean François Carpentier** *"Organometallic Chemistry and Hydroelementation Catalysis of Heavy Alkaline-and Divalent Rare-Earth Elements"*
13:00 – 13:15	**S5-OC-03**	**Arjan Kleij** *"Al(III) and Fe(III) Catalysts for the Conversion of Carbon Dioxide into Value-Added Organic Compounds and Polymers"*
13:15 – 13:30	**S5-OC-04**	**María Fernández-Millán** *"Chiral Main Group Derivatives Bearing Ligands of Natural Origin: Catalytic Properties"*
13:30 – 13:45		**Factoría de Cristalizacion** por **Fermín Otarola**
13:45 – 15:30		Comida

18:30	***Sesión de Pósteres***

Comunicaciones Invitadas (IL)

S5: *Derivados de Metales Representativos: Estructura, Reactividad y Propiedades Únicas*

MAIN GROUP MIXED-METAL CHEMISTRY: NEW PERCEPTIONS AND PRACTICES

Eva Hevia[1]

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Keywords: *s-block metals, bimetallic, metalation, catalysis, ate chemistry*

Recent advances have established that cooperative characteristics can be instilled into main group bimetallic systems by combining two different metals with distinct bond polarities within the same compound. The outcome of this cooperativity is that the bimetallic is capable of delivering new chemistry irreproducible by either of its single-metal components. Despite many synthetic organic studies having utilised these reagents, the key factors governing their reactions and cooperative behaviour still remain to be elucidated and fully understood.

To complement these organic-focused studies and gain a better understanding of this intriguing area, we have approached it from an alternative inorganic/structural/metal perspective. This presentation will highlight our recent results that provide valuable insights into the often blurred identities of the organometallic intermediates involved in key reactions such as deprotonation,[1] metal-halogen exchange and Pd-catalysed cross-couplings (see Figure 1).[2] The first catalytic applications of these multicomponent reagents will also be discussed focussing on hydroamination reactions of unsaturated organic molecules such as isocyanates and olefins.[3] The opening applications of mixed ammonium-magnesiate salts in Green Chemistry will also be revealed through addition reactions of Grignard reagents to ketones under air and at room temperature using *Deep Eutectic Solvents*.[4]

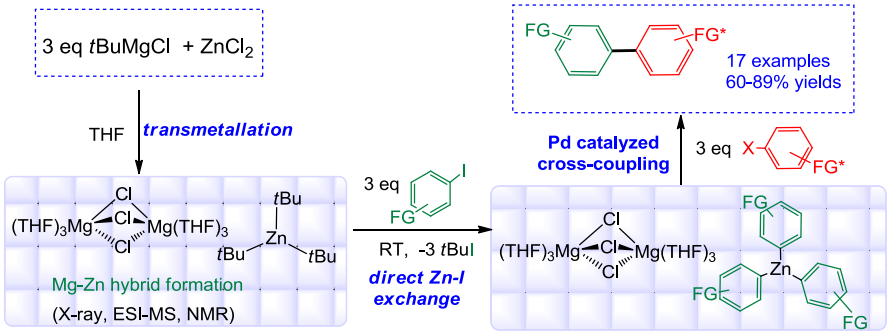

Figure 1

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S5: *Derivados de Metales Representativos: Estructura, Reactividad y Propiedades Únicas*

VERSATILE BORANES FOR SYNTHETIC BOARD GAMES

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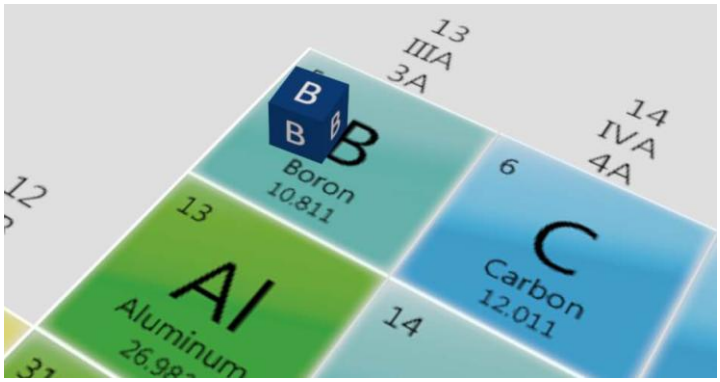
Keywords: *catalytic organoboron chemistry*

Organoboranes are at the forefront of synthetic organic chemistry due to their versatile reactivity, stability and straightforward accessibility. In particular, the C-B bond formation can be considered as an ideal mean to introduce functionalities that opens the access to a multiple target compounds with high control of chemo-, regio- and stereoselectivity.[1,2]

We have experimentally proved the metal-free viability of 1,2-diboration, 1,1-diboration and -boration of unsaturated substrates with symmetrical and non-simmetrical diboron reagents. The heterolytic cleavage of the diboron reagent by simple alkoxyde interaction and the formation of two vecinal or geminal C-B bonds has been rationalised based on spectroscopic and DFT calculations and mechanisms have been suggested.



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S5: *Derivados de Metales Representativos: Estructura, Reactividad y Propiedades Únicas*

PREPARATION AND PROPERTIES OF NEW GROUP 13 BASED METAL-ORGANIC FRAMEWORKS

M. A. Monge, L. M. Aguirre-Díaz, F. Gándara, E. Gutiérrez-Puebla, M. Iglesias, N. Snejko
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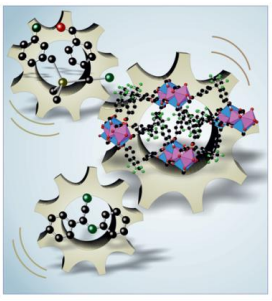
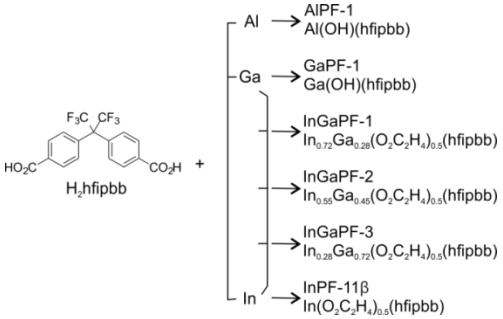
Keywords: *MOF materials, heterogeneous catalysis,*

Metal-organic frameworks, MOFs, are a class of crystalline materials formed by the linkage of metal ions or clusters (SBUs) through organic ligands. MOFs have many applications, including gas storage or separation, luminescence, drug delivery, or heterogeneous catalysis. Compared to traditional heterogeneous catalysts, MOFs exhibit the advantage of offering a wide range of different chemical compositions, as well as topological and structural features. Thus, MOFs can be prepared with different metal ions and in different coordination environments, suitable to be used as catalytic active sites in organic transformations. In addition, it is possible to use different metal elements to obtain MOFs with the same framework type so that the properties of the materials vary depending on the selected metal atom while keeping the same structural features. More recently, it has also been demonstrated that different metal atoms can be incorporated within the same MOF, occupying equivalent positions in the crystalline framework, which we denote solid solution MOFs

Herein we report[1] the synthesis and characterization of three new isostructural MOFs, AlPF-1, [Al(OH)(hfipbb)], GaPF-1, [Ga(OH)(hfipbb)] and InPF-11β, [$In(O_2C_2H_4)_{0.5}$(hfipbb)] (H_2hfipbb = 4,4'-(hexafluoroisopropylidene) bis(benzoic acid), (scheme 1) which show catalytic activity in the solvent free, one pot Strecker reaction. These three materials showed different behaviorin this catalytic reaction affording three different products. In case of AlPF-1 the expected α-aminonitrile product was obtained; however when using GaPF-1 and InPF-11β, the cyanosilylation and the imine formation products were respectively obtained. These differences are attributed to the various possible reaction pathways related to the reactant activation process for each catalyst. Thus, in order to probe whether the combination of both paths could reach the desired α-aminonitrile product, we have prepared solid solution MOFs with the combinations of gallium and indium cations. Our results demonstrate for the first time that it is possible to control the catalytic activity of the MOFs in a multicomponent reaction by using specifically selected metal ratios.





Scheme 1. The organic ligand 4,4'-(hexafluoroisopropylidene)*bis*(benzoic acid), H_2hfipbb reacts with aluminium, gallium, indium, and combination of gallium and indium to form a series of new MOFs.

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S5: *Derivados de Metales Representativos: Estructura, Reactividad y Propiedades Únicas*

ORGANOMETALLIC CHEMISTRY AND HYDROELEMENTATION CATALYSIS OF HEAVY ALKALINE- AND DIVALENT RARE-EARTH ELEMENTS

Bo Liu,[1] Sorin Rosca,[1] Yann Sarazin,[1] and Jean-François Carpentier[1,*]

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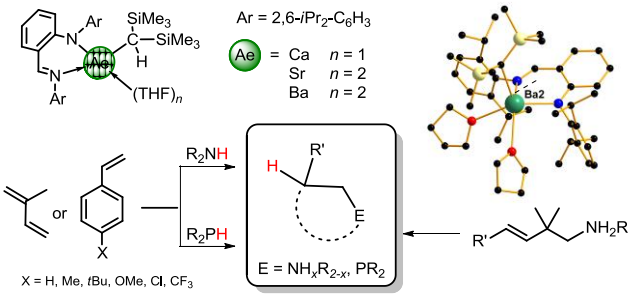
Keywords: *Alkaline-earth elements, Catalysis, Hydroelementation, Mechanisms*

Means to stabilize complexes of the large, oxophilic and benign alkaline-earth metals (Ae = Ca, Sr and Ba) against ligand scrambling have become available, and as a result the interest in the reactivity of these main group metals is rising sharply. We have shown that non-covalent interactions such as Ae•••H–Si and Ae•••F–C afford stable, yet highly reactive complexes which catalyze polymerization and hydroelementation reactions.[1-3]

The preparation of families of heteroleptic alkyl and amide complexes will be presented here, highlighting the importance of the ancillary ligand (aminophenolate, β-diketiminate and imino-anilide) and Ae•••H–Si agostic bonding in their stability.[2,3,4] The reactivity of the new Ae complexes is examined in relation with four key organic transformations leading to C–P and C–N bond formation: ketone hydrophosphonylation,[5] intermolecular and hydroamination and hydrophosphination of activated alkenes,[3,6] and cyclohydroamination of aminoalkenes.[4,6,7] Intermolecular alkene hydroamination and hydrophosphination give strictly anti-Markovnikov products, and the catalytic activity systematically increases with metal size: Ca < Sr < Ba. Key structure-reactivity trends will be discussed in light of kinetic and mechanistic investigations. Recent results obtained in the hydrophosphination of alkenes with catalysts based on divalent lanthanides, which are closely related to Ae elements, will be discussed as well [8].



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Comunicaciones Orales (OC)

S5: *Derivados de Metales Representativos: Estructura, Reactividad y Propiedades Únicas*

DEVELOPING POROUS HETEROMETALLIC SCANDIUM(III)/ALKALINE/PYRIMIDINE-4,6-DICARBOXYLATE FRAMEWORKS AS IONIC CONDUCTORS

Sonia Pérez-Yáñez,[1] Javier Cepeda,[1,2] Garikoitz Beobide,[1] Oscar Castillo,[1] Eider Goikolea,[3] Frederic Aguesse,[3] Antonio Luque,[1] Paul A. Wright[4]

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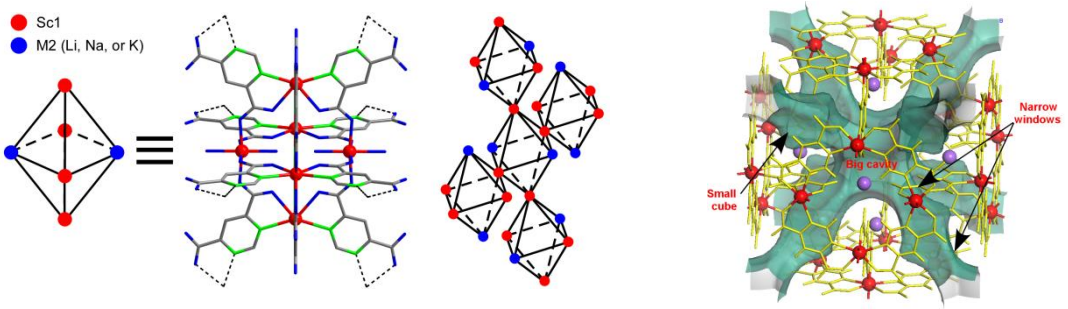
Keywords: *MOFs, adsorption, ionic conductivity*

Metal-organic frameworks (MOFs) constitute a rapidly growing class of materials due to their permanent porosity, high surface area, large pore volume, adjustable pore size, uniform distribution and shape. Moreover, these materials have been largely investigated for possible applications in sensing, drug delivery, catalytic activity, optoelectronics, and magnetism, since they benefit from their hybrid metal-organic nature. However, although conductivity of lithium ions into such materials has been observed, only few reports concerning the use of MOFs as Li-ion battery electrolytes have been published to date.

Herein we present a family of heterometallic 3D porous scandium(III)/alkaline/pyrimidine-4,6-dicarboxylato frameworks. The replacement of alkaline metals during the synthesis generates lighter compounds, which raises the accessible specific surface area. Moreover, these compounds show a remarkable CO_2 uptake due to strong interactions with the pore surface. The heterometallic nature of the materials provides, in addition to a higher specific surface area, an ordered distribution of alkaline ions able to migrate through a 3D void system, promoting ionic conductivity to the material. Compounds have been doped with Cd^{II} and Mn^{II} to force the presence of interstitial Li^+ and Na^+ occupying the void, leading to a substantial increase of the intrinsic conductivity.



(a) (b)

Figure 1: (a) Structural analysis and (b) pore size distribution of $\{[ScM(\mu_4\text{-pmdc})_2(H_2O)_2]\cdot solv\}_n$

S5: *Derivados de Metales Representativos: Estructura, Reactividad y Propiedades Únicas*

SYNTHESIS OF CYCLIC CARBONATES CATALYSED BY ALUMINIUM HETEROSCORPIONATE COMPLEXES

A. Lara-Sánchez[1*], J. Martínez,[1] A. Otero[1], J. Fernández-Baeza[1], C. Alonso-Moreno[1], J. A. Castro-Osma[2], M. North[2]

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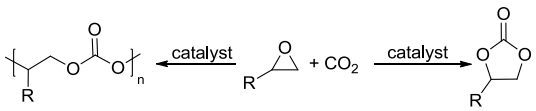
Keywords: *Cyclic carbonates • Carbon dioxide • Aluminium Complexes • Catalysis*

Due to the utilisation of fossil fuels to produce energy, the concentration of carbon dioxide in the atmosphere is increasing every year. Therefore, carbon dioxide is increasingly being seen as a sustainable chemical feedstock for the chemicals industry as it is abundant, economic and non-toxic. It can be used for as starting material for the synthesis of organic molecules, polymeric materials and as a phosgene replacement. One of the most studied reactions of carbon dioxide is its reaction with epoxides to afford either cyclic- or polycarbonates (Scheme 1) which are 100% atom-economical reactions and amongst the most important commercial processes using carbon dioxide as starting material. The synthesis of cyclic carbonates has been extensively investigated in recent years and many highly active catalyst systems which combine a metal complex and an onium salt as cocatalyst have been developed.[1]



Scheme 1

The nature of the metal centre in metal complexes plays an important role in their catalytic performance and aluminium complexes are one of the most efficient catalyst systems for this reaction.[2] Inspired by the high catalytic activity displayed by the aluminium complexes, the work described herein, is the result of a rational development of a new family of bimetallic aluminium(scorpionate) complexes containing an oxo-bridge between the two aluminium centres and their application as catalysts for the conversion of epoxides into the corresponding cyclic carbonates. Notably, a combination of these complexes and TBAB is a very efficient catalyst system for the conversion of a broad range of internal epoxides to cyclic carbonates with, unusually, higher catalytic activity for the synthesis of cyclopentene carbonate than cyclohexene carbonate.

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S5: *Derivados de Metales Representativos: Estructura, Reactividad y Propiedades Únicas*

Al(III) AND Fe(III) CATALYSTS FOR THE CONVERSION OF CARBON DIOXIDE INTO VALUE-ADDED ORGANIC COMPOUNDS AND POLYMERS

V. Laserna,[1] G. Fiorani,[1] Leticia Peña Carrodeguas,[1] Jeroen Rintjema,[1] Arjan W. Kleij[1,2]

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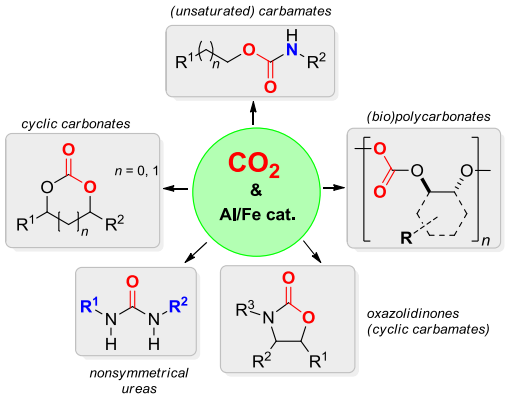
Palabras Clave: *Sustainable metal catalysis, CO_2, Carbonates, Polymers*

The area of carbon dioxide conversion and catalysis is gaining momentum and research communities in academia and industry have as a primary focus using this formal waste material from combustion processes as a renewable and cheap feed stock to prepare organic matter with added value [1,2]. Recently our group has become engaged in the use of amino-triphenolate ligands and particularly in the use of Al(III) and Fe(III) complexes to design new and powerful catalytic strategies for the conversion of CO_2 into functional organic carbonates [3] and CO_2 based polymers [4]. The use of earth-abundant, cheap and readily available metals for catalytic CO_2 applications helps to create value from waste and increases the overall sustainability of chemical synthesis.



Particular examples will be demonstrated where such Al/Fe complexes have been successfully applied as catalysts for the stereo-selective formation of diols [5] and carbamates, and the formation of 100% bio-based polymers derived from renewable limonene, an example of the terpene family of structures. A mechanistic rationale will be presented to explain the observed reactivity and selectivity patterns providing new insights and valuable information for iterative catalyst/process development. The results therefore emphasize the current and future impact of the use of metals such as Al and Fe in the field of homogeneous catalysis [6] and material science and underline the importance of ongoing efforts to explore their full potential in these areas.

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S5: *Derivados de Metales Representativos: Estructura, Reactividad y Propiedades Únicas*

CHIRAL MAIN GROUP DERIVATIVES BEARING LIGANDS OF NATURAL ORIGIN: CATALYTIC PROPERTIES

M. Fernández-Millán[1], G. Chahboun, J. Cano, T. Cuenca, M. E. G. Mosquera

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Keywords: *Main group, Chirality, C-H Activation, ROP*

In the last few decades main group coordination chemistry have gone through a resurgence due to the fascinating structural diversity and chemical properties shown by coordination compounds bearing these metals. The number of well-defined main group complexes described bearing chiral ligands is surprisingly low, even though main group coordination compounds are active in a variety of important catalytic processes.[1]

In this context, one of our ongoing research areas is focused on the preparation of homo and heterometallic aluminium complexes with O- and N- donor ligands and the study of their activity in catalytic polymerization processes.[2] We have extended these studies to O- and N- donor chiral ligands using naturally occurring compounds. In particular, we used terpenoids since they are excellent ligand precursors, due to they are chiral and commercially available as enantiomerically pure products. As well, the presence of instaurations in their structures gives the opportunity of performing further functionalization in a stereo-selective way. [3] These studies have led us to prepare new chiral derivatives with unusual structures, which are active in catalytic ROP polymerization processes and also in the activation of C-H bonds in carbonyl compounds.

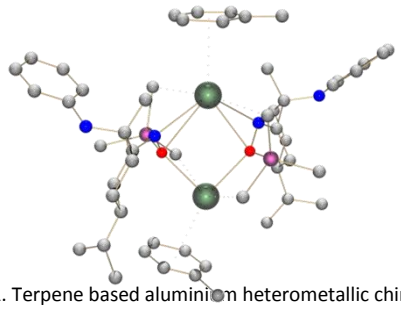

Figure 1. Terpene based aluminium heterometallic chiral compound

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Presentaciones Póster (PP)

Listado de presentaciones póster

ARYL EXCHANGE REACTIONS INVOLVING ORGANOTIN AND GOLD COMPLEXES

J. A. Casares

METALAZIDES IN THE CONSTRUCTION OF MULTIMETAL STRUCTURES

L. Casarrubios

ALKALI METAL SCHIFF-BASE COMPLEXES: SYNTHESIS AND APPLICATIONS

F. M. García-Valle

SINTESIS Y ACTIVIDAD CATALITICA DE COMPUESTOS HETEROMETALICOS DE ALUMINIO Y METALES ALCALINOS DE BAJA NUCLEARIDAD

M. T. Muñoz

S5: *Derivados de Metales Representativos: Estructura, Reactividad y Propiedades Únicas*

ARYL EXCHANGE REACTIONS INVOLVING ORGANOTIN AND GOLD COMPLEXES

D. Carrasco[1], M. Pérez-Iglesias[1], J. A. Casares[1] , M. García-Melchor[2] , P. Espinet[1]

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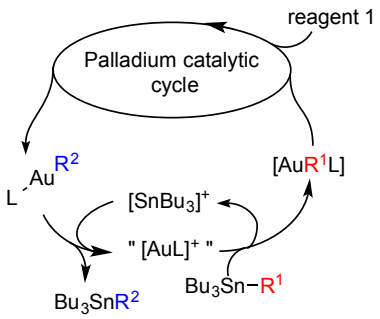
Keywords: *Transmetalation, bimetallic catalysis, reaction mechanisms*

In previous works, we found that gold(I) complexes catalyze the transmetalation step in the Stille reaction, and that an equilibrium between species with the aryl group in the tin or in the gold is established (Eq. 1), which depends on the nature of the halogen and the bulkiness of the aryl.[1]

On a related topic, Blum *et.al.* reported the vinyl exchange between gold and tin in the carbo-stannylation of alkynes co-catalyzed by palladium and gold.[2] In this reaction, the participation of cationic organotin intermediates was hypothesized (Scheme 1). Also Chen *et al*. reported the gold-catalyzed cycloisomerization/stannylation cascade reaction of 1,6-diyne-4-en-3-ols, leading to stannyl naphthalenes,[3] and also in these reactions the transmetalations between organotin and gold complexes take place.



Scheme 1. In the palladium catalytic cycle R^1 is transformed into R^2. The gold plays the role of a carrier of R^1 from tin to palladium and R^2 from palladium to tin.

Now we have undertaken a more extensive study of this group of reactions, and in this communication we present a combined experimental and theoretical study on some relevant reactions involving organotin and organogold(I) complexes, such as reactions in which the organic group R is exchanged by halogen, triflate or another organic group.

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S5: *Derivados de Metales Representativos: Estructura, Reactividad y Propiedades Únicas*

METALAZIDES IN THE CONSTRUCTION OF MULTIMETAL STRUCTURES

Elena A. Giner,[1] M. Gómez-Gallego,[1] L. Casarrubios,[1] M.C. de la Torre,[2] M. A. Sierra[1]

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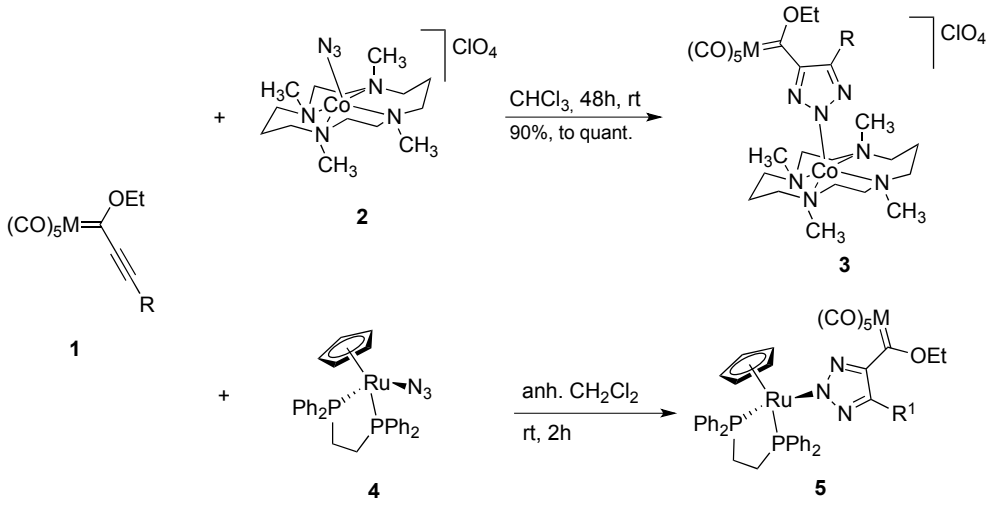
Keywords: *CuAAC, multimetallic, cycloaddition, metal-azide*

Although the Cu(I)-catalyzed 1,3-cycloaddition of azides and alkynes (CuAAC) is widely employed to assemble complex organic molecules through a 1,2,3-triazole tether, the use of metal azides is much more restricted.[1] Here we report the combination of metal azides and metal alkynes as a useful tool for the construction of polymetallic complexes. Thus, reaction of equimolar amounts of mono- and biscarbenes **1** and [(Me_4cyclam)$Co^{II}(N_3)$]-ClO_4 (**2**) in $CHCl_3$ at RT for 48 h, leads to the quantitative formation of bi- and polymetallic triazolates **3** . The structure of the products was established by means of spectroscopic data and confirmed by X-Ray diffraction analysis of **3a**. In a similar manner, the reaction of **1** and ruthenium-azide complexes **4** leads to quantitative formation of bi-and polymetallic complexes **5**.



The electronic properties of the polymetallic systems prepared and the study of the interaction between the metal centers will be discussed.

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S5: *Derivados de Metales Representativos: Estructura, Reactividad y Propiedades Únicas*

ALKALI METAL SCHIFF-BASE COMPLEXES: SYNTHESIS AND APPLICATIONS

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Keywords: *Schiff-base, alkali metal, ROP*

Schiff-base compounds are attractive ligand precursors due to their steric and electronic properties and their amenability to modification. These species constitute simple N, O-donor non-symmetric species that impose control over the metal coordination geometry with a sterically demanding chelating structure. Their easy preparation and purification make them remarkable candidates for the synthesis of a wide variety of metallic compounds.[1,2] One of the ongoing projects in our groups is focused in the study these species as ligands for p-block metals such as aluminium.[3] We have extended our work to the preparation of Schiff-base complexes with alkali metals. These studies have allowed us to isolate new alkali metal derivatives that present high catalytic activity in ROP processes of renewable monomers such as lactide.[4]

Moreover, for the alkali metal complexes prepared, when the Schiff-base precursors have fluoro substituents in the aromatic rings an interesting activation of C-F bonds is observed. These processes give an easy access to the preparation of polycyclic organic molecules with pharmacological activity.

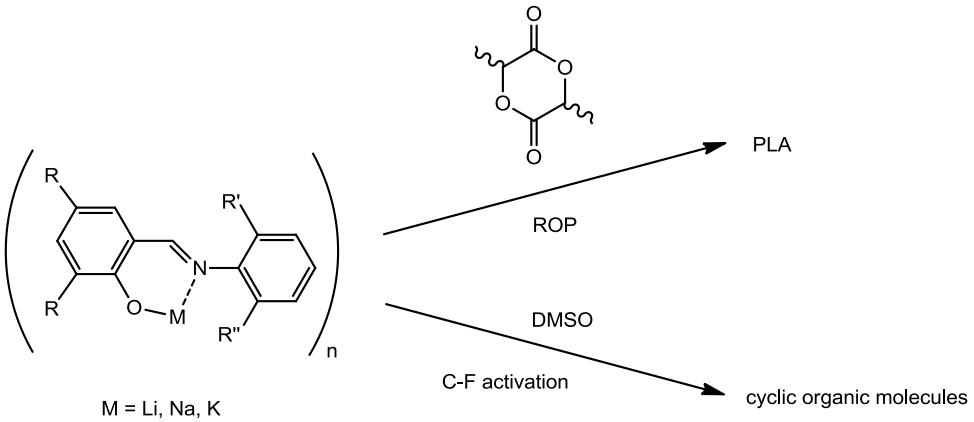

Figure 1. Applications of alkali metal Schiff-base complexes.

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S5: *Derivados de Metales Representativos: Estructura, Reactividad y Propiedades Únicas*

SINTESIS Y ACTIVIDAD CATALITICA DE COMPUESTOS HETEROMETALICOS DE ALUMINIO Y METALES ALCALINOS DE BAJA NUCLEARIDAD

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Palabras Clave: *aluminio, heterometálicos, metales alcalinos*

Los compuestos de aluminio despiertan un gran interés debido a su rica química estructural e importante actividad en catálisis.[1] En particular, los derivados alcóxido y arilóxido de aluminio han demostrado ser eficientes catalizadores en procesos de polimerización por apertura de anillo. Asimismo, los compuestos heterometálicos de aluminio son especies catalíticas muy atractivas, especialmente cuando los metales están conectados por un átomo de oxígeno, debido a la posibilidad de que se produzcan efectos cooperativos entre los diferentes metales del mismo compuesto. En este tipo de especies con frecuencia se mejoran las propiedades catalíticas en comparación con los homólogos homometálicos.[2]

Nuestra investigación se centra en la preparación de nuevos compuestos arilóxido de aluminio homo y heterometálicos que sean activos en procesos de polimerización catalítica.[3] Hemos observado que la presencia de grupos funcionales en el anillo aromático de los grupos arilóxido ofrece puntos de coordinación extra confiriéndoles nuevas características estructurales (figura 1) y consiguiendo así un buen control de la nuclearidad en los compuestos sintetizados.[4] Los derivados preparados son activos en procesos de polimerización de monómeros funcionalizados.

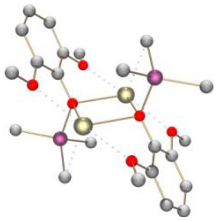

Figura 1. Compuesto heterometálico de aluminio y sodio.

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S6. Avances en Organocatálisis Asimétrica (AOA) / Advances in Asymmetric Organocatalysis

Desde que hace unos 15 años se establecieran los principios generales de la Organocatálisis Asimétrica, la disciplina ha evolucionado en varias direcciones, aportando nuevas soluciones a la síntesis orgánica estereoselectiva. En este simposio se presentarán los más recientes avances en el campo, abarcando aspectos como el diseño de nuevos catalizadores y modos de activación, la investigación de mecanismos, la implementación de métodos sostenibles, o las aplicaciones en síntesis.

Since the foundation of the principles of Asymmetric Organocatalysis some 15 years ago or so, the discipline has evolved in many directions, providing original solutions to problems in stereoselective organic synthesis. This one-day Symposium is aimed to show the most recent advances in the area, covering from the design of new catalysts and activation modes, mechanistic investigations, sustainable implementations, to applications in synthesis.

Organizadores:

Claudio Palomo Nicolau (UPV-EHU)

Mikel Oiarbide Garmendia (UPV-EHU)

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Martes 21 de Julio 2015

08:40 – 09:40	**PL-3**	***Conferencia Plenaria*** (Común a todos los simposios) **Samuel I. Stupp** *"Supramolecular Materials Chemistry"*

Chairman: J. Manuel González

		Conferencia Lilly
10:00 – 10:30	**S6-IL-01**	**José Alemán** *"A Beautiful Journey: From Sulfur Chemistry to Catalysis"*

Chairman: Claudio Palomo

10:30 – 11:00	**S6-IL-02**	**Helma Wennemers** *"Bioinspired Catalysis with Peptides and other Small Molecules"*
11:00 – 11:30		Pausa Café

Chairman: Josep Bonjoch

11:30 – 12:00	**S6-IL-03**	**Darren J. Dixon** *"Catalytic Approaches to Simplifying Synthesis"*
12:00 – 12:15	**S6-OC-01**	**Marisa Carrillo** *"Utilidad Sintética de Dihidropiran-3-onas en Organocatálisis Asimétrica"*
12:15 – 12:30	**S6-OC-02**	**Gabriela Guillena** *"Organocatalyzed Aldol Reaction in Deep Eutectic Solvents"*
12:30 – 12:45	**S6-OC-03**	**Olga García-Mancheño** *"Novel Chiral Helical Triazole-Based C–H·Chloride Anion-Binding Catalysts for the Enantioselective Dearomatization of Heteroarenes"*
12:45 – 13:00	**S6-OC-04**	**Javier Vicario** *"Enantioselective Synthesis of Tetrasubstituted α-Aminophosphonic Acid Derivatives through Organocatalyzed Addition of Nucleophiles to Phosphorated Imines"*
13:00 – 13:30	**S6-FC-01 a 05**	**Comunicaciones Flash / Flash Communications**
13:30 – 15:30		Comida

Chairwoman: Rosario Fernández

15:30 – 16:00	**S6-IL-04**	**Alessandra Lattanzi** ***"****Bifunctional Non-Covalent Organocatalysis: From Small to Medium-Ring Heterocycles Synthesis****"***
16:00 – 16:15	**S6-OC-05**	**Raquel P. Herrera** *"New Trends in Hydrogen Bonds Based Catalysts"*
16:15 – 16:30	**S6-OC-06**	**Carlos Vila** *"Organocatalytic Enantioselective Friedel-Crafts Reactions of Naphthols and Electron-Rich Phenols"*
16:30 – 17:00		Pausa Café

Martes 21 de Julio 2015

Chairman: José Luis Vicario

17:00 – 17:30	**S6-IL-05**	**Miquel A. Pericàs** *"Organocatalytic Asymmetric Flow Processes with Supported Systems"*
17:30 – 17:45	**S6-OC-07**	**Silvia Reboredo** *"Nuevas Estrategias Organocatalíticas en la Síntesis de Derivados Fullerénicos"*
17:45 – 18:00	**S6-OC-08**	**Carlos del Pozo** *"Organocatalytic Intramolecular aza-Michael reaction: New Perspectives"*
18:00 – 18:30	**S6-FC-06 a 09**	**Comunicaciones Flash / Flash Communications**

Comunicaciones Invitadas (IL)

S6: *Avances en Organocatálisis Asimétrica*

Premio Lilly al joven Investigador 2015

A BEAUTIFUL JOURNEY: FROM SULFUR CHEMISTRY TO CATALYSIS

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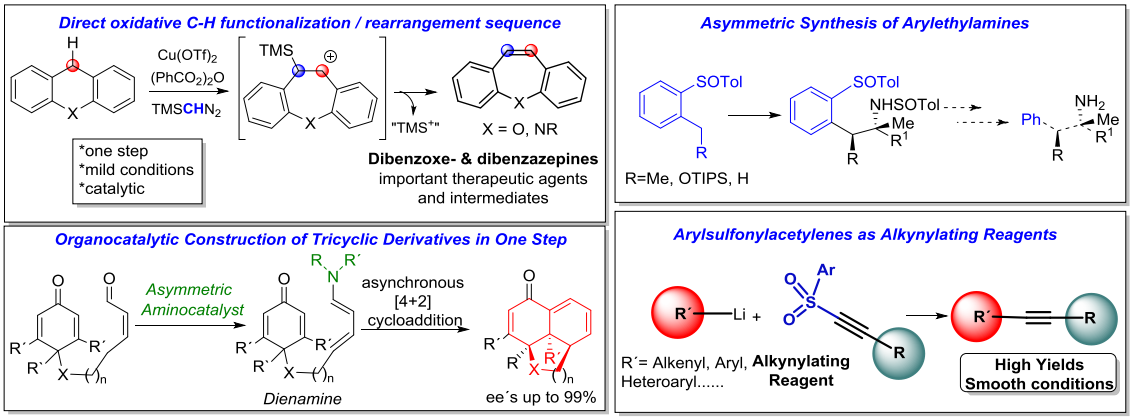
Keywords: *sulfur chemistry, organocatalysis, asymmetric synthesis*

During these last three Lustrums I have been looking for new reactivities and applications of sulfur compounds to stequiometric or catalytic reactions and medicinal chemistry (see www.uam.es/jose.aleman). *Only some examples of different topics of my research trajectory will be selected and shown during this presentation*.

In the first part of this talk (sulfur compounds), different aproaches for the asymmetric synthesis of arylethylamines[1] and then a new approach for the synthesis of alkynes, starting from ethynylsulfones will be presented.[2] As an example in the organocatalytic area, the asymmetric synthesis of tricyclic compounds via desymmetrization of cyclohexadienones will be presented.[3] Finally, I will show the synthesis of tricyclic dibenzoxepines and dibenzazepines which are important therapeutic agents for the pharmaceutical industry and academia. In this work, we present the first copper(I)-catalyzed oxidative C–H bond functionalization–ring expansion reaction with $TMSCHN_2$ to yield these important derivatives in a facile and straightforward way.[4]



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S6: *Avances en Organocatálisis Asimétrica*

BIOINSPIRED CATALYSIS WITH PEPTIDES AND OTHER SMALL MOLECULES

Helma Wennemers

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Keywords: *C-C bond formations, peptides, cinchona alkaloids*

In nature, proteins fulfill manifold different functions and are crucial as, for example, enzymes or templates for the controlled formation of structural components such as bones. The Wennemers group is intrigued by the question whether peptides and other molecules with significantly lower molecular weights compared to proteins can fulfill functions for which nature evolved large macromolecules. Specifically we ask whether peptides can serve as effective asymmetric catalysts, templates for the controlled formation of inorganic materials, or tumor targeting vectors. The lecture will focus on the development of peptides as asymmetric catalysts for stereoselective C-C bond forming reactions and the use of malonic acid derivatives as thioesterenolate equivalents.

Tripeptides of the general type H-Pro-Pro-Xaa (Xaa = amino acid with a carboxylic acid) will be presented that are effective catalysts for aldol reactions and conjugate addition reactions between aldehydes and nitroolefins. The peptides allow for aminocatalysis with catalyst loadings of as little as 0.1-1 mol% and provide synthetically versatile products in high stereoselectivities. The scope of these peptide-catalyzed reactions will be discussed and recent insight into the mechanism will be presented.

The lecture will also highlight the use of malonic acid half thioesters (MAHTs) and monothiomalonates (MTMs) as thioesterenolate equivalents for organocatalytic reactions. The methodology provided straightforward access to numerous types of compounds (e.g. activated β-amino acids, γ-nitrothioesters, indolines) under mild reaction conditions, and even acyclic compounds bearing quaternary stereogenic centers were accessible in excellent yields and stereoselectivities.

S6: *Avances en Organocatálisis Asimétrica*

CATALYTIC APPROACHES TO SIMPLIFYING SYNTHESIS

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Keywords: *bifunctional organocatalysis, iminophosphorane organic superbases, enantioselectivity, Mannich reaction, Michael addition, desymmetrization*

Achieving new reactivity, high turnover numbers and high turnover frequencies in asymmetric organocatalysis remains a major challenge requiring the further development of existing catalyst systems and the invention of new catalyst classes. In an ongoing effort to address the reactivity issues of the commonly used tertiary amine derived bifunctional organocatalysts we have designed and developed a new and highly modular catalyst class based on the high and tunable Bronsted basicity of iminophosphoranes [1]. These new catalysts have demonstrated upto 1000 fold enhancements in reaction rates relative to existing best in class catalysts and have allowed us to develop reactions that were not previously possible.

In this presentation, the background, design, development and repeated application of bifunctional iminophosphorane superbase organocatalysts in a range of important and fundamental asymmetric reactions will be described [2]. Examples demonstrating the application of the catalyst family to heterogeneous organocatalysis [3] and the application of newly developed reactions to the rapid and efficient stereoselective synthesis of natural products and drug molecules will also be described [4].

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S6: *Avances en Organocatálisis Asimétrica*

BIFUNCTIONAL NONCOVALENT ORGANOCATALYSIS: FROM SMALL TO MEDIUM-RING HETEROCYCLES SYNTHESIS

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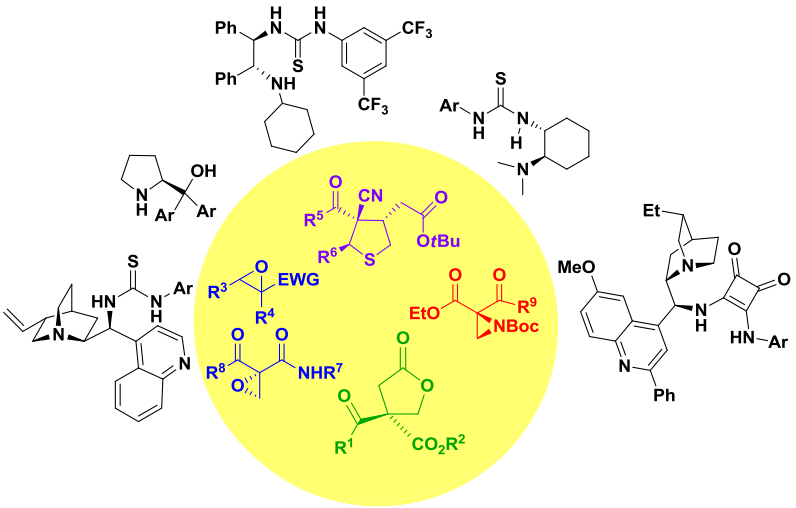
Keywords: *epoxides, aziridines, tetrahydrothiophenes, γ-butyrolactones, quaternary stereocenters*

Ring forming reactions are fundamental processes useful for the synthesis of molecular scaffolds found in a plethora of products having different biological activities. The development of stereoselective cascade reactions to access heterocyclic compounds received a huge interest in recent years, mostly in the realm of organocatalysis.[1,2] Inherent advantages over multistep classical synthesis rely on environmentally friendliness of reaction conditions, cost and time-savings, high atom economy. Aminocatalysis played a major role in the development of cascade reactions leading to heterocycles bearing different stereocenters. Additionally, bi- and multifunctional organocatalysts have been increasingly used to address this goal by means of noncovalent activation of the reagents. This communication will focus on our efforts to access small and medium heterocyclic compounds, bearing quaternary stereocenters, exploiting noncovalent asymmetric organocatalytic tandem reactions.[3,4,5,6]



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S6: *Avances en Organocatálisis Asimétrica*

ORGANOCATALYTIC ASYMMETRIC FLOW PROCESSES WITH SUPPORTED SYSTEMS

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The design and preparation of immobilized catalysts that keep intact the characteristics (activity and selectivity) of their homogeneous counterparts represents a major goal in view of more efficient chemical production. When enantioselective processes are considered, the opportunities offered by this approach (recovery and reuse of expensive catalytic species, highly simplified work-up, implementation of continuous flow processing) become even more evident.

In this lecture we will present different strategies followed in our laboratory for the modification of homogeneous ligands and catalysts, in order to make possible its supporting,[1] with special emphasis on the use of the copper-catalyzed alkyne-azide cycloaddition (CuAAC) as a supporting strategy.[2] Examples of the development of highly active catalytic species for enantioselective processes immobilized on either insoluble polymers[3] or magnetic nanoparticles[4] will be presented, and the development of continuous flow processes[5] based on these immobilized species will be discussed.

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Comunicaciones Orales (OC)

S6: *Avances en Organocatálisis Asimétrica*

UTILIDAD SINTÉTICA DE DIHIDROPIRAN-3-ONAS EN ORGANOCATÁLISIS ASIMÉTRICA

M. Carrillo[1], A. Orue[1], U. Uria[1], E. Reyes[1], J. L. Vicario[1]

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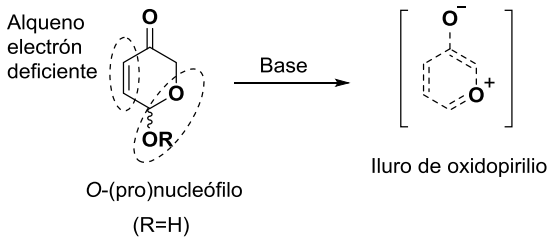
Palabras Clave: *Dididropiran-3-onas, aminocatálisis asimétrica, reacciones en cascada*

En nuestro grupo de investigación recientemente se ha explorado el potencial sintético de 6-hidroxi-2*H*-piran(6*H*)-onas como sustratos versátiles en el diseño de reacciones organocatalíticas asimétricas empleando aminas secundarias quirales como catalizadores. Así, un análisis de la estructura de este tipo de sustratos muestra la presencia de un doble enlace electrón deficiente que, potencialmente, puede ser un buen aceptor de Michael en reacciones de adición conjugada con nucleófilos así como un dienófilo adecuado en reacciones Diels-Alder. [1] Adicionalmente, la presencia de un grupo hidroxilo en posición 6 ofrece la posibilidad de que estos compuestos actúen como (pro)nucleófilos oxigenados. Esta posibilidad de actuar como O-(pro)nucleófilos y como aceptores de Michael los convierte en sustratos ideales para realizar reacciones oxa-Michael/Michael aminocatalíticas con enales bajo activación iminio/enamina. [2] Finalmente, transformando la posición 6 de la estructura de dihidropiran-3-ona en un buen grupo saliente, la molécula resulta ser un excelente precursor de iluros de oxidopirilio en presencia de una base, abriendo la posibilidad de llevar a cabo cicloadiciones [5+2] con un dipolarófilo adecuado. [3]



Agradecimientos: Los autores agradecen a la UPV/EHU (UFI QOSYC 11/22 y EHUA 12/09), al MICINN (CTQ2011-22790 y contrato Juan de la Cierva a U.U), al EJ/GV (IT328-10, OSALAN 14/02, beca a A.O) por la financiación recibida.

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S6: *Avances en Organocatálisis Asimétrica*

ORGANOCATALYZED ALDOL REACTION IN DEEP EUTECTIC SOLVENTS

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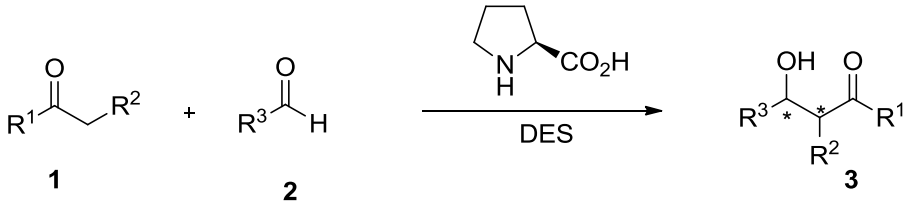
Keywords: *Aldol, DES, enantioselective, proline*

Deep eutectic solvents are considered “green solvents” to carry out chemical transformations, due to their low costs, biodegradability and possible recovery and reuse.[1] However, these type of solvents have been rarely used in organic synthesis, with only a few examples of their application involving the use of a transition metal catalysts.[2] The combination of these media with organocatalysed processes, where the catalysis involves a simple organic molecule, is even scarcer.[3] This type of reactions would be highly interesting for industrial segments such as pharmaceuticals and agrochemicals because the achieved products would be free of metallic traces and obtained through simple, clean, safe and efficient processes. In this work, the use of different deep eutectic solvents to carry out the proline organocatalysed aldol reaction will be described (Scheme 1).



Scheme 1.

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S6: *Avances en Organocatálisis Asimétrica*

NOVEL CHIRAL HELICAL TRIAZOLE-BASED C–H···CHLORIDE ANION-BINDING CATALYSTS FOR THE ENANTIOSELECTIVE DEAROMATIZATION OF HETEROARENES

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Keywords: *Anion-binding catalysis, triazoles, dearomatization, N-heterocycles*

The asymmetric dearomatization of N-heteroarenes constitutes a straightforward synthetic methodology to gain bioactive and synthetic value chiral heterocycles. Conversely, enantioselective catalytic dearomatizations are still rare.[1] In this regard, an interesting approach would consist on the use of neutral H-donor molecules as anion-binding catalysts.[2] However, till date essentially only chiral (thio)ureas have been efficiently employed. With the aim of providing alternative structures for anion acceptor catalysis, our group has recently developed a novel family of chiral triazoles (TetraTri) as C-H-based hydrogen donor catalysts.[3],[4] These catalysts are able to efficiently transfer the chirality to the dearomatized products via formation of a contact chiral ion-pair complex with a preformed N-acyl ionic substrate. Herein, their outstanding performance for the asymmetric dearomatization reaction of quinolines and the more demanding simple pyridines will be presented.[4]

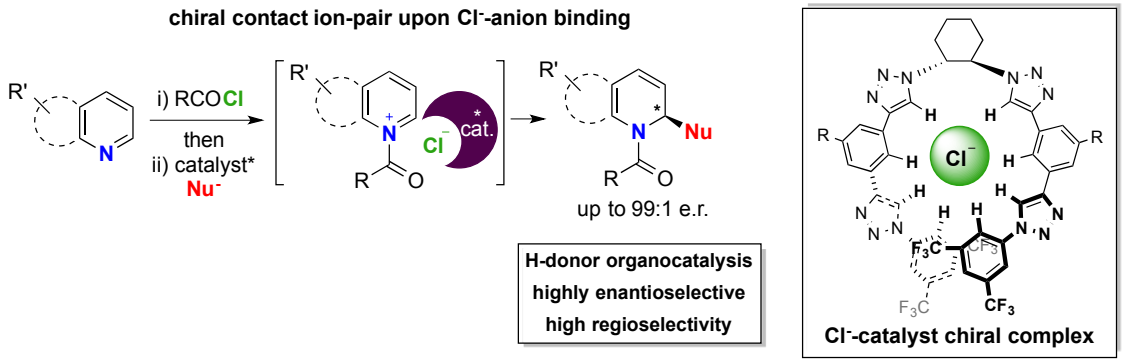

Figure. Anion-binding catalysis for the dearomatization of 6-membered ring N-heteroarenes

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S6: *Avances en Organocatálisis Asimétrica*

ENANTIOSELECTIVE SYNTHESIS OF TETRASUBSTITUTED α-AMINOPHOSPHONIC ACID DERIVATIVES THROUGH ORGANOCATALYZED ADDITION OF NUCLEOPHILES TO PHOSPHORATED IMINES

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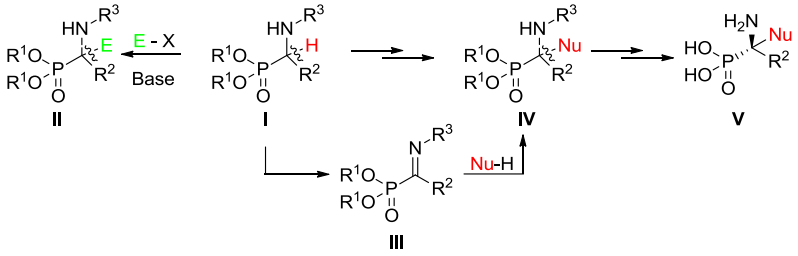
Keywords: *α-Aminophosphonic acids, quaternary centers, organocatalysis*

Aminophosphorus derivatives constitute a significant family of compounds in Organic and Medicinal Chemistry,[1] and interest is especially focused on the α-aminophosphonates. The biological potential of α-aminophosphonates has aroused considerable attention in the development of improved methods for their synthesis,[2] but few methods have been reported for the preparation of α-aminophosphonates containing tetrasubstituted α-carbons.[4]

Some limited examples can be found in the literature, reporting the substitution of a hydrogen atom by an electrophilic alkyl group to afford tetrasubstituted α-aminophosphonates **II**.[3]We report a new route for the substitution of a hydrogen atom in a tertiary α-aminophosphonate by a nucleophilic reagent to obtain quaternary α-aminophosphonates **IV** which may be considered as the complementary process ("umpolung reaction") of the electrophilic substitution of a α-aminophosphonate. This approach allows the functionalization using, for example, nucleophilic aryl groups, not as easily available if electrophilic reagents are used.



The key step in this approach is the generation of α-ketiminophosphonates **III** through a formal oxidation of the parent α-aminophosphonates **I**. The subsequent addition of nucleophilic reagents to species **III**, applying either diastereoselective or asymmetric catalytic strategies, allows the preparation of a bunch of optically active tetrasubstituted α-aminophosphonic acid derivatives **V**.[4]

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S6: *Avances en Organocatálisis Asimétrica*

NEW TRENDS IN HYDROGEN BONDS BASED CATALYSTS

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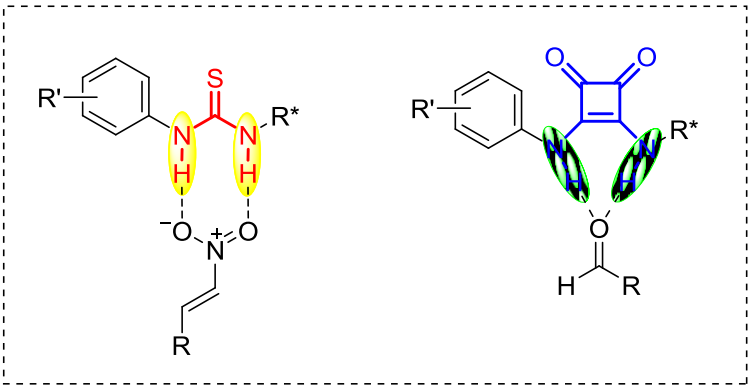
Keywords: *thiourea, squaramide, hydrogen-bond, asymmetry*

Among all kind of explored organocatalysts, those acting by hydrogen bond interactions have received special attention in the last fifteen years,[1] and represent a significant contribution to this great area of research. Herein, we will disclose our recent results in this field in which the use of hydrogen bond-based catalysts has become an efficient tool for the aim of our research.

In the context of our research program focused on the synthesis of new chiral organocatalysts, we have also centered our attention in the exploration of different properties of our catalyst structures beyond the catalytic activity of these scaffolds in different efficient processes, such as biological and luminescence properties and their capacity to form gels, which will be briefly shown.



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S6: *Avances en Organocatálisis Asimétrica*

ORGANOCATALYTIC ENANTIOSELECTIVE FRIEDEL-CRAFTS REACTIONS OF NAPHTHOLS AND ELECTRON-RICH PHENOLS

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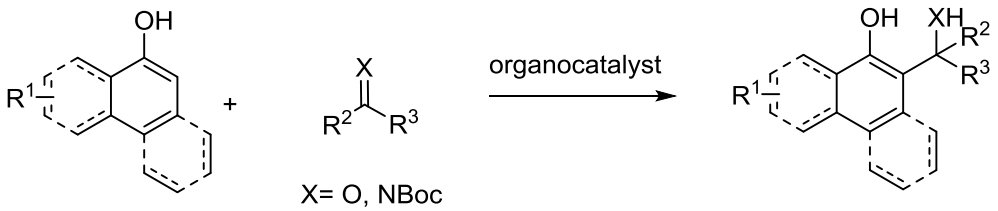
Kew Words: *Friedel-Crafts, organocatalysis, asymmetric synthesis, naphthol, imines, ketimines, trifluoropyruvate*

Catalytic enantioselective methodologies for an efficient carbon-carbon bond formation are at the heart of the chemical sciences and in particular the Friedel-Crafts reaction continues to be one of the cornerstones of our discipline.[1] Despite the progress over the past years on the asymmetric Friedel-Crafts reaction, the major efforts have been focused on the use of indoles and pyrroles as nucleophiles.[2] The application of less reactive arenes such naphthols in the F-C reaction is more demanding, as a result of their lower nucleophilicity. In this communication, we present our efforts in the study of enantioselective alkylation of naphthols or activated phenols with different electrophiles, such imines, ketimines[3] or ethyl trifluoropyruvate. The corresponding chiral benzylic compounds are obtained with good yields and high to excellent enantioselectivities.



X= O, NBoc

R^2=Ar, CF_3

R^3= H,CO_2Et, $CONR_2$

Acknowledgment

Financial support from the MINECO (Gobierno de España) (CTQ2013-47494-P) and from Generalitat Valenciana (ISIC2012/001) is gratefully acknowledged. C. V. thanks MINECO for JdC contract. M.M.-M. thanks the Universitat de València for a predoctoral grant.

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S6: *Avances en Organocatálisis Asimétrica*

NUEVAS ESTRATEGIAS ORGANOCATALÍTICAS EN LA SÍNTESIS DE DERIVADOS FULLERÉNICOS

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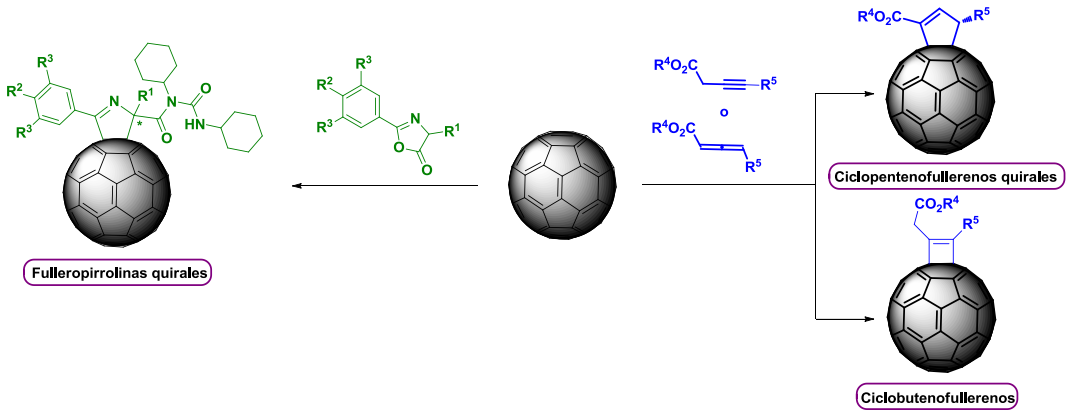
Palabras Clave: *Fullerenos, síntesis asimétrica, organocatálisis, fosfinas, carbenos*

Desde el descubrimiento de la molécula de [60]fullereno en 1985, se han publicado un elevado número de trabajos dirigidos a su funcionalización química. Más recientemente, la preparación de fullerenos y otras nanoformas de carbono enantio-enriquecidos ha demostrado ser de vital relevancia en campos tales como la química médica y la ciencia de materiales, logrando en este último incluso la modificación de sus propiedades físicas.[1] Sin embargo, dada la difícil activación de los fullerenos, la introducción de quiralidad en este tipo de compuestos supone un reto de gran interés dentro de la comunidad científica.

En este sentido, nuestro grupo de investigación ha sido pionero en la preparación de derivados de [60] y [70]fullerenos ópticamente activos utilizando como catalizadores sistemas metálicos[2] y, posteriormente, métodos organocatalíticos.[3,4] En el presente trabajo se describen las diferentes estrategias organocatalíticas empleadas en la síntesis de ciclopenteno[4,5:1,2][60]fullerenos y fulleropirrolinas, así como la formación de interesantes compuestos fullerénicos portadores de un anillo de ciclobuteno, utilizando tanto catálisis nucleófila con fosfinas quirales como carbenos *N*-heterocíciclos.



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S6: *Avances en Organocatálisis Asimétrica*

ORGANOCATALYTIC INTRAMOLECULAR *aza*-MICHAEL REACTION: NEW PERSPECTIVES

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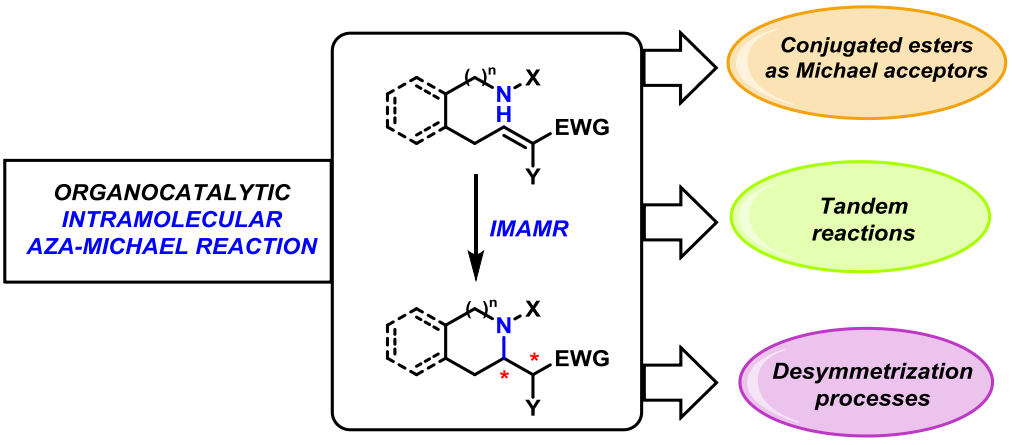
Keywords: Intramolecular *aza*-Michael reaction; nitrogen heterocycles; organocatalysis, tandem reactions, desymmetrization

Enantiomerically enriched nitrogen-containing heterocycles can be assembled by means of the organocatalytic intramolecular *aza*-Michael reaction (IMAMR) [1]. Since *N*-heterocyclic compounds are common structural features in a great variety of biologically active substances, this transformation has found wide applicability in the synthesis of heterocycles and natural products [2].

The organocatalytic IMAMR has been subject of intense research in our group. We have developed efficient methodologies to perform this cyclization with enals [3] and enones [4] as Michael acceptors and moderate nitrogen nucleophiles such as carbamates or sulphonamides as nitrogen donors. Recent achievements in the organocatalytic IMAMR comprise the extension of this protocol to conjugated esters as Michael acceptors [5]. Furthermore, new tandem reactions involving an organocatalytic IMAMR have been recently devised as well as the application of this transformation to desymmetrization processes on conveniently substituted prochiral substrates [6].



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Comunicaciones Flash (FC)

Listado de comunicaciones flash

S6-FC-01 *UNIFIED SYNTHETIC APPROACH TO THE cis-PHLEGMARINE ALKALOIDS*

C. Bosch

S6-FC-02 *NEW CYCLOBUTANE CONTAINING HYBRID PEPTIDES AS CHIRAL ORGANOCATALYSTS FOR ASYMMETRIC ALDOL REACTIONS*

O. Illa

S6-FC-03 *PHOTOCHEMICAL ENANTIOSELECTIVE β - ALKYLATION OF ENONES BY MEANS OF IMINIUM ION ACTIVATION*

David Bastida

S6-FC-04 *QUININE-DERIVED THIOUREA-CATALYZED ENANTIOSELECTIVE ADDITION OF NAPHTHOLS AND ACTIVATED PHENOLS TO ISATIN-DERIVED KETIMINES*

M. Montesinos-Magraner

S6-FC-05 *CATALYTIC ENANTIOSELECTIVE SYNTHESIS OF α,α-DISUSTITUTED α-MERCAPTO CARBOXYLIC ACID DERIVATIVES FROM 5H-THIAZOL-4-ONES*

I. Olaizola

S6-FC-06 *BIFUNCTIONAL BRØNSTED BASES CATALYZED DIRECT ALDOL REACTION OF α - KETO AMIDES*

Haizea Echave

S6-FC-07 *CATALYTIC ENANTIOSELECTIVE SYNTHESIS OF N,C^{α},C^{α}-TRISUBSTITUTED α-AMINO ACID DERIVATIVES USING 1H-IMIDAZOL-4(5H)-ONES AS KEY TEMPLATE*

J. Etxabe

S6-FC-08 *DIASTEREO- AND ENANTIOSELECTIVE VINYLOGOUS POVAROV REACTIONS FOR THE SYNTHESIS OF TETRAHYDROQUINOLINES BEARING A C-4 QUATERNARY STEREOCENTER*

G. Bianchini

S6-FC-09 *REACCIONES HETERO-CARBONIL-ÉNICAS SELECTIVAS SOBRE α-CETOÉSTERES ALIFÁTICOS CATALIZADAS POR TIOUREAS DERIVADAS DE CARBOHIDRATOS*

Gonzalo de Gonzalo

S6: *Avances en Organocatálisis Asimétrica*

UNIFIED SYNTHETIC APPROACH TO THE *cis*-PHLEGMARINE ALKALOIDS

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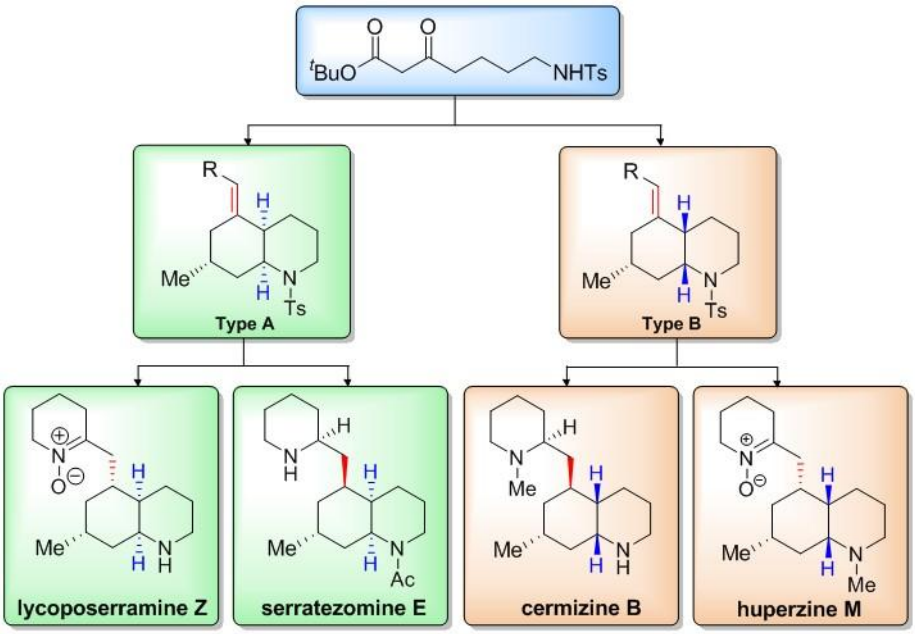
Keywords: *Organocatalysis, Stereodivergent hydrogenation, Phlegmarine alkaloids*

The phlegmarine alkaloids, a subset of the *lycopodium* alkaloids are of interest for their biological properties and synthetic challenges. These compounds feature a decahydroquinoline ring system linked to a 2-piperidylmethyl unit arranged in a diverse range of stereochemistries.[2]

Synthetic access to the four different stereochemical arrangements of the decahydroquinoline ring core of *cis*-phlegmarine alkaloids has been achieved after a short and efficient synthesis including the use of organocatalysis,[3] tandem reactions,[4] stereodivergent hydrogenations and "pot and time economy" strategies.[5]



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S6: *Avances en Organocatálisis Asimétrica*

NEW CYCLOBUTANE CONTAINING HYBRID PEPTIDES AS CHIRAL ORGANOCATALYSTS FOR ASYMMETRIC ALDOL REACTIONS

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Keywords: *organocatalysis, cyclobutane amino acids, proline*

The search for new highly enantioselective and reactive organocatalysts is still necessary to successfully compete with metal catalysts for large scale applications commonly sought after in industry.

Our group has extensively studied the properties of cyclobutane amino acids, especially β-aminocyclobutane carboxylic acid and its homo- and heterooligomers in the field of Foldamers and Materials Science.[1] In a recent research program, chiral *vic*-disubstituted-cyclobutane scaffolds have been used to synthesize a variety of products, some of which have been tested as bifunctional organocatalysts.[2] In turn, γ-aminocyclobutane carboxylic acid has been derivatized into several compounds, which have served, for instance, as stabilizers of ruthenium nanocatalysts. [3]

In this work, four tripeptides have been synthesized (Figure 1). Both enantiomers of cis-β- and cis-γ-aminocyclobutane carboxylic acid, respectively, have been combined with two (L)-proline residues. Their activity as chiral organocatalysts in asymmetric aldol reactions has been explored. Experimental results have been rationalized with the help of NMR experiments as well as with computational calculations.

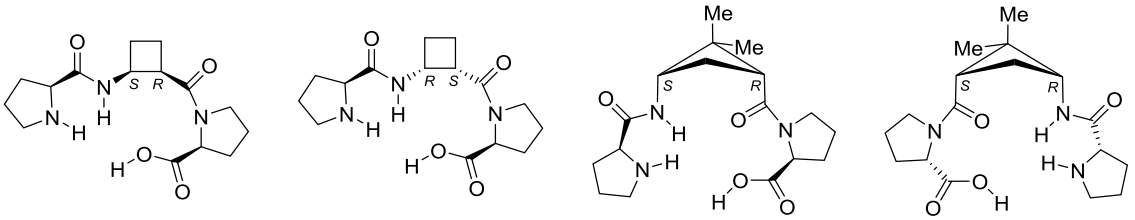

Figure 1. cis-β- and cis-γ-aminocyclobutane carboxylic acid–based catalysts studied in this work

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S6: *Avances en Organocatálisis Asimétrica*

PHOTOCHEMICAL ENANTIOSELECTIVE β - ALKYLATION OF ENONES BY MEANS OF IMINIUM ION ACTIVATION

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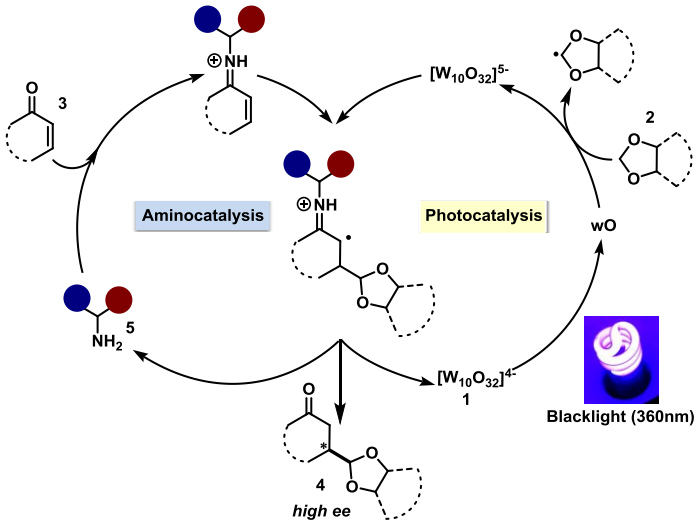
Keywords: *Photocatalysis, Asymmetric Synthesis, Iminium Ion, Enantioselective* β *– Alkylation.*

The ability of the decatungstate anion **1** to absorb UV (ultraviolet) light and produce (*via* LMCT and a short lived excited state) wO is well established.[1] This reactive species (wO) can efficiently generate alkyl radicals through hydrogen atom abstraction from alkanes.[2] Despite the extensive work in this field, an asymmetric transformation has yet to be developed.

Merging the ability of chiral amines to generate a chiral iminium ion intermediate,[3] and the ability of wO to generate alkyl radicals, we developed an asymmetric radical conjugate addition of benzodioxolanes **2** with unsaturated ketones **3**. The β-alkylated products **4** were obtained in good yield and high enantioselectivity using the tungsten-based photocatalyst **1** and a newly designed chiral aminocatalyst **5**.

The possibility of using open-shell species in combination with iminium ion activation opens up new opportunities for the design of enantioselective radical conjugate additions.



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S6: *Avances en Organocatálisis Asimétrica*

QUININE-DERIVED THIOUREA-CATALYZED ENANTIOSELECTIVE ADDITION OF NAPHTHOLS AND ACTIVATED PHENOLS TO ISATIN-DERIVED KETIMINES

M. Montesinos-Magraner, C. Vila, R. Cantón, G. Blay, I. Fernández and J. R. Pedro*

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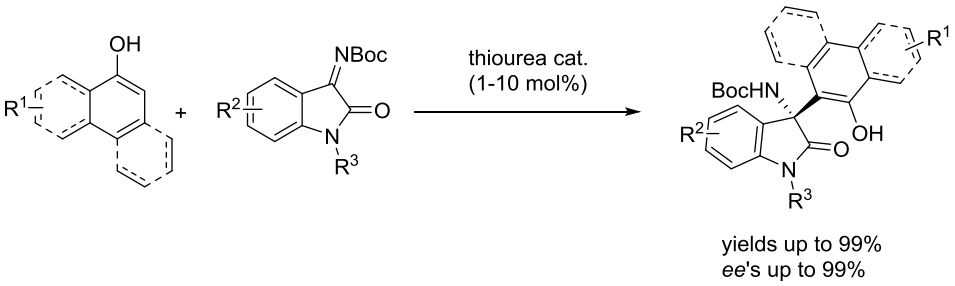
Keywords: *Friedel-Crafts, organocatalysis, asymmetric synthesis, naphthol, imines, ketimines.*

The asymmetric addition of aromatic compounds to imines provides enantioenriched benzylic amines, which are an important scaffold in organic synthesis.[1] In this context, the catalytic enantioselective addition of indoles and pyrroles to different imines has been deeply studied using either organic or metal based catalysts.[2] However, the aza-Friedel-Crafts reaction using naphthols has been less developed and just the addition to aldimines has been described.[3] In this communication, we report the highly enantioselective aminoalkylation of naphthols and activated phenols with ketimines using a quinine-derived thiuourea.[4] The corresponding chiral oxindole derivatives, which can be of interest in medicinal chemistry, were obtained in good yields with a high degree of enantiocontrol.



Acknowledgements

Financial support from the MINECO (Gobierno de España) (CTQ2013-47494-P) and from Generalitat Valenciana (ISIC2012/001) is gratefully acknowledged. M. M.-M. thanks the Universitat de València for a predoctoral grant. C. V. thanks MINECO for JdC contract.

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S6: *Avances en Organocatálisis Asimétrica*

CATALYTIC ENANTIOSELECTIVE SYNTHESIS OF α,α-DISUSTITUTED α-MERCAPTO CARBOXYLIC ACID DERIVATIVES FROM 5*H*-THIAZOL-4-ONES

E. Badiola, S. Diosdado, J. Etxabe, B. Fiser, J. M. García, E. Gómez-Bengoa, I. Izquierdo, A. Landa, R. López, A. Mielgo, J. M. Odriozola, M. Oiarbide, I. Olaizola, C. Palomo, J. Razkin, I. Urruzuno.

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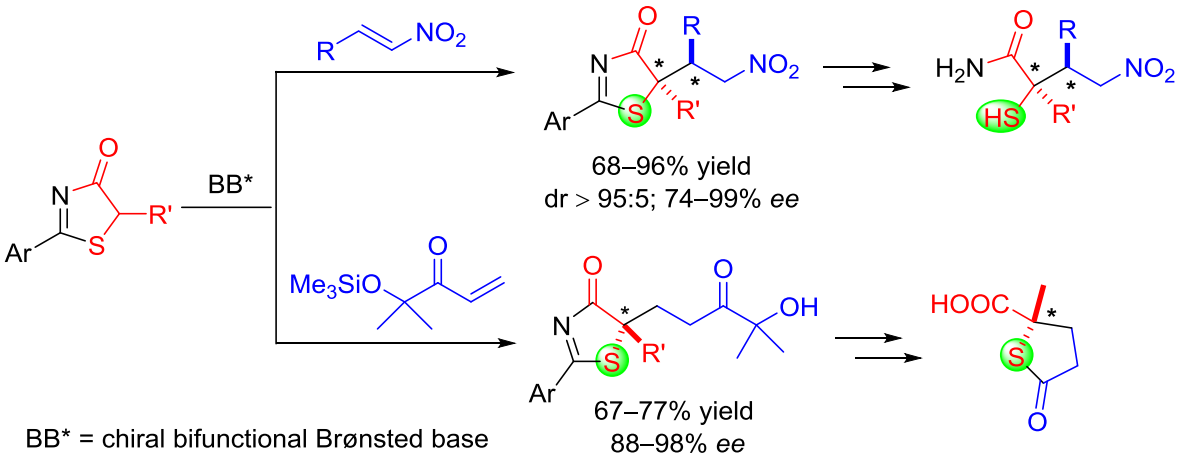
Keywords: *Tertiary thiols · organocatalysis · bifunctional Brønsted bases*

Tertiary thiols are structural motifs present in some biologically active compounds and therefore play an important role in biological and medicinal chemistry. However, and in contrast to secondary thiols, relatively few examples of asymmetric protocols for the preparation of tertiary thiols in optically pure form have been reported.

In this context, we have described the usefulness of 5*H*-thiazol-4-ones as new prochiral Michael donors to provide α,α-disubstituted α-mercapto carboxylic acid derivatives. Before our work, these pronucleophiles, as far as we know, had never been used in asymmetric synthesis. They are easily deprotonated by bifunctional Brønsted bases, such as chiral ureidopeptide-like Brønsted bases developed in our research group or by squaramide derived Brønsted bases. In the presence of these bases they react with Michael acceptors like nitroolefins[1] or α'-oxy enones[2] to produce adducts with good chemical yields and very high diastereo- and enantioselectivities.

α,α-disubstituted α-mercapto carboxylic acid derivatives



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S6: *Avances en Organocatálisis Asimétrica*

BIFUNCTIONAL BRØNSTED BASES CATALYZED DIRECT ALDOL REACTION OF α -KETO AMIDES

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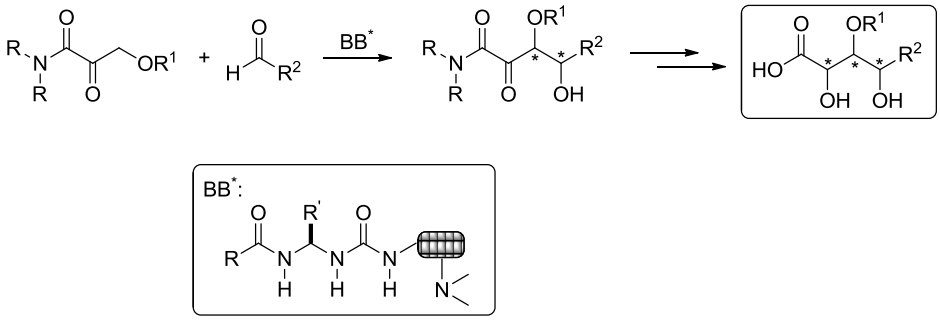
Keywords: *Aldol reaction, Brønsted bases*

The aldol reaction constitutes one of the most powerful methods for the construction of α -hydroxy carbonyl units that are fundamental building blocks in the synthesis of biologically active and pharmaceutically important compounds.[1] Given their synthetic utility, a tremendous effort has been made to develop catalytic asymmetric direct aldol reactions since the first report by Shibasaki.[2] Nevertheless, scarce examples have been described employing poor acidic aldol donors, such those having a carboxylic oxidation state, to produce α -hydroxy carboxyl compounds. On the other hand, there are no examples of BBs catalyzed direct aldol reactions using enolizable aldehydes as aldol acceptor due to their tendency to produce self-condensation.

In this communication, we present an organocatalyzed direct aldol reaction of α-keto amides and enolizable aldehydes that provides polyoxygenated fragments which have not been prepared by means of catalytic and stereoselective aldol reactions yet.[3] Main problems related to the stereoselective generation of the enolate, face shielding of the aldol acceptor, reactivity and prevention of the aldol condensation have been addressed by employing a new family of bifunctional BBs, recently described by our group.[4]



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S6: *Avances en Organocatálisis Asimétrica*

CATALYTIC ENANTIOSELECTIVE SYNTHESIS OF *N*,C^{α},C^{α}-TRISUBSTITUTED α-AMINO ACID DERIVATIVES USING 1*H*-IMIDAZOL-4(5*H*)-ONES AS KEY TEMPLATE

J. Etxabe, J. Izquierdo, A. Landa, M. Oiarbide, C. Palomo.

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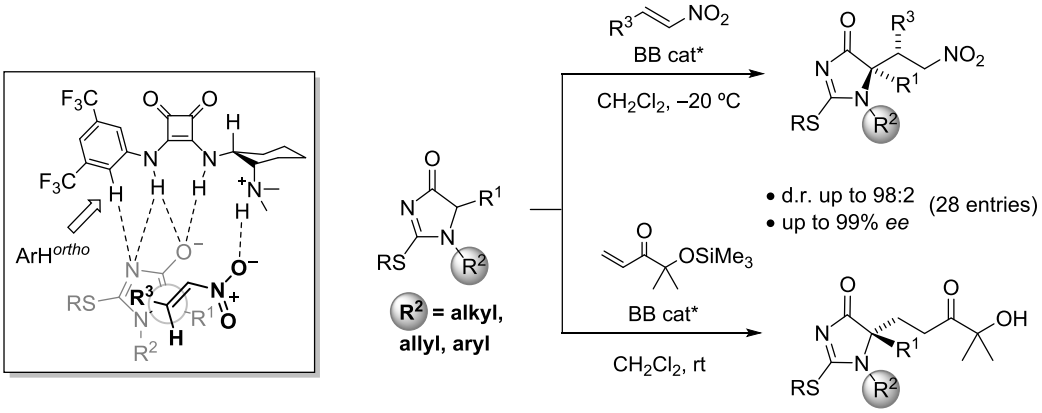
Keywords: *Noncovalent, Organocatalysis, Imidazolones, Hydantoins.*

1*H*-Imidazol-4(5*H*)-ones are introduced as novel nucleophilic α-amino acid equivalents in asymmetric synthesis. These compounds not only allow highly efficient construction of tetrasubstituted stereogenic centers, but unlike hitherto known templates provide direct access to *N-substituted* (-alkyl, -allyl, -aryl) α-amino acid derivatives.



Further elaboration of thus obtained adducts opens a straightforward access to an array of different *N*-substituted quaternary α-amino acid derivatives, including 5,5-disubstituted hydantoins and other complex *N*-heterocycles, in enantiomerically pure form.

Financial support was provided by UPV/EHU (UFI QOSYC 11/22), Basque Government (Grant No IT-628-13 and Saiotek 2014), MEC (Grant CTQ2013-47925-C2-1-P), Spain. J. E. thanks MEC and J. I. thanks UPV/EHU for Fellowships. We also thank SGIker (UPV/EHU) for providing NMR, HRMS, and X-Ray resources.

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S6: *Avances en Organocatálisis Asimétrica*

DIASTEREO- AND ENANTIOSELECTIVE VINYLOGOUS POVAROV REACTIONS FOR THE SYNTHESIS OF TETRAHYDROQUINOLINES BEARING A C-4 QUATERNARY STEREOCENTER

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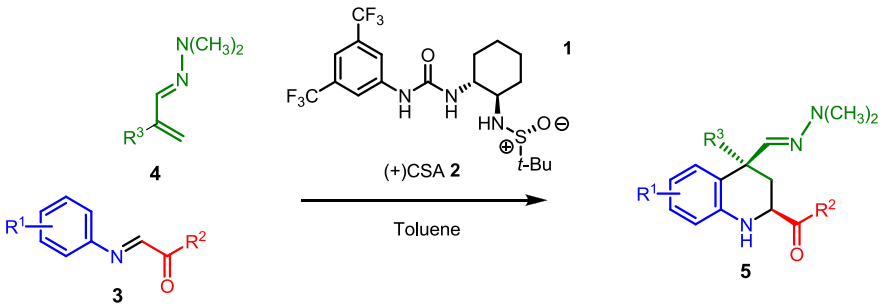
Keywords: *Povarov reactions, chiral sulfinamidourea, tetrahydroquinolines, α,β-unsaturated N,N-dimethylhydrazones*

We present here the first catalytic enantioselective vinylogous Povarov reaction using an α,β-unsaturated N,N-dimethylhydrazone as the dienophile. The aza Diels-Alder reaction between aromatic imines **3**, prepared from anilines and aromatic glyoxals, and α,β-unsaturated N,N-dimethylhydrazones **4**, affords 1,2,3,4-tetrahydro-2-acylquinolines **5** in high yields (up to 85%) with good diastereoselectivity (9:1) and enantioselectivity (up to 95% ee). This reaction was co-catalyzed by chiral sulfinamidourea **1** [1] and camphorsulphonic acid **2** as a strong Brønsted acid.

Our method allows the formation in a one-pot process of two C-C bonds and two stereocenters, one of which is quaternary. The polysubstituted 1,2,3,4-tetrahydroquinolines **5** thus obtained represent, besides being biologically relevant, a good starting point to obtain a wide range of natural and unnatural pharmacologically important compounds.



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S6: *Avances en Organocatálisis Asimétrica*

REACCIONES HETERO-CARBONIL-ÉNICAS SELECTIVAS SOBRE α-CETOÉSTERES ALIFÁTICOS CATALIZADAS POR TIOUREAS DERIVADAS DE CARBOHIDRATOS

Inmaculada Serrano,[1] David Monge,[1] Gonzalo de Gonzalo,[1] Rosario Fernández,[1] José M. Lassaletta[2]

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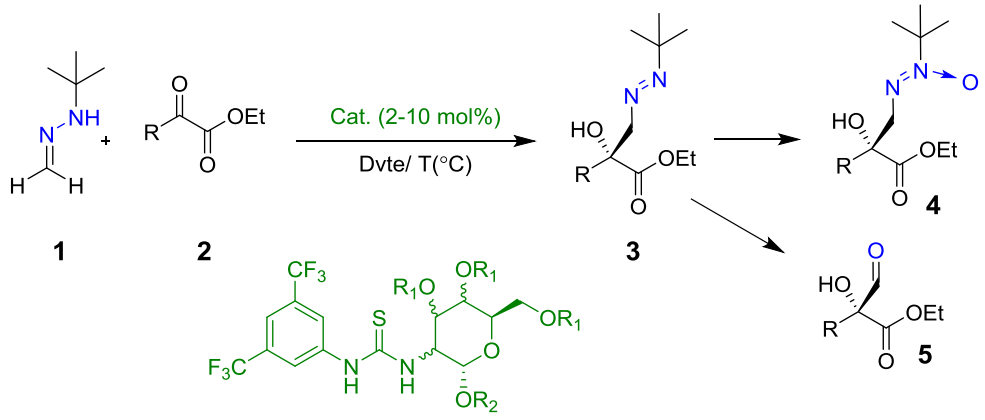
[2] Instituto de Investigaciones Químicas, CSIC-US, c/ Américo Vespucio 49, 41092, Sevilla

Palabras Clave: *Organocátalisis, tioureas, carbohidratos, azoxicompuestos, carbinoles*

En los últimos años, las tioureas ópticamente activas han demostrado ser organocatalizadores muy eficientes en diversas reacciones químicas empleando sustratos con funciones sensibles a la activación mediante enlaces de hidrógeno múltiples [1]. Dentro de la diversidad estructural que presentan las tioureas, los carbohidratos, compuestos quirales de gran abundancia natural, estabilidad conformacional y alta densidad de grupos funcionales, constituyen una alternativa de interés [2]. Los estudios previos de nuestro grupo de investigación han demostrado que las bis-(tio)ureas derivadas de BINAM catalizan la reacción hetero-carbonil-énica entre la *terc*-butil hidrazona del formaldehído (**1**) y diversos α-cetoésteres aromáticos y heteroaromáticos (**2**) para la síntesis de diazenos (**3**) con excelentes rendimientos y enantioselectividades [3]. Sin embargo, los resultados no son tan buenos en la adición de la hidrazona a los α-cetoésteres alifáticos análogos, por lo que se han preparado y analizado nuevas tioureas derivadas de carbohidratos con el objetivo de mejorar la selectividad y actividad es estos procesos catalíticos. Los diazenos ópticamente activos así obtenidos han sido convertidos en los correspondientes azoxicompuestos (**4**) y carbinoles (**5**), compuestos de alto valor añadido en síntesis orgánica.



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S7. Metodología Sintética y Síntesis Total (MSST) / Synthetic Methodology and Total Synthesis

Este simposio abordará, de modo genérico, los siguientes temas: metodología sintética, métodos generales de síntesis, síntesis total de productos naturales, síntesis enantioselectiva, síntesis biomimética.

This symposium will deal, widely, with the following topics: synthetic methodology, general methods of synthesis, total synthesis of natural products, enantioselective synthesis, biomimetic synthesis.

Organizador:

Joan Bosch Cartes (UB)

e-mail de contacto: joanbosch@ub.edu

Miércoles 22 de Julio 2015

08:40 – 09:40	**PL-4**	***Conferencia Plenaria*** (Común a todos los simposios) **Luis Liz-Marzán** *"Chemical Growth of Metal Nanoparticles: Why and How?"*

Chairman: Kilian Muñiz

10:00 – 10:30	**S7-IL-01**	**Markus Kalesse** *"Natural Products: From Evolutionary Analysis to Stereoselective Synthesis"*
10:30 – 10:45	**S7-OC-01**	**Susana Álvarez** *"Approach to the Total Synthesis of Heronamide C"*
10:45 – 11:00	**S7-OC-02**	**Peter Fodran** *"Convergent Synthesis of Mycolic Acid and Its Derivatives"*
11:00 – 11:30		Pausa Café
11:30 – 11:50		**Entrega de las Medallas del GEQOR**

Chairwoman: Mar Gómez Gallego

11:50 – 12:20	**S7-IL-02**	**Juan Manuel Cuerva** *"Bioinspired Terpene Synthesis: A Radical Approach"*
12:20 – 12:50	**S7-IL-03**	**Mercedes Amat** *"Chiral Lactams as Multipurpose Scaffolds for the Synthesis of Complex Natural Products"*
12:50 – 13:05	**S7-OC-03**	**José Carlos González-Gómez** *"A General Synthesis to All Natural Tetraponerines"*
13:05 – 13:20	**S7-OC-04**	**Hugo Rego-Campello** *"Asymmetric Catalytic Hydrogenation of Enamides Towards the Synthesis of (-)Cytisine and Heterocyclic Building Blocks"*
13:20 – 13:25	**S7-FC-01**	**Guilhem Coussanes** *"Synthesis of the Tetracyclic ABCD Ring system of Calciphylline A-Type Alkaloids"*
13:25 – 13:30	**S7-FC-02**	**Iago Alonso-Vicente** *"Total Synthesis of (-)-Aspergilazine A"*
13:30 – 13:35	**S7-FC-03**	**Guillaume Guignard** *"Access to Enantiopure δ-Hydroxy Acid Derivatives from Phenylglycinol-Derived Lactams"*
13:35 – 15:30		Comida

Miércoles 22 de Julio 2015

Chairman: Víctor S. Martín

15:30 – 16:00	**S7-IL-04**	**Juan Granja** *"Taxane Synthesis by Sequential Metathesis Reactions"*
16:00 – 16:15	**S7-OC-05**	**Claudio Martínez** *"First Iodine Catalysed Hofmann-Löffler Reaction"*
16:15 – 16:30	**S7-OC-06**	**Daniel Solé** *"Palladium: A Versatile Metal for the Synthesis of Nitrogen Heterocycles"*
16:30 – 17:00		Pausa Café

Chairman: Ángel Rodríguez de Lera

17:00 – 17:30	**S7-IL-05**	**Dirk Trauner** *"Natural Biomimetic Synthesis Of Heterocyclic Products"*
17:30 – 17:45	**S7-OC-07**	**José A. Souto** *"Enabling Technology to Organic Chemistry. A Gate to Efficiency"*
17:45 – 18:00	**S7-OC-08**	**Silvia Castro-Fernández** *"Enhanced Chiroptical Response by Constraining the Conformational Space of Pyridoallenophanes"*
18:00 – 18:05	**S7-FC-04**	**Andrea Areal** *"Synthesis of Ditryptoleucines"*
18:05 – 18:10	**S7-FC-05**	**Diana Rodríguez** *"Towards an Efficient Synthesis of 6-Alkylidene Penacillanic and Derivatives for the Treatment of Multi-Resistant Nosocomial Infections"*
18:10 – 18:15	**S7-FC-06**	**Ane Otermin** *"Intramolecular Domino Diels-Alder Reactions of a Difulvene Derived from Bicyclo[3.3.0]Octane-3,7-dione and Transformations Thereof"*
18:15 – 18:20	**S7-FC-07**	**David Lozano** *"Synthesis of New Polycyclic Compounds by Single or Double Domino Nucleophilic Substitution / Diels Alder Reaction"*
18:20 – 18:25	**S7-FC-08**	**José María Gil-Negrete** *"Transition-Metal-Free Cross-Copuling of Triorganoindium Reagents with Chromene and Isochroman Acetals Mediated by $BF_3{\cdot}OEt_2$"*
18:25 – 18:30	**S7-FC-09**	**José Carlos Menéndez** *"Transition Metal-Free Synthesis of Highly Substituted and Functionalized Carbazoles via a Multicomponent Process that Includes a C-H Activation Step"*
18:30 – 18:35	**S7-FC-10**	**Irene R. Márquez** *"A New Synthetic Strategy to Construct Seven-Membered Carbocycles Embedded in a Hexagonal Network"*
18:35 – 18:40	**S7-FC-11**	**Alessandra Lacetera** *"From the Computer to the Bench: Novel Selective Glycomimetics Take Life"*
18:40 – 18:45	**S7-FC-12**	**Mykyta Iazykov** *"The S_N3 Dilemma: Characterization of the Transition State for Solvolysis Reactions of Hindered Sulfonyl Halides"*

18:45	***Sesión de Pósteres***

Jueves 23 de Julio 2015

08:40 – 09:40	**PL-5**	***Conferencia Plenaria*** (Común a todos los simposios) **Avelino Corma Canós** *"Intentos para Establecer Puentes entre la Catálisis Homogénea y Heterogénea"*

Chairman: José M. Lassaletta

10:00 – 10:30	**S7-IL-06**	**David Procter** *"Designing Radical Cyclization Cascades: New Methods for Total Synthesis"*
10:30 – 10:45	**S7-OC-09**	**Lucía Guillade** *"Approach to the Synthesis of Nahuoic Acid"*
10:45 – 11:00	**S7-OC-10**	**Faiza Diaba** *"A Rapid Access to Morphans and Normorphans through Enamines from Dichloro- and Trichloroacetamides"*
11:00 – 11:30		Pausa Café

Chairman: Carlos Valdés

12:00 – 12:15	**S7-OC-11**	**Jesús Herraiz-Cobo** *"Total Synthesis of Mayotlide"*
12:15 – 12:30	**S7-OC-12**	**Jairo González** *"Catalytic and Synergistic σ-Gold(I) Activation-Acetylide Addition and Consecutive σ- and π-Gold(I) Alkyne Activations. Synthesis of Indene Derivatives"*
12:30 – 12:45	**S7-OC-13**	**Fernando García Tellado** *"The Microwave-Assisted Organocatalyzed Rearragement of Propargyl Vinyl Ethers to Salicyladehydes Derivatives"*
12:45 – 13:00	**S7-OC-14**	**Antonio Leyva-Pérez** *"Carbon-Carbon and Carbon-Heteroatom Bond-Forming Reactions Catalyzed by in-situ Generated, Extremely Active, Ligand-Free Metallic Aggregates of <10 Atoms"*
13:00 – 13:05	**S7-FC-13**	**Marta Domínguez** *"The Use of Olefin Cross Metathesis in the Synthesis of Carotenoids and Apocarotenoids"*
13:05 – 13:10	**S7-FC-14**	**Nicola Lucchetti** *"Iodine(III) Reagents for C-N Bond Formation with Unprecedented Scope"*
13:10 – 13:15	**S7-FC-15**	**Tatiana Suárez-Rodríguez** *"IPy_2BF_4 Mediated Triple Bond Activation of Propargylic Esters for the Synthesis of α-Iodoenones"*
13:15 – 13:20	**S7-FC-16**	**M. Carmen Pérez-Aguilar** *"Synthesis of Chiral Pyrazoles through a 1,3-Dipolar Cycloaddition/1,5-Sigmatropic Rearrangement Cascade with Migration of a Stereogenic Group"*
12:20 – 13:25	**S7-FC-17**	**Manuel Plaza** *"Setereoselective Reductive Coupling of N-Tosylhydrazones with Alkenylboronic Acids"*
13:25 – 13:30	**S7-FC-18**	**Judit Oliver-Meseguer** *"Ligand-Free Cu Clusters Catalyze C-N, C-C, C-O, C-S and C-P Bond-Forming Reactions"*

13:30	***Ceremonia de Clausura***

Comunicaciones Invitadas (IL)

S7: *Metodología Sintética y Síntesis Total*

NATURAL PRODUCTS CHEMISTRY – FROM GENETIC ANALYSIS TO STEREOSELECTIVE SYNTHESIS

H.-H. Lu,[3] Aruna Raja,[2] T. Tautz,[3] J. Li,[1] R. Franke,[2] F. Sasse,[2] M. Kalesse*[1, 3]

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Keywords: *Soraphen, Synthesis, Evolution, Polyketides, Chemical Biology*

Natural products are the source of biologically active compounds and in particular secondary metabolites isolated from microorganisms have been in the focus of natural product chemistry for quite some time. One of the most fundamental questions associated with natural products is the question on the origin of their biological activity and the ultimate purpose of their existence. While questions on the genuine relevance of natural products are answered by working groups concerned with the ecological aspects of natural products, the question of how the activity was generated in the first place is still unknown. With this state of knowledge, we started a program that aimed at providing natural products as if they were derived by the precise specification of polyketide synthases. Based on this concept and previous contributions on the biosynthesis of the soraphens we will present the synthesis and biological evaluation of so-called paleo-soraphens of which one exhibited a biological activity completely different from natural soraphen A.[1]

In order to shed more light on this topic we completed the syntheses of overall six paleo-soraphens, which exhibit modifications associated with the hypothetical evolutionary optimization. To compare biological activities of the paleo-soraphens, we characterized them via impedance profiling. Time-dependent cellular response profiles (TCRP) recorded by the xCelligence system were used to identify compounds with similar mode of action as characterized by similar time-dependent response profiles. These results supported the hypothesis that biological activities can be altered by turning off distinct enzymatic activities within polyketide synthases. The design of these additional variations of the soraphen family was based on hypothetical biosynthetic precursors that could provide evidence for the evolutionary optimization of these compounds in retrospect. The paleo-soraphens C and D are lacking the methylation at C11 which was shown to be a postketidal transformation. The hierarchical cluster analysis shows that these soraphens are more distant from soraphen A than the paleo-soraphens A and B which from an evolutionary point of view is consistent with an optimization of its biological activity.

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S7: *Metodología Sintética y Síntesis Total*

BIOINSPIRED TERPENE SYNTHESIS: A RADICAL APPROACH

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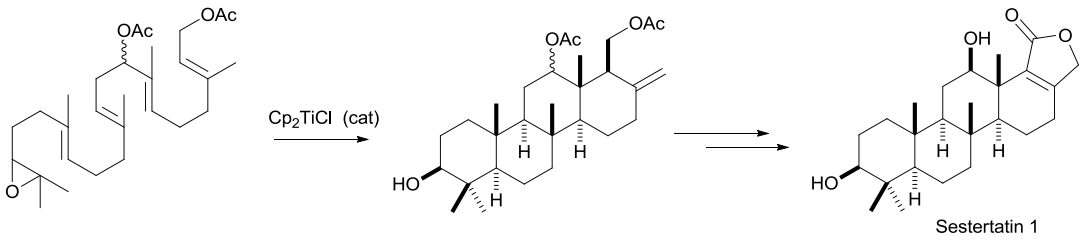
Keywords: *natural products, radicals, synthetic methods, titanium*

Radical-based bioinspired synthesis of terpenes represents a straightforward approach to obtain many natural products from readily available starting materials. Within this context, titanocene(III) complexes, essentially titanocene(III) chloride (Cp_2TiCl), have recently emerged as a powerful tool in organic synthesis. They are mild single-electron-transfer (SET) reagents capable of promoting different kinds of reactions, such as homolytic epoxide and oxetane openings, Barbier-type reactions, Wurtz-type reactions, Reformatsky-type reactions, reduction reactions, and pinacol coupling reactions [1].

Despite the interest of Cp_2TiCl in many synthetic steps, one of the most remarkable characteristic of this reagent is its capability to efficiently build different polycyclic carbon skeletons. This key characteristic has been used to develop a general Cp_2TiCl-based approach to polycyclic terpenic skeletons [2]. Thus for example, the potential of this methodology has been shown in the synthesis of sestertatin 1, a bioactive tetracyclic scalarane (Scheme 1) [3]. The efficiency of these radical-based bioinspired processes nicely complements the known cationic polyolefin cyclisations and even suggests that modern radical methods could provide improvements upon Nature's synthetic pathways.



Scheme 1. Synthesis of sestertatin 1

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S7: *Metodología Sintética y Síntesis Total*

CHIRAL LACTAMS AS MULTIPURPOSE SCAFFOLDS FOR THE SYNTHESIS OF COMPLEX NATURAL PRODUCTS

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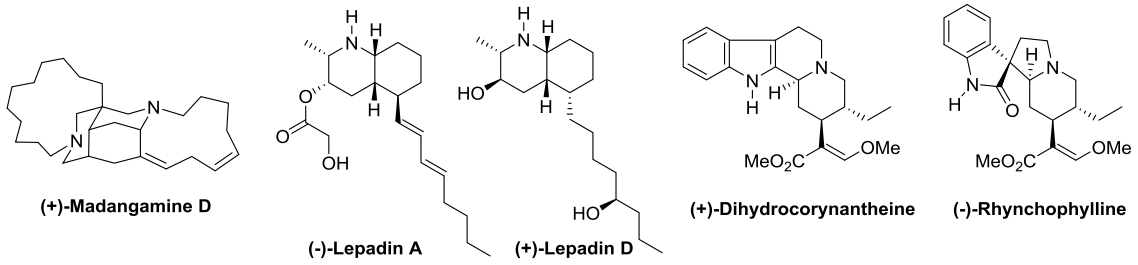
Keywords: *Stereoselective synthesis, Alkaloids, Nitrogen heterocycles.*

The development of new procedures for the synthesis of enantioenriched chiral nitrogen-containing heterocycles, with the final goal of applying them to the synthesis of natural products, has focused our attention during the last years. To this end, we have explored a methodology based on the use of chiral, conformationally rigid and highly functionalized aminoalcohol-derived lactams as enantiomeric scaffolds, and have carried out a systematic study on their scope and limitations for the enantioselective synthesis of a variety of nitrogen heterocycles.[1] As a result of this work, we have now in hand a flexible and versatile tool for the preparation of a broad range of piperidine, *cis*-decahydroquinoline, *cis*- and *trans*-octahydroindole, indolo[2,3-*a*]- and benzo[*a*]quinolizidine derivatives that allows the generation of new stereocenters with a high degree of stereoselectivity and a predictable absolute configuration.

In this contribution, an overview of the methodology and its application to the synthesis of the marine alkaloids madangamine D[2] and lepadins A-D[3] as well as the indole alkaloids dihydrocorynantheine[4] and rhynchophylline[5] will be presented.



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S7: *Metodología Sintética y Síntesis Total*

TAXANES SYNTHESIS BY SEQUENTIAL METATHESIS REACTIONS

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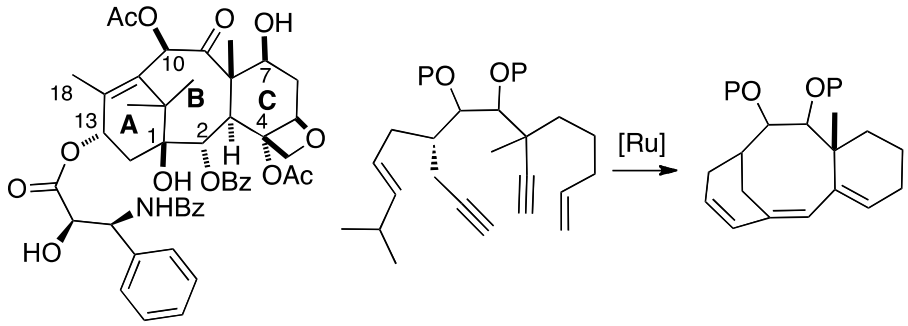
Keywords: *taxanes, metathesis reactions, cascade, dienynes*

Total synthesis of biological relevant compounds has changed in the last decades from the consideration of almost an art to a very mature science thanks to the apparition of novel concepts such as atom, step or redox economy in synthesis.[1] In this way the complex organic molecules must be prepared in a reduced number of transformations, without almost the generation of waste and from simple commercially available substrates. At this respect, the cascade transformations, reactions in which several bonds are formed in a sequential way in a single synthetic transformation without adding any additional reactant, are very attractive tools for modern and efficient synthesis.[2]

In the last few years we have been working in the efficient synthesis of taxane skeleton and analogues in an efficient way.[3] Our strategy was based on the ring closing metathesis reaction of dienynes to construct the [5.3.0] bicyclic system of taxanes. In this communication we will present our latest results to efficiently construct the carbocyclic system of taxol in one synthetic transformation.



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S7: *Metodología Sintética y Síntesis Total*

NATURAL BIOMIMETIC SYNTHESIS OF HETEROCYCLIC PRODUCTS

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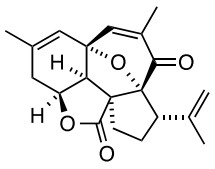
Natural products continue to inspire synthetic chemist with their structural beauty and functional sophistication. I will discuss the synthesis of a variety of terpenoids, polyketides, alkaloids and phenolic natural products that have recently occupied our minds. Some of them were assembled though crafty biomimetic cascades whereas others were reached through decidedly non-biomimetic strategies that often included an element of surprise.



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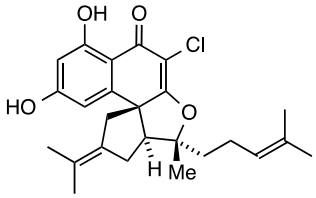
Nature Commun. **2014**, *5*, 5597

photochemical formation!



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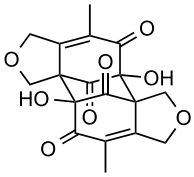

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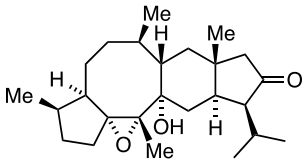

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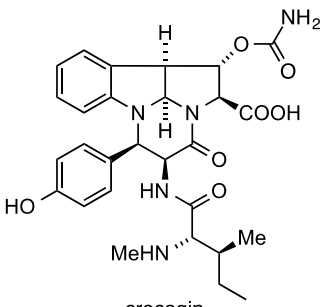

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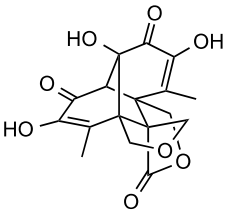

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S7: *Metodología Sintética y Síntesis Total*

DESIGNING RADICAL CYCLIZATION CASCADES: NEW METHODS FOR TOTAL SYNTHESIS

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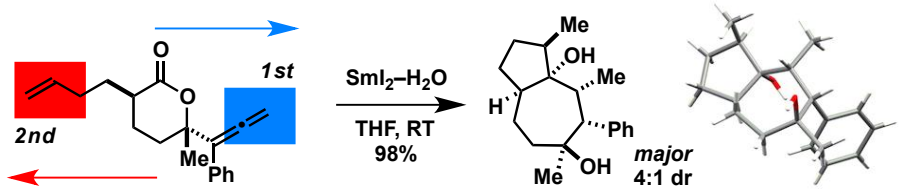
Keywords: *cascades, electron transfer, samarium, natural products*

Reductive electron transfer (ET) to organic compounds is a powerful method for the activation of substrates via the formation of radicals and anions that can be exploited in bond-cleaving and bond-forming processes. Since its introduction to the synthetic community in 1977 by Kagan, SmI_2[1,2] has become one of the most important reducing agents available in the laboratory. Despite its widespread application in aldehyde and ketone ET reduction, it was widely accepted that carboxylic acid derivatives could not be reduced by SmI_2 and only recently has our work led to this dogma being overturned and the ET reduction of carboxylic acid derivatives using SmI_2 can now take its place as a powerful activation mode for synthesis.[3]



We will focus on the development of complexity-generating cascade approaches to biologically-significant molecular architectures triggered by ET from Sm(II)–H_2O to carbonyl feedstocks.[4] The presentation will conclude with the application of a Sm(II)-mediated cascade cyclization in the total synthesis of the antibacterial natural product (+)-pleuromutilin.[5]

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Comunicaciones Orales (OC)

S7: *Metodología Sintética y Síntesis Total*

APPROACH TO THE TOTAL SYNTHESIS OF HERONAMIDE C

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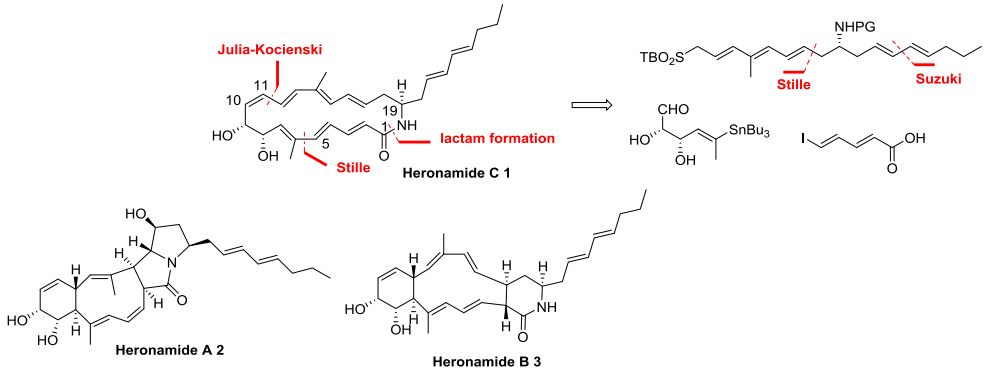
Keywords: *Natural products, total synthesis, heronamides, macrolactam, cross-coupling, polyenes.*

Polyenic macrolactams are a growing class of microbial metabolites, many of which endowed with potent biological activities. Heronamide C **1** was discovered together with heronamides A **2** and B **3** from cultures of *Streptomyces sp.* CMB-M0406, which was isolated from a shallow water sediment collected in Heron Island (Australia).[1]Only heronamide C **1**was reported to have a pronounced and unique effect on the morphology of cultured cell.Structurally, heronamide C **1**features an unsaturated macrocyclic system with threechiral centers,avicinal diol at C8 and C9 and theamine at C-19 that connect diene, triene and tetraene chains.Capon et al. postulated a plausible biosynthetic relationship among the heronamides and proposed the configuration of the heronamide C stereocenters on the basis of those of heronamide A**2**.However,a recent synthesis of this proposed structured did not produce the expected natural product,[2]and more comprehensiveNMR studies confirmed the opposite absolute configuration of the C8 and C9 sterocenters.[3]

Based on these precedents, we targeted the total synthesis of the reassigned structure of heronamide C **1**to unambiguosly confirm the stereostructure of the natural isolate. The construction of the macrocycle was addressed using three highly functionalized fragments, which will be sequentiallyconnected by amidation, Stille cross coupling reaction and intramolecular Julia-Kocienski condensation. The stereocenters of the diol fragments were derived from the chiral pool andthat of the chiral amine from the enantioselective addition of organometals to a chiral sulfonamide.



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S7: *Metodología Sintética y Síntesis Total*

CONVERGENT SYNTHESIS OF MYCOLIC ACID AND ITS DERIVATIVES

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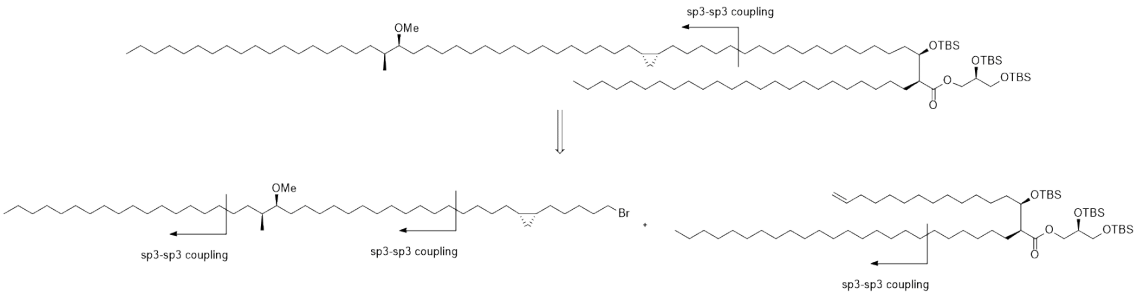
[3] Public Health England, Porton Down, Porton, Salisbury, United Kingdom

[4] Division of Rheumatology, Immunology and Allergy, Brigham and Women's Hospital, Boston, MA 02115, United States of America

Keywords: *Mycolic acids, antigens, total synthesis.*

Mycolic acid and its derivatives are promising antigens for tuberculosis vaccination[1]. They are available as the major component of the *Mycobacterium tuberculosis* cell wall, however, the isolation and purification of a single, defined compound is virtually impossible due to the large number of homologues and isomers present.



Despite the apparent simplicity of the structure of Mycolic acid, its total synthesis is laborious. The only published approach requires over 40 steps.[2] We wish to present our convergent approach based on C(sp3)-C(sp3) cross-couplings[3], which significantly reduced the necessary steps and is easy to scale-up, thus enabling synthesis of gram amounts of Mycolic acid and its derivatives.

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S7: *Metodología Sintética y Síntesis Total*

A GENERAL SYNTHESIS TO ALL NATURAL TETRAPONERINES

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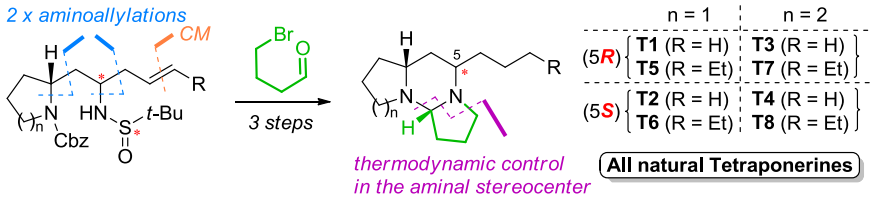
Palabras Clave: *stereoselective synthesis, alkaloids, tetraponerines*

Tetraponerines constitute a unique family of alkaloids which share an indolizidine moiety with a quinolizidine or another indolizidine fragment, including a singular aminal stereocenter. These compounds are segregated by *Pseudomyrmecine* ants of the genus *Tetraponera*, and used as chemical warfare against their enemies.[1] Recent studies categorize tetraponerines as inhibitors of a range of nicotinic acetylcholine receptors (nAChRs),[2a] and it has also found that they display important cytotoxic activities.[2b] Despite their interesting biological activities, only one method had been reported at the outset of our work for the general synthesis of all natural tetraponerines.[3]

An exhaustive DFT configurational study of (+)−**T3** and (+)−**T4** allowed as to conclude that the configuration at the aminal carbon stereocenter could be thermodynamically controlled.[4a] Our synthesis make use of two consecutive indium-mediated aminoallylations with the appropriate enantiomer of chiral *N*-*tert*-butylsulfinamide and presume a thermodynamic control at the aminal stereocenter of all natural tetraponerines.[4b] The use of 4-bromobutanal in the first aminoallylation leads to the formation of 5-6-5 tetraponerines whilst 5-bromopentanal is required to build the scaffold of 6-6-5 tetraponerines. A cross-metathesis reaction of the second aminoallylation product with *cis*-3-hexene is used to elongate the side chain up to 5 carbons so as to prepare the tetraponerines **T5** to **T8**. The antiproliferative activity of these heavier tetraponerines is also disclosed in this work.



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S7: *Metodología Sintética y Síntesis Total*

ASYMMETRIC CATALYTIC HYDROGENATION OF ENAMIDES TOWARDS THE SYNTHESIS OF (-)-CYTISINE AND HETEROCYCLIC BUILDING BLOCKS

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Key words: *asymmetric hydrogenation, enamides, catalysis, cytisine, total synthesis.*

Asymmetric catalytic hydrogenation of enamides in a novel transition metal catalyzed reaction has been established as a readily available pathway for the synthesis of several heterocyclic building blocks. The scope of the reaction has been investigated over 5-, 6-, and 7-membered-cyclic enamides, generating the resulting amides in high enantiomeric excess.

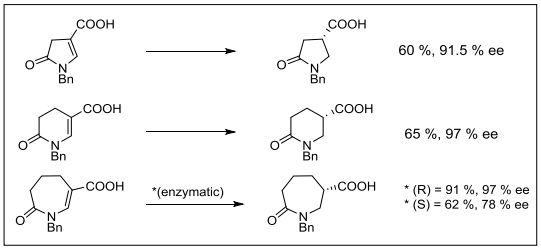
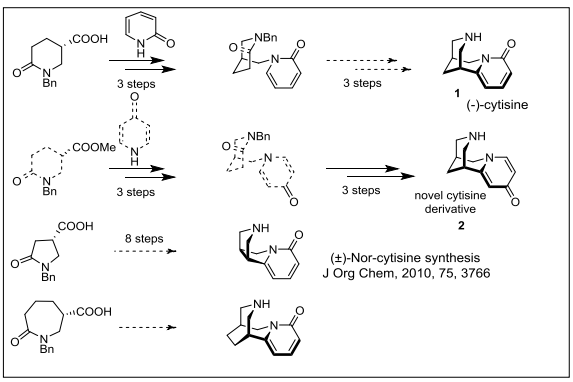


Figure 1: Asymmetric heterocyclic building blocks which may be used as future templates to synthesize many asymmetric organic compounds.

Furthermore, this chemistry provides a novel asymmetric route towards the synthesis of the naturally occurring alkaloid (-)-cytisine **1**, enabling a general way to synthesize core and pyridone modified derivatives asymmetrically. Cytisine **1** behaves as a partial agonist of nicotinic acetylcholine receptors in the brain, and it was taken by Pfizer as the lead compound in the development of Varenicline, a smoking cessation agent. Moreover, one interesting pyridone-modified cytisine analogue **2**, which is thought to hold greater biological activity than cytisine, has been synthesized racemically.



S7: *Metodología Sintética y Síntesis Total*

FIRST IODINE CATALYSED HOFMANN-LÖFFLER REACTION

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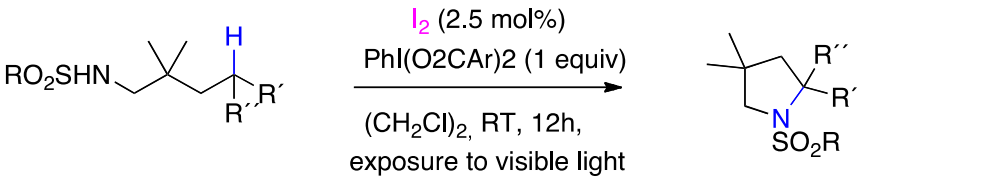
Keywords: *Amination, Catalysis, C-H Functionalization, Iodine, Oxidation*

Iodine reagents have been identified as economically and ecologically benign synthetic alternatives to transition metals, although their application as molecular catalysts in challenging C-H oxidation has remained elusive. An attractive iodine oxidation catalysis is now shown to promote the convenient conversion of ubiquitous carbon-hydrogen into carbon-nitrogen bonds with unprecedented complete selectivity.[1] The reaction combines catalytic amounts of molecular iodine and a modified hypervalent iodine(III) reagent and proceeds within two interlocked catalytic cycles comprising a radical chain reaction, which is initiated by visible light as energy source. It represents the realisation of a first truly catalytic Hofmann-Löffler reaction.[2] This unorthodox synthetic oxidation strategy of direct catalytic alkane amination has no biosynthetic precedence and provides an efficient and straightforward access to pyrrolidines, which constitute an important general class of saturated nitrogenated heterocycles.



unfunctionalised remote C-H bond

C-H amination products (applicable to primary, secondary and tertiary C-H bonds)

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S7: *Metodología Sintética y Síntesis Total*

PALLADIUM: A VERSATILE METAL FOR THE SYNTHESIS OF NITROGEN HETEROCYCLES

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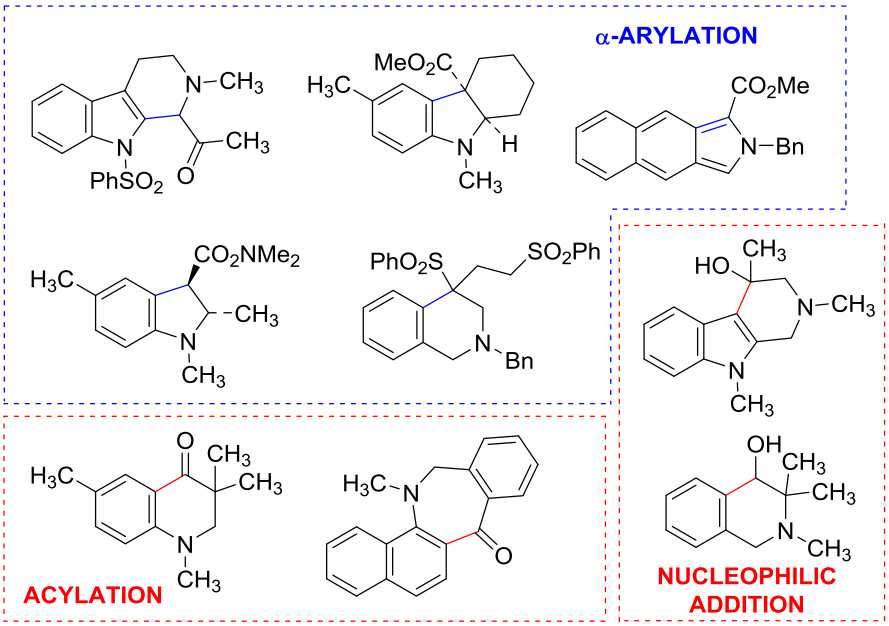
Key words: *palladium, nitrogen heterocycles, arylation, acylation*

During the past years we have been exploring the versatility of palladium-catalyzed reactions for the synthesis of nitrogen heterocycles. Our initial studies on Pd(0)-catalyzed intramolecular cross-coupling reactions of (2-iodoanilino) ketones showed that two competitive processes, namely the enolate arylation and the nucleophilic attack on the carbonyl group, can be promoted.[1] More recently, we have demonstrated that both reactions can also be selectively promoted when starting from (2-haloanilino) esters,[2] carboxamides[3] and carbaldehydes[4] by subtle modification of the reaction conditions. The α-arylation reaction has also been studied using anions derived from sulfones as the nucleophilic counterpart.[5]

These studies have allowed us to develope a variety of efficient methodologies for the synthesis of nitrogen heterocycles.



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ENABLING TECHNOLOGY TO ORGANIC CHEMISTRY. A GATE TO EFFICIENCY.

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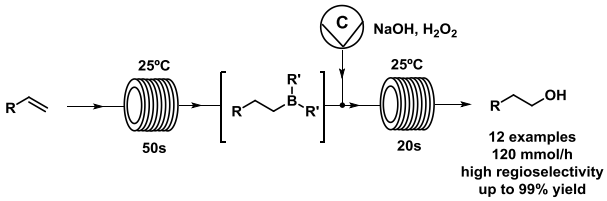
Keywords: *flow chemistry, continuous synthesis, green chemistry.*

During previous investigations on the functionalisation and polymerisation of olefin-containing natural products, we were performing hydroxylation reactions (i.e. hydroboration/oxidation and carbonyl reduction) of olefins.[1] Although the used methodologies proved to be very efficient in terms of conversion and selectivity, the needs for large scale production of the desired alcohol to overcome further functionalisation and subsequent polymerisation, made this production process tedious and time consuming.



In that sense, flow technology provides a practical solution to overcome some of these limitations due to better mixing, more efficient heat transfer in highly exothermic reactions and the improved ability to moderate the rate of the transformation, compared to the batch mode. Furthermore, the possibility for continuous production of the desired product with in-line purification techniques, or for the development of a telescoped protocol offers an efficient generation of the alcohol functional group.[2]

Herein, we describe a method for the continuous preparation of alcohols by hydroboration/oxidation of olefins using flow techniques. The process allows the isolation of up to 120 mmol/h of the desired alcohol in a very rapid manner with good functional group tolerance. The flow setup can be modified to perform a continuous extraction of the desired alcohol from the biphasic mixture produced by the reaction.[3]

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ENHANCED CHIROPTICAL RESPONSE BY CONSTRAINING THE CONFORMATIONAL SPACE OF PYRIDOALLENOPHANES

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Keywords: *allenophanes, conformational stability, chiroptical response*

Shape-persistent chiral macrocycles constitute potential molecular receptors applicable in a wide variety of areas: from ligands for catalysis to sensors. Obtaining an appropriate compound involves getting compounds with intense chiroptical responses. These responses are very sensitive to conformational changes, as a consequence, a compound with many different conformations presents low chiroptical intensities. Therefore, the construction of conformationally stable chiral molecules can be used to optimize chiroptical response intensity. Allenophanes, presenting diethynylallene moieties as chiral motifs and aromatic units as functionality sites, have resulted to be good candidates for such aim.[1] Particularly, we have synthetized **(P_4)-DEA**, with four diethynylallene moieties, presenting a single conformation and strong responses. In order to enhance molecular recognition, we have introduced aromatic spacers leading to **[7_4]** and **[14_2]** allenophanes. However, this increase in functionality led to a decrease in conformational stability.

In this work, we have synthesized the first **[14_1]**-pyridoallenophane which presents a single conformation. We have probed that increasing the conformational stability of the chiral macrocycle, despite having reduced the number of chiral units, makes the chiroptical response even stronger.

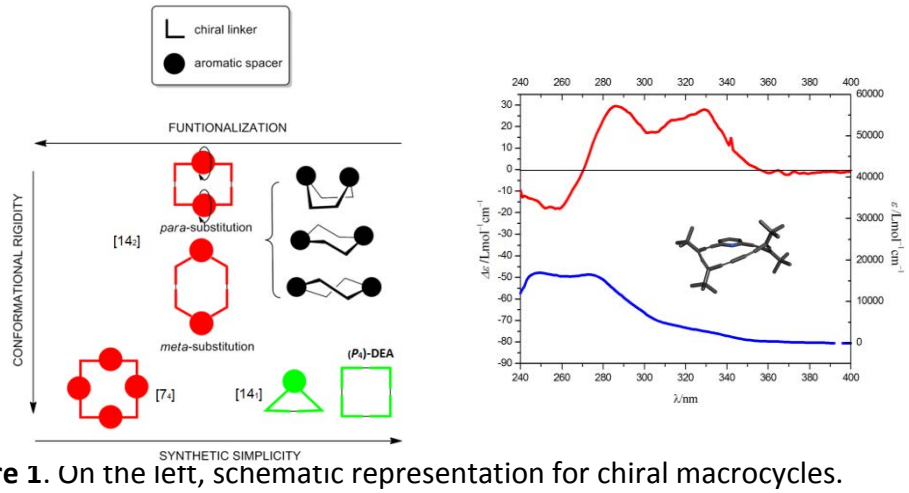

Figure 1. On the left, schematic representation for chiral macrocycles. Vertex denote chiral axes while circles denote aromatic rings used as connectors. In green, general structures for chiral macrocycles with only one possible conformation. In red, general structures for macrocycles with several possible conformations. In black the representation of different possible conformations for a particular system. On the right; CD (in red) and UV (in blue) spectra of [14_1]pyridoallenophane.

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APPROACH TO THE SYNTHESIS OF NAHUOIC ACID

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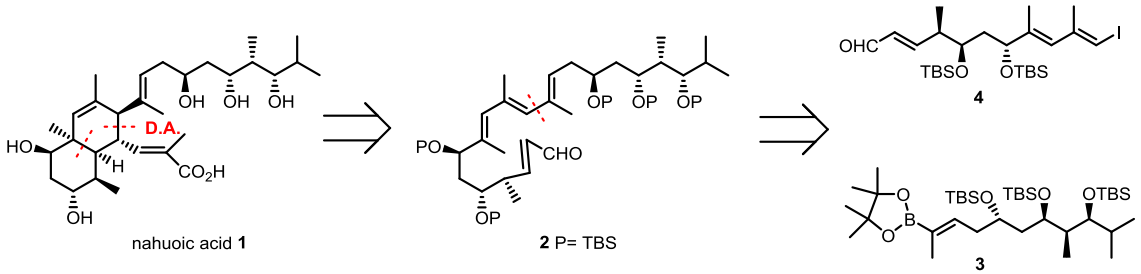
Keywords: *epigenetics, lysine methyltransferases, nahuoic acid, intramolecular Diels-Alder, enantioselective synthesis.*

Epigenetics is one of the most promising approaches to the knowledge of the etiology of cancer and the discovery of new therapies. Human tumors have a number of epigenetic alterations that result from modifications of histones and DNA methylation.[1] Histone methylation plays a major role by regulating transcription, maintaining genomic integrity and contributing to epigenetic effects. The methylation of specific lysine residues is highly regulated and it is asociated to transcriptional activation or repression.

Nahuoic acid **1**, a metabolite produced by cultures of Streptomyces, is a competitive and selective inhibitor of lysine methyltransferase SAM SETD8 (PR-Set7 / KMT5a) in vitro.[2] We have the synthesis of nahuonic acid inspired by its biogenesis in which the construction of cyclic fragment octahydronaphthalene is based on an intramolecular Diels-Alder reaction (IDA).[3] The configuration of the natural product requires the cycloaddition of a precursor of E geometry following an exo orientation to the Si face of the dienophile. Computational studies of the four stereoisomeric transition states were performed to check whether the desired approach is the most favored one. Tetraene **2** will be built by the Suzuki coupling reaction between two complex fragments containing 4 and 3 stereocenters and functionalized as boronic acid **3** and alkenyl halide **4**. To generate those fragments with total stereocontrol, addition of enantiopure allylic organometallic compounds to carbonyl groups, as well as Evans diastereoselective aldol condensation reactions using oxa(thia)zolidinethiones will be used.



Acknowledgements. We thank MINECO (SAF2013-48397-R; FPU Fellowship to L.G.) and EC 7FP (BIOCAPS) for financial support.

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A RAPID ACCESS TO MORPHANS AND NORMORPHANS THROUGH ENAMINES FROM DICHLORO- AND TRICHLOROACETAMIDES

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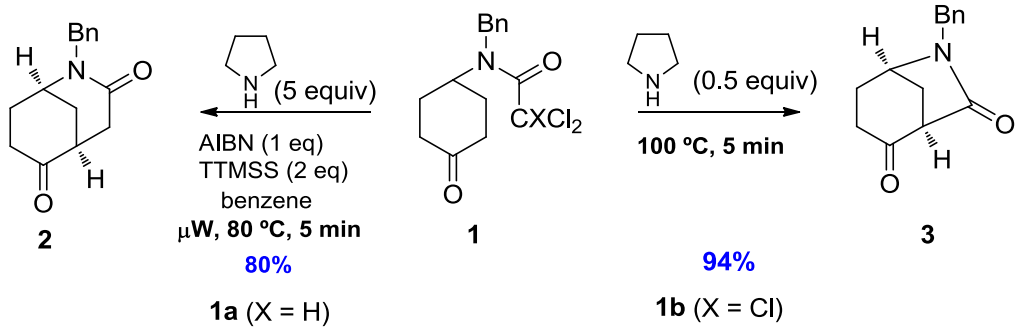
Key words: *Enamines, Radical Chemistry, Carbamoylation, Bridged azabicycles, Organocatalysis*

Methodologies involving the intramolecular formation of carbon-carbon bonds at the α-position of ketones are important tools for the construction of molecular frameworks in organic synthesis. New protocols for the rapid access to either morphans[1,2] or normorphans [3] have been developed, using enamine intermediates formed in situ, from dichloro- and trichloroacteamides of type **1**. Two divergent processes are described: (i) starting from dichloroacetamide **1a**, using AIBN and TTMSS, under microwave activation and after only 5 min at 80 °C, the reaction provided the bridged azabicyclic compound **2**; (ii) alternatively, starting from trichloroacetamide **1b** and using conventional heating and free-solvent conditions and a substoichiometric quantity of pyrrolidine, normorphan **3** was isolated in an excellent yield. The mentioned reactions are currently under study to achieve and asymmetric version through organocatalysis.



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TOTAL SYNTHESIS OF MAYOTLIDE

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Keywords: *hexahydropirroloindole, peptide-heterocycles, natural products*

Every year, marine invertebrates offers an important source of new bioactive compounds[1]. Mayotlide is a marine peptide isolated by Pharmamar S.A. from *Spongia sp.* in the coasts of Alicante.

Mayotlide is a bicyclic peptide containing eight L-aminoacids with a particular tryptophan-hexahydropyrroloindole (Trp-HPI) framework. The structure and stereochemistry of mayotlide were stablished by spectroscopy and Marfey degradation. Concerning its biological activity, mayotlide possesses cytotoxic activity against three human cancer cell lines: MDA-MD-231, A-549 and HT-29 in micromolar concentrations.

In this presentation the results of synthetic experiments towards the total synthesis of that heterocyclic-peptide will be described. The strategy followed for the total synthesis of mayotlide combines both solution and solid phase synthetic methodologies for the preparation of the building blocks and the peptide skeleton, as well as for the coupling between them. Furthermore, an according selection of the protecting groups utilized is fundamental for a selective deprotections and subsequent properly conectivity formation.

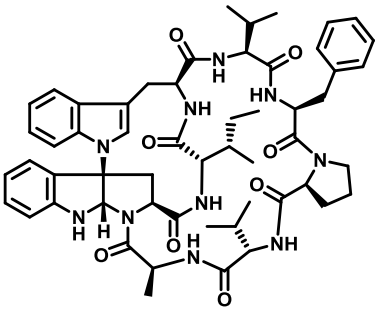

Figure 1. Structure of Mayotlide

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CATALYTIC AND SYNERGISTIC σ-GOLD(I) ACTIVATION-ACETYLIDE ADDITION AND CONSECUTIVE σ- AND π-GOLD(I) ALKYNE ACTIVATIONS. SYNTHESIS OF INDENE DERIVATIVES.

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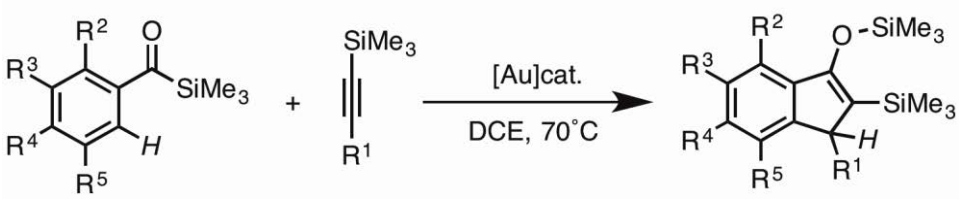
Keywords: *Gold, carbenoid, synergistic.*

Among the large number of gold(I) catalyzed organic transformations,[1] gold(I) carbenoids[2] have been proposed as key intermediates for several of them. A variety of methods to generate gold carbenoids has been described, such as decomposition of diazocompounds, 1,2-acyloxy migrations of propargyl esters, cyclization of enynes or oxidation transfer reaction of alkynes, among others.

In this work, we present a catalytic and simple methodology to obtain indene derivatives through a C-H functionalization, from acylsilanes and silylacetylenes. The methodology described here consists in a simple and intermolecular procedure that is proposed to involve the participation of Au(I) carbenoid. This gold(I) carbenoid is proposed to be generated in a new way through an intermolecular cascade reaction initiated by a synergistic[3] σ-gold(I) activation-acetylide addition and involving a consecutive double σ- and π-gold(I) alkyne activation.



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THE MICROWAVE-ASSISTED ORGANOCATALYZED REARRANGEMENT OF PROPARGYL VINYL ETHERS TO SALICYLALDEHYDES DERIVATIVES

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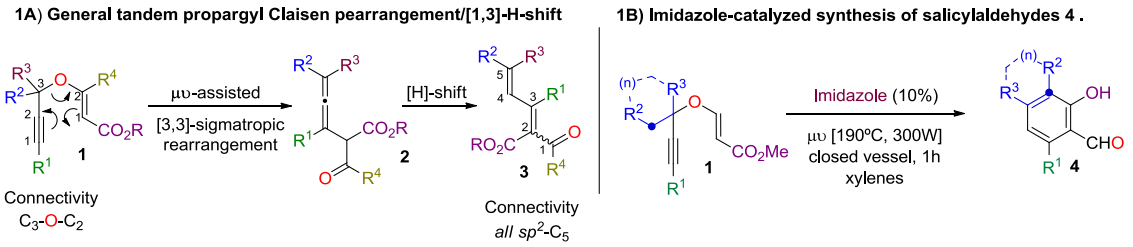
Keywords: *salicylaldehydes, propargyl vinyl ethers, 6π-electrocyclization, microwave.*

Propargyl vinyl ethers **1** constitute a privileged group of small size, densely functionalized and readily accessible linear scaffolds. The main key to the chemical reactivity encoded in these structures is the [3,3]-sigmatropic rearrangement (propargyl Claisen rearrangement) shown in Scheme **1A**,[1] which takes place irreversibly and under thermodynamic control to generate the allene **2** which isomerizes to dienal **3**. We have developed a microwave-assisted, catalytic (imidazole 10 mol-%) and scalable methodology to transform these allenes into salicylaldehyde motives supported on a broad range of topologies, which spanned from simple aromatic monocycles to complex fused polycyclic systems.[2] The reaction manifold is depicted in Scheme **1B**. We have performed a theoretical study of this reaction which is in full agreement with the observed experimental results. The reaction scope and the proposed mechanism will be commented in our presentation.



Scheme 1

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S7: *Metodología Sintética y Síntesis Total*

CARBON-CARBON AND CARBON-HETEROATOM BOND-FORMING REACTIONS CATALYZED BY IN-SITU GENERATED, EXTREMELY ACTIVE, LIGAND-FREE METALLIC AGGREGATES OF <10 ATOMS

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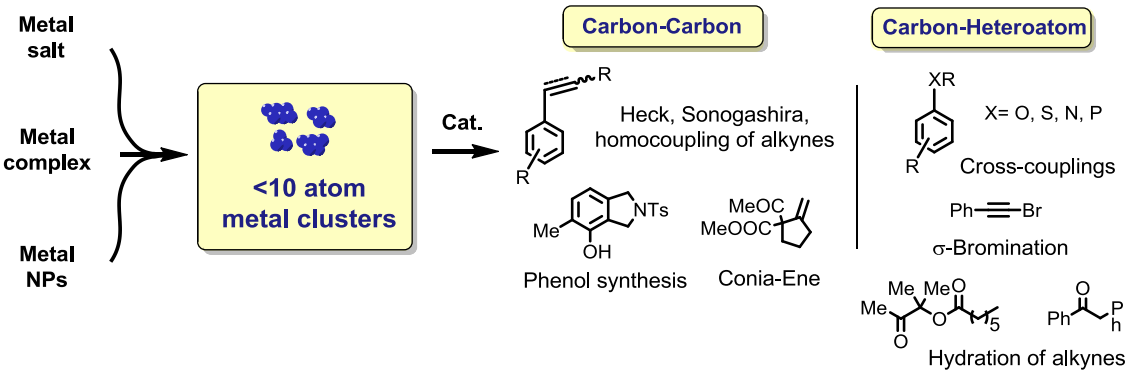
Keywords: *catalysis, sub-nanometric metal clusters, gold, palladium, copper*

The catalytically active species for some metal-catalyzed C-X (X= C, O, S, N, P, Br) bond-forming reactions are not the starting metal salt, complex or nanoparticle, but small metal aggregates with <10 atoms, formed in-situ during reaction.[1-4] These ligand-free metal aggregates (clusters) catalyze the reaction with very high activity (turnover frequencies up to 10^5 h^{-1} and turnover numbers up to 10^7), and can be prepared independently and isolated, thus having a new tool to accelerate organic reactions of interest. In addition, an unexpected selectivity can be found in some cases, for instance during the homocoupling of alkynes catalyzed by two gold atoms in different oxidation states.[5]



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Comunicaciones Flash (FC)

S7: *Metodología Sintética y Síntesis Total*

SYNTHESIS OF THE TETRACYCLIC ABCD RING SYSTEM OF CALYCIPHYLLINE A-TYPE ALKALOIDS

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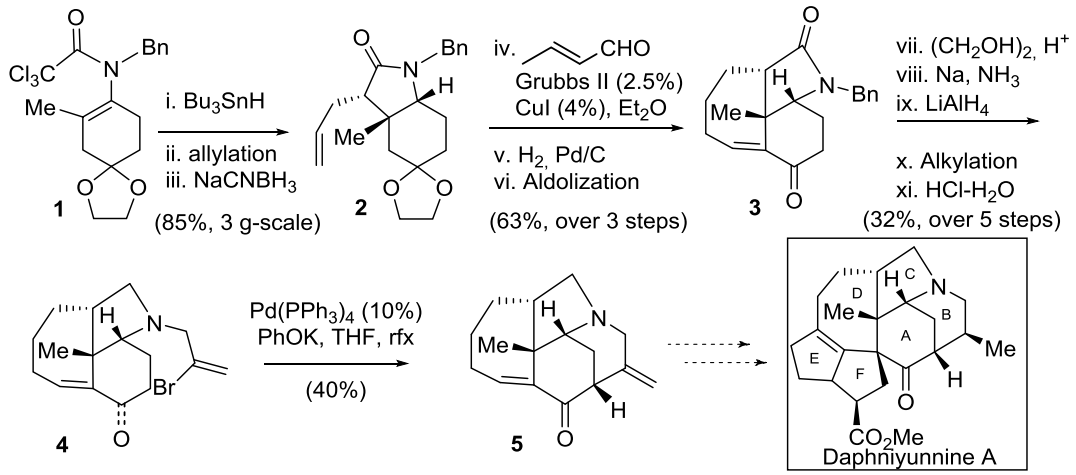
Keywords: *Radical cyclization, Alkenylation of ketone enolates, Total synthesis,*

Many years after the classical synthetic work of Heathcock, a renewed interest in the synthesis of Daphniphyllum alkaloids[2] has resulted in a plethora of new strategies towards these highly complex compounds. However, very few total syntheses have been reported to date.[3] Here, following our synthetic methodology of Pd-catalyzed intramolecular enolate alkenylation,[4] an approach to the ABCD fragment of calyciphilline A-type alkaloids is reported.

The tetracyclic core ring of calyciphylline A has been synthesized, the key steps being: (a) a 5-*endo* radical cyclization of trichloroenamide **1**, which after diastereoselective allylation and reduction of the enamide gave **2**; (b) a seven-membered ring formation (D ring) by a ring-closing aldolization leading to **3** and (c) a palladium-catalyzed intramolecular coupling of an amino-tethered vinyl bromide with a ketone (*i.e.* **4**) using potassium phenoxide as the base to generate azatetracyclic compound **5** embodying the ABCD-ring. Studies on the transformation of **5** to the targeted alkaloids are in course.



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S7: *Metodología Sintética y Síntesis Total*

TOTAL SYNTHESIS OF (-)- ASPERGILAZINE A

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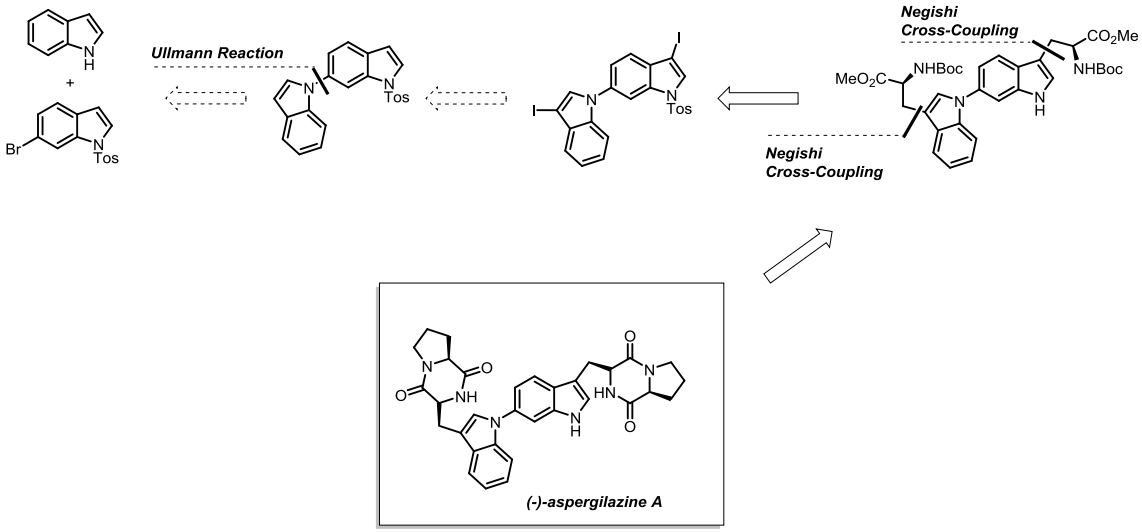
Keywords: *Copper, Palladium, Cross-coupling, diketopiperazine, bis-indole*

Aspergilazine A[1], a 2,5-diketopiperazine (DKP) dimer, was first isolated from the marine fungus *Aspergillus taichungensis.* Its structure, an heterodimer that presents four stereocenters enclosed in two tryptophan-proline DKP moieties, was elucidated by one and two dimensional NMR experiments and Marfey´s analysis, becoming the first congener of the family with the N(1)-C(6) linkage. Furthermore, the antiviral activity of aspergilazine A was evaluated and proved to be active against Influenza A virus (H_1N_1).

Due to our interest in the stereoselective synthesis of natural products and related compounds [2] with potential activities as epigenetic modulators, we present our strategy towards the stereoselective synthesis of aspergilazine A, which involves the use of transition metal catalyzed reactions such as the Cu(I)-promoted *Ullmann* reaction [3] and the Pd(0)-catalyzed Negishi C_{Ar}-C_{sp3} cross-coupling [4].



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ACCESS TO ENANTIOPURE δ-HYDROXY ACID DERIVATIVES FROM PHENYLGLYCINOL-DERIVED LACTAMS

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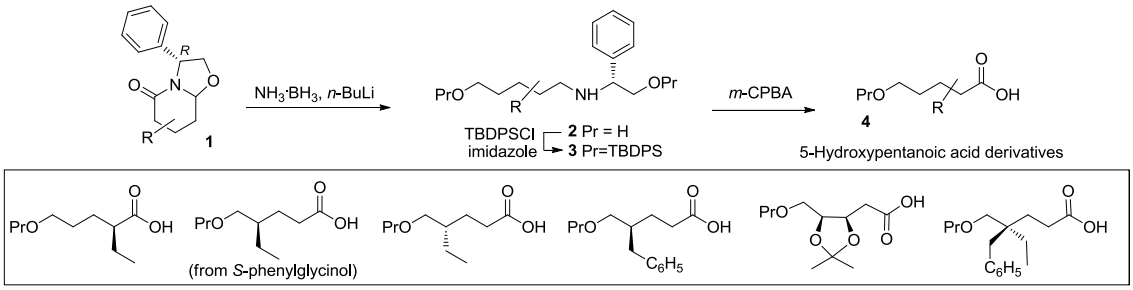
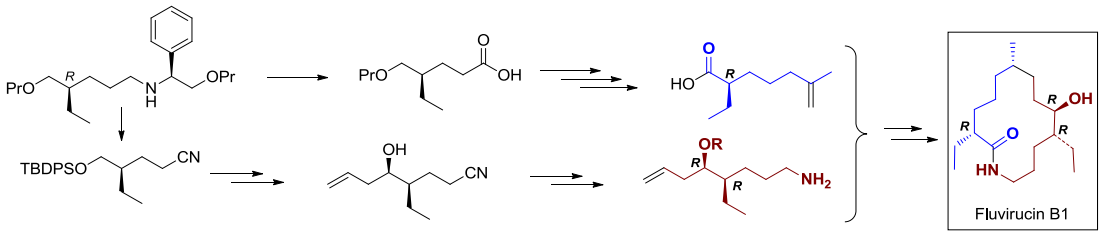
Keywords: *enantioselective synthesis, δ-hydroxy acids, oxidation, phenylglycinol-derived lactams*

In previous work we have reported the conversion of lactams **1** into enantiopure aminodiols **2** under $LiNH_2BH_3$ reduction conditions and the use of these functionalized linear-chain amino derivatives as enantiomeric scaffolds for the synthesis of *Haliclona* alkaloids.[1] We present here a straightforward procedure for the conversion of these easily accessible aminodiols **2** into enantiopure δ-hydroxy acids under *m*-CPBA oxidative conditions, in an unprecedented process that involves the oxidation of the secondary amine to a carboxylic acid with simultaneous removal of the chiral auxiliary. Following this strategy, we have prepared a variety of enantiopure 2-, 4-, 3,4-, and 4,4-substituted 5-hydroxypentanoic acid derivatives.



Our progress on the application of these enantiopure scaffolds to the total synthesis of *Fluvirucin* B1 will be presented.



We acknowledge financial support from MINECO (projecte CTQ2012-35250) and the AGAUR, Generalitat de Catalunya (Grant 2014-SGR-0155).

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SYNTHESIS OF DITRYPTOLEUCINES

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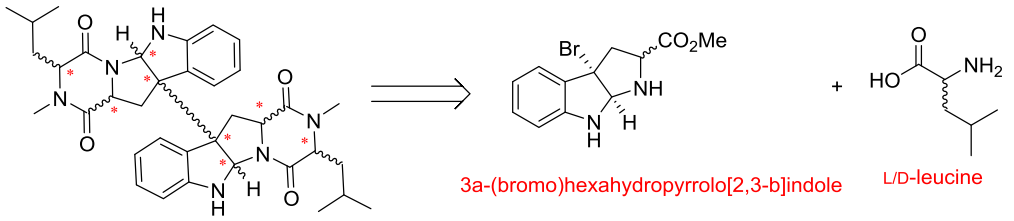
Keywords: *natural products, total synthesis, ditryptoleucine, pyrrolidinoindoline, diketopiperazine.*

Alkaloids are natural products, abundant in plants and microorganisms. In 2012 two indole alkaloids named ditryptoleucines A and B, were isolated from the fungus *Aspergillus oryzae*[1] and their structure was elucidated by NMR spectroscopy. The gross structure of those diastereomers consist of homodimers of pyrrolidinoindoline diketopiperazines with four stereogenic centers in each monomer, the relative and absolute configuration of which are unknown. By analogy with similar compounds present in nature of known configuration among them (+)-asperdimin, (+)-cristatumin C[2] and WIN 64745, a set of 4 diastereomers were proposed.



Here, we have addressed the stereoselective synthesis of ditryptoleucines, with the aim to confirm the proposed structure and the absolute configuration of the chiral centers. The synthesis will be based on the stereoselective bromocyclization[3] of trytophan derivatives to form the pyrrolidino-indoline, the radical dimerization of the two units catalyzed by a Co(I)[4] complex forming the C_3-$C_{3'}$ bond and, finally, the formation of the diketopiperazine rings after peptide couplings with both enantiomeric leucines (L/D).

These compounds are also of biological interest, since structural analoguos, such as chaetocine, acts as epigenetic modulator and shows citotoxic activity.

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TOWARDS AN EFFICIENT SYNTHESIS OF 6-ALKYLIDENE PENACILLANIC ACID DERIVATIVES FOR THE TREATMENT OF MULTI-RESISTANT NOSOCOMIAL INFECTIONS

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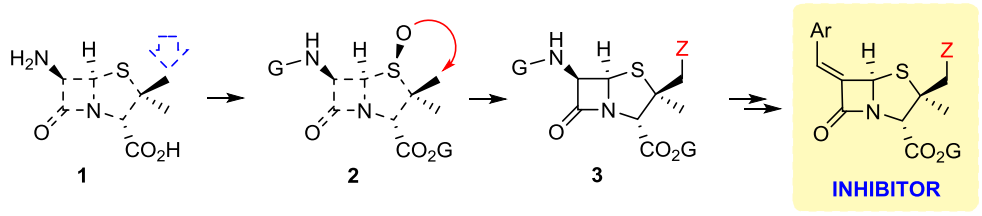
Keywords: *antibiotic drug resistance, β-lactam synthesis, stereoselectivity*

The development of antibiotic drug resistance has become one of the most important public health issues of the early 21st century. Severe hospital- and community-acquired bacterial infections are on a sharp rise, being antibiotic-resistant nosocomial infections of major concern. The most common resistance mechanism is the enzymatic inactivation of the antibiotic due to β-lactamases enzymes that hydrolyze the most widely used antibiotics in an acylation-deacylation-based process that represents the most prevalent cause of antibiotic resistance in Gram-negative bacteria. The most rapidly growing and diverse group of β-lactamases are the class D enzymes, which are also known as oxacillinases (OXA). Recently, a new type of oxacillinases that they also display resistance to carbapenems has been identified.[1] Considering that carbapenems are the remaining drug of choice to treat these multi-resistant nosocomial infections, the emergence of OXA-type carbapenemases raises a disturbing problem.[2] Therefore, potent inhibitors of class D oxicillinases are urgently needed in order to preserve the current β-lactam antibiotics. It has been recently shown that the incorporation of a substituent into position 2´ of sulfopenicillines provides compounds that inhibit class D β-lactamases.[3] In our group we are interested in the development of novel inhibitors of this enzyme, as well as the development of an efficient synthetic strategy for the stereoselective functionalization of the pro-*R* methyl group of 6-aminopenacillanic acid (**1**). Our recent results on this project will be presented.[4]



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INTRAMOLECULAR DOMINO DIELS-ALDER REACTIONS OF A DIFULVENE DERIVED FROM BICYCLO[3.3.0]OCTANE-3,7-DIONE AND TRANSFORMATIONS THEREOF

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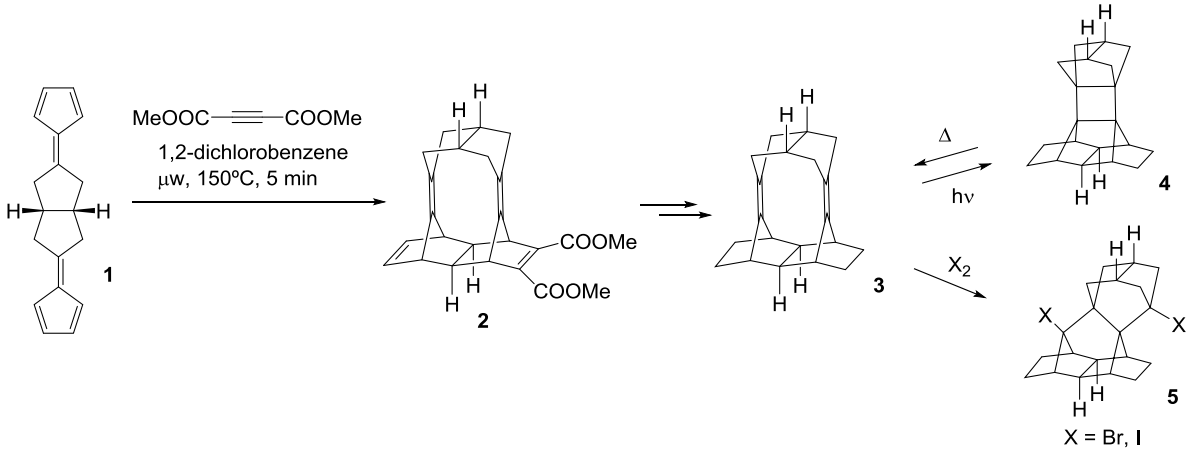
Keywords: *Domino reactions, photochemistry, polycycles, belt compounds*

A short preparation of belt compounds with spatially close C=C bonds is described. The key step consists of a domino Diels-Alder (DA) reaction among the known[1] difulvene (**1**) and dimethyl acetylenedicarboxilate or *N*-methylmaleimide under microwave irradiation.

The polycyclic hydrocarbon $C_{20}H_{20}$ (**3**) was obtained by Zn/AcOH reduction, hydrolysis, oxidative decarboxylation and selective hydrogenation of the domino DA adduct (**2**).

Photochemical [2+2] cycloaddition of this diene (**3**) gave a thermally unstable cyclobutane derivative (**4**) which reverts to the diene (**3**). However, irradiation of a crystal of diene (**3**) gave a new crystal containing 50% molecules of (**3**) and 50% molecules of (**4**), as established by X-ray diffraction analysis.

The transannular addition of bromine and iodine of the diene (**3**) led to adducts (*N*-type, C_s symmetry) with formation of new six-membered rings (**5**).



Sheme 1. Preparation of domino DA adduct (**2**) and several derivatives.

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SYNTHESIS OF NEW POLYCYCLIC COMPOUNDS BY SINGLE OR DOUBLE DOMINO NUCLEOPHILIC SUBSTITUTION / DIELS ALDER REACTION

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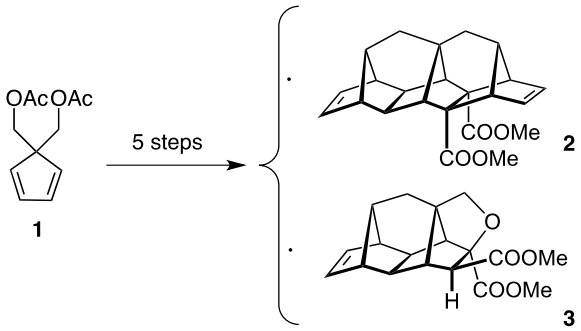
Keywords: *Polycyclic compounds, nucleophilic substitution-Diels Alder reaction, cyclopentadiene.*

Polycyclic and cage compounds are of current interest in medicinal chemistry. Drugs containing cage structures are very limited, probably due to the lack of easily accessible polycyclic scaffolds as their synthesis often requires multistep routes. An important challenge is the development of novel methodologies which allow the construction of these complex skeletons. [1]

In this context, our research group has reported several synthetic methods to rapidly access to a wide range of polycyclic compounds, which are of significant interest for the treatment of diseases such as Alzheimer, flu caused by influenza A virus or diabetis. [2]

On the basis of our previous insights, a short access to new functionalized hexacyclo (**3**) and octacyclo (**2**) compounds is herein described. [3] The key-step of the route consists of a single or double domino nucleophilic substitution of neopentyl-type iodides with potassium cyclopentadienide followed by intramolecular Diels-Alder cycloaddition.

An important feature of these syntheses was the preparation of cyclopenta-2,4-diene-1,1-diylbis(methylene) diacetate (**1**). Many approaches to 1,1-disubstituted cyclopentadiene derivatives have been tried with negative results. However, allylic bromination followed by dehydrobromination of a diacetate cyclopentene derivative gave us the desired cyclopentadiene substructure, which is the cornerstone of the developed syntheses.



Scheme 1. Schematic approach to hexacyclo and octacyclo derivatives.

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TRANSITION-METAL-FREE CROSS-COUPLING OF TRIORGANOINDIUM REAGENTS WITH CHROMENE AND ISOCHROMAN ACETALS MEDIATED BY BF_3•OET_2

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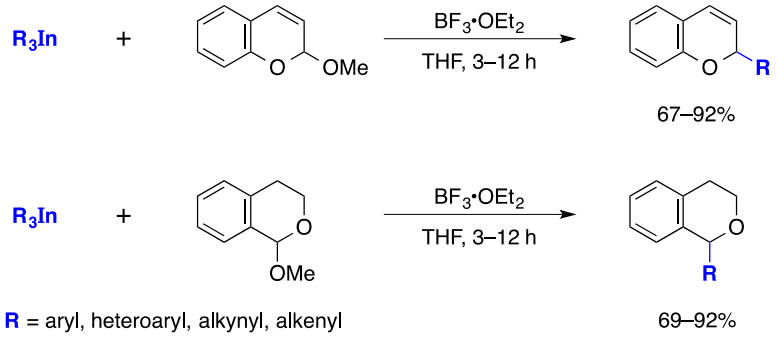
Keywords: *Oxocarbenium ions; Indium organometallics; Cross-coupling*

Reactions involving in situ generated reactive oxocarbenium ions play an important role in the synthesis of natural products, bioactive molecules an in particular, in the chemistry of carbohydrates. These species, formed by reactions of cyclic acetals —such as chromene and isochroman acetals— with Lewis acids or transition-metal catalysis react with soft nucleophiles to afford the coupling products.[1] As part of a program devoted to the development of new applications of indium and its derivatives in organic synthesis,[2] in this communication we report a novel transition-metal free BF_3•OEt_2-mediated coupling of indium organometallics with oxocarbenium ion precursors.

After optimizing the reaction parameters such as the Lewis acid, solvent, reaction temperature and time, in a typical example chromene or isochroman acetals were treated with BF_3•OEt_2 (110 mol %) after subsequent addition of a trioganoindium reagent (50 mol %) in THF and the reaction was followed at the optimum temperature (rt to 80 °C) for 3–12 h to isolate the coupling products in good yields. Reactions occur efficiently for aryl, heteroaryl, alkynyl and alkenyl indium reagents. Additionally, the atom economy of the process and the absence of transition metal catalysis should be also highlighted.



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TRANSITION METAL-FREE SYNTHESIS OF HIGHLY SUBSTITUTED AND FUNCTIONALIZED CARBAZOLES *VIA* A MULTICOMPONENT PROCESS THAT INCLUDES A C-H ACTIVATION STEP

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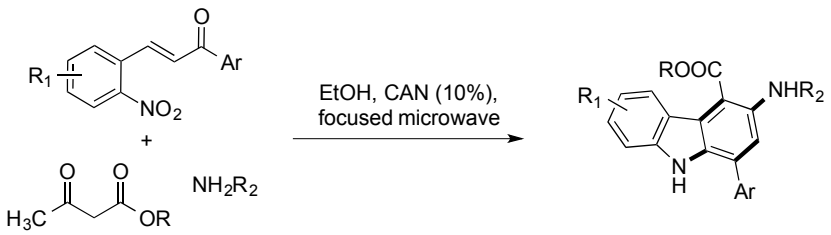
Keywords: *Multicomponent reactions, carbazoles, focused microwave.*

The carbazole system constitutes the structural core of a large family of alkaloids [1] and is also of crucial importance in medicinal chemistry and materials science. While there is a wide array of methods for carbazole synthesis [1-3], most modern procedures rely on the use of transition metals as catalysts. We report here a multicomponent access to this ring system based on a CAN-catalyzed three-component reaction between primary amines, β-ketoesters and *o*-nitrochalcones under focused microwave irradiation. This method affords good to excellent yields of highly substituted and functionalized carbazole derivatives *via* the generation of two rings, two C-N and two C-C bonds, and is noteworthy in that there are very few multicomponent reactions that include a CH functionalization step.



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A NEW SYNTHETIC STRATEGY TO CONSTRUCT SEVEN-MEMBERED CARBOCYCLES EMBEDDED IN A HEXAGONAL NETWORK

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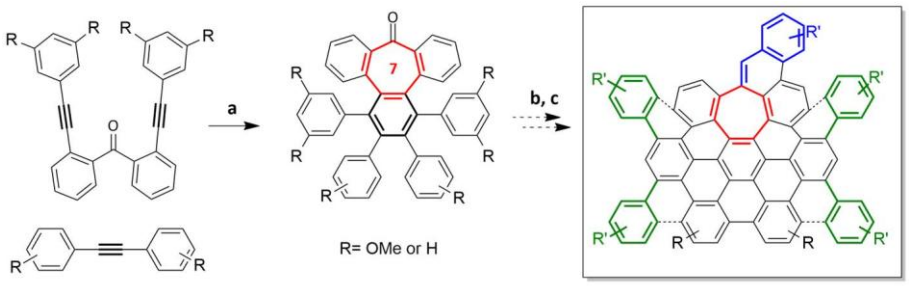
Keywords: *cyclotrimerization, dehydrogenation, cross-coupling reaction.*

Conjugated carbon nanomaterials based in pure hexagonal network have received major attention due to their extraordinary properties. The introduction of non-hexagonal carbocycles in flat sheets of hexagonal rings has tremendous impact not only in the geometry but also in the properties of the material. In particular, the construction of seven-membered carbocycles embedded into otherwise pure hexagonal lattices may lead to new carbon nanostructures with unprecedented geometries and therefore properties. Recently, curved carbon nanostructures including non-hexagonal carbocycles have been reported. [1]

Here we report a new versatile route to construct a variety of compounds including a seven-membered carbocycle partially surrounded by benzene rings. Subsequent cyclodehydrogenation reaction gives rise to a heptagon-including polycyclic arenes.



Scheme 1. a) Co(0)-mediated cyclotrimerization; b) Cyclodehydrogenation reaction; c) Nucleophilic addition and Ni(0)-catalyzed cross coupling reactions

Our modular approach is based on a Co-mediated intermolecular cyclotrimerization reaction of adequate precursors. This strategy is very flexible and just by choosing the suitable building blocks we can directly construct a variety of structures. The subsequent oxidative cyclodehydrogenation can also be controlled and therefore we have obtained different polycyclic arenes depending on the chosen substitution pattern of the cyclotrimerization precursors.

We have used building blocks bearing adequate functional groups to further expand the polycyclic π-framework in three different directions. Hence, we consider three strategies: nucleophilic addition to the ketone moiety, cross-coupling reaction by using methoxy groups as electrophiles[2] and cyclotrimerization reaction with functionalized diphenylacetylenes.

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S7: *Metodología Sintética y Síntesis Total*

FROM THE COMPUTER TO THE BENCH: NOVEL SELECTIVE GLYCOMIMETICS TAKE LIFE

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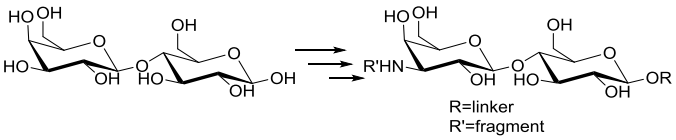
Keywords: *Carbohydrates, Drug Design, Synthesis*

Carbohydrates are a family of molecules involved in physiological and pathological processes. The sugars represent a very big challenge for the chemists, due to their characteristics: on the one side, the wide variety and possible final combinations they may lead to, and, on the other side, the complexity of their synthesis (Scheme 1).

Galectins are a family of lectins which recognize selectively β-galactoside moiety. They are involved in cancer, HI, inflammatory disease, rheumatoid arthritis [1]. To date, 14 members of the galectins have been identified in mammals. All galectins share a carbohydrate recognition domain (CRD) which makes difficult to aim selective binding (Figure 1). Among the family, we have focused on galectin-1, -3 and -7 due to their biological/pathological roles. Following a combined virtual screening and docking approach, we have designed a series of novel ligands with predicted improved affinity and selectivity towards galectins, and synthesis is being undertaken.

Here we report some details about the design and optimization of the synthesis method of these novel compounds with putative biological/therapeutic applications. Docking studies for other galectin binders are also reported.



Scheme 1

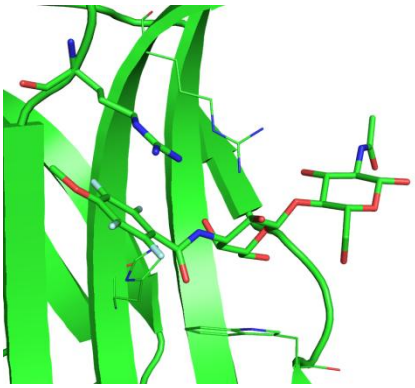


Figure 1. Lactose derivative in complex with hGal-3.[2]

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S7: *Metodología Sintética y Síntesis Total*

THE S_N3 DILEMMA: CHARACTERIZATION OF THE TRANSITION STATE FOR SOLVOLYSIS REACTIONS OF HINDERED SULFONYL HALIDES

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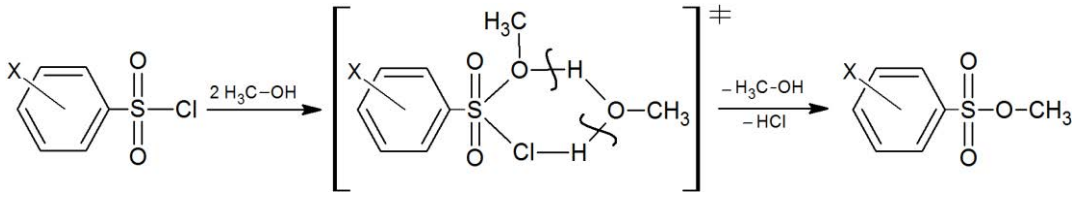
Keywords: *methanolysis, positive steric effect, structure-reactivity effects, S_N2*

Recently, nucleophilic substitution processes at sulfonyl sulfur have received attention because of the proposal of a termolecular S_N3 mechanism for their solvolysis,[1] and because sterically hindered sulfonyl derivatives show unexpectedly enhanced reactivities ("positive" ortho-effect). To characterize the transition state (TS) for solvolysis of hindered arenesulfonyl chlorides, we studied the methanolysis of X-$ArSO_2Cl$ (X=H-, 4-Me-, 4-*t*-Bu-, 4-Cl-, 4-Br-, 3-NO_2-, 2,4,6-Me_3-, 2,4,6-Et_3-, 2,4,6-*i*-Pr_3-, 2-Me-, 2,4-Me_2-, 2,5-Me_2-, 2-Me-5-*t*-Bu-, 2,6-Me_2-4-*t*-Bu-, 2,3,5,6-Me_4-, 2-Me-5-NO_2-, 2,4-Me_2-5-NO_2- and 2,4,6-Me_3-3-NO_2-)in the temperature range303-323 K.

Hammett's correlation for substituted arenesulfonyl chlorides is linear, with a negative slope (ρ=-0.49; R^2=0.97) for unhindered substrates, indicating a significant decrease in electron density at the reaction center. The most reactive compounds, those bearing -Me groups in both *ortho*- positions, fall out of the correlation. Despite kinetic differences, all studied compounds show similar activation values ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$), which is indicative of a compensation effect (enthalpic and entropic factors). The existence of: a $logk_{T1}$ *vs.* $logk_{T2}$ isokinetic dependence, similar solvent kinetic isotope effect, the effect of the change of nucleophile, and activation parameters, all point to a common reaction mechanism for all the studied compounds. Large negative $\Delta S^{\ddagger}$ values, similar $\Delta H^{\ddagger}$ values and magnitudes of reaction order on nucleophile are consistent with a S_N2 mechanism with participation of, at least, a second solvent molecule in the TS, most possibly with formation of a cyclic transition state in which a reduced number of solvent molecules form chains, as in general-base catalysis:



This mechanistic interpretation avoids the use of the S_N3 concept, that would imply the trouble some idea of a termolecular process in solution.

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S7: *Metodología Sintética y Síntesis Total*

THE USE OF OLEFIN CROSS METATHESIS IN THE SYNTHESIS OF CAROTENOIDS AND APOCAROTENOIDS

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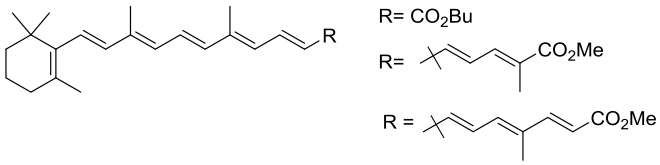
Keywords: *carotenoids, olefin metathesis, pigments.*

Carotenoids are a large and widely distributed group of pigments, which are biosynthesized by plants, some animals and microorganisms but not by humans. The role of carotenoids in the coloration of Nature, as well as in photosynthesis and the photoprotection of plants and animals is well established.[1]

Carotenoids have traditionally been synthesized using condensation methods, such as Wittig, Horner–Wadsworth–Emmons and Julia reactions to form C*sp*2=C*sp*2 bonds, and more recently using palladium-catalyzed cross-coupling reactions (Stille, Suzuki and Negishi) to form C*sp*2–C*sp*2 bonds.[2] In the last few years, the olefin metathesis reaction has emerged as a third general approach to the synthesis of these conjugated polyene chains despite the concerns about the control of site-selectivity, stereoselectivity, and the stability of polyenes to the reaction conditions.[3]



Herein, we show our progress in the synthesis of carotenoids and apocarotenoids using the olefin cross metathesis as key reaction allowing us to obtain the desired conjugated polyene chains stereoselectively in good overall yield.

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S7: *Metodología Sintética y Síntesis Total*

IODINE(III) REAGENTS FOR C-N BOND FORMATION WITH UNPRECEDENTED SCOPE

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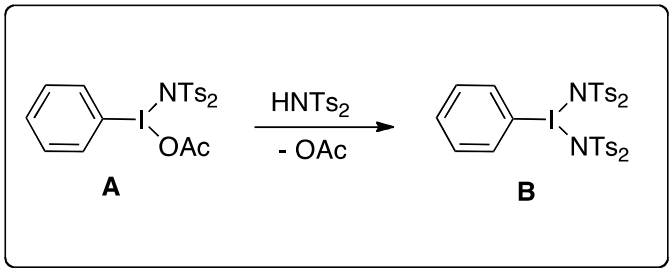
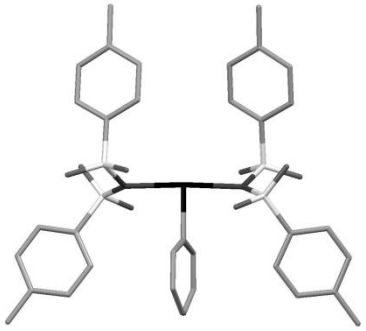
Palabras Clave: *Amides, Amination, Halide Reagents, Iodine, Oxidation*

Hypervalent iodine reagents represent versatile synthetic tools for a series of selective oxidative transformations.[1] This approach is of particular synthetic value where reactions are concerned that enable entirely new transformations. We have been particularly interested in the development of new synthetic methodology for direct amination of a diverse range of different hydrocarbon molecules such as alkenes, alkanes, acetylenes, arenes and allenes.[2] We have recently found that simple protonolysis events enable incorporation of nitrogenated groups into the coordination sphere of common iodine(III) complexes, as for example, in case of the previously described compound **A**, which contains a rare iodine-nitrogen single bond.[2a] Further protonolysis furnishes the new iodine(III) compound $PhI(NTs_2)_2$ **B** containing two defined iodine-nitrogen single bonds.[3] It is of utmost synthetic importance that the new compound **B** contains iodine-nitrogen entities, which upon solution dissociation lead to electrophilic iodine centres and nucleophilic nitrogen groups. They enable unprecedented amination reactions.





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S7: *Metodología Sintética y Síntesis Total*

IPy_2BF_4 MEDIATED TRIPLE BOND ACTIVATION OF PROPARGYLIC ESTERS FOR THE SYNTHESIS OF α-IODOENONES.

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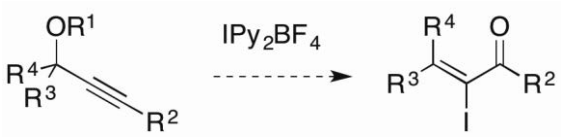
Propargylic alcohol derivatives constitute an interesting class of organic compounds and have been extensively used as synthetic intermediates due to their particular reactivity. For instance, *propargylic rearrangement* by electrophile triple bond activation of the corresponding ester derivatives has been applied in the past years as an access to other organic functionalities. [1]

Within this context, there are several examples in the literature to obtain *α-haloenones*, an important class of synthetic intermediates, by propargylic rearrangement using a metal catalyst and an external source of halogen. [2] However, there are few examples in which the triple bond activation is directly exerted by the electrophilic halogen without the use of a carbophilic metal catalyst. [3]

In this regard we describe an easy new access to α-iodoenones from propargylic esters using IPy_2BF_4 both as carbophilic triple bond activator and electrophilic iodine source. The reaction takes place with good yields in the presence of an acid and under mild conditions. It also has demonstrated group tolerance, since it goes well for primary, secondary or terciary propargylic alcohol derivatives containing either alkyl, aryl or heteroaryl groups.

In summary, we have developed an efficient synthesis of α-iodoenones by the use of propargylic esters and IPy_2BF_4 as both carbophilic activator and iodine source.



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S7: *Metodología Sintética y Síntesis Total*

SYNTHESIS OF CHIRAL PYRAZOLES THROUGH A 1,3-DIPOLAR CYCLOADDITION/1,5-SIGMATROPIC REARRANGEMENT CASCADE WITH MIGRATION OF A STEREOGENIC GROUP

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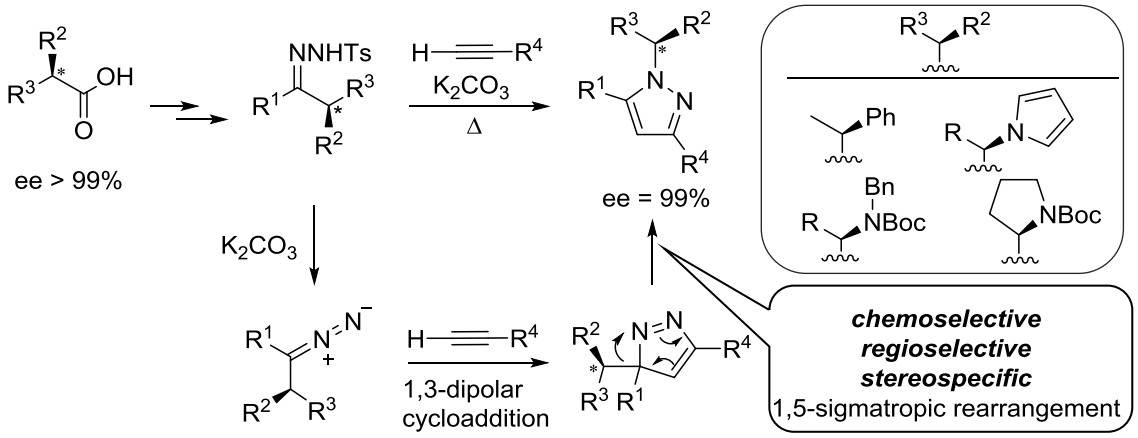
Keywords: *alkyne, heterocycles, hydrazones, rearrangement, synthetic methods*

The pyrazole ring has emerged as a very important heterocycle on account of its presence in a large number of molecules with applications in pharmaceutical, agrochemical and materials chemistry [1]. Indeed, substituted pyrazoles are constantly employed as building blocks in drug discovery programs, ligands for transition metal-catalyzed reactions, receptors in supramolecular chemistry, liquid crystals and polymers. [2,3]

We have recently reported the regioselective synthesis of 1,3,5- and 3,4,5-trisubstituted pyrazoles from the reaction of tosylhydrazones and terminal alkynes by a 1,3-dipolar cycloaddition/1,5-sigmatropic rearrangement sequence [4]. Taking into account the expected concerted nature of the [1s, 5s]-sigmatropic rearrangement, we report herein the formation of *N*-chiral pyrazoles from α-chiral-*N*-tosylhydrazones and terminal alkynes through the same cascade process (*Scheme*). Importantly, the migration of the stereogenic group proceeds with retention of configuration providing the final pyrazoles with very high e.e.s. Noteworthy the reactions are highly selective at three different levels: i) chemoselectivity in the migration group; ii) regioselectivity on the sense of the migration; iii) stereospecificity of the rearrangement. Finally, these reactions represent a very rare example of 1,5-sigmatropic rearrangements with retention of configuration on the migrating group.



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STEREOSELECTIVE REDUCTIVE COUPLING OF N-TOSYLHYDRAZONES WITH ALKENYLBORONIC ACIDS

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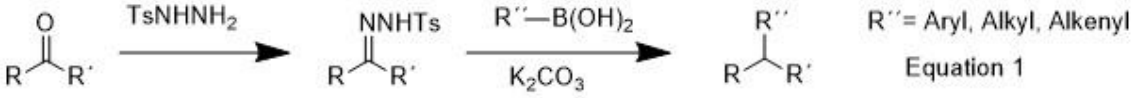
Keywords: *N-Tosylhydrazone, stereoselective, alkenylboronic acid.*

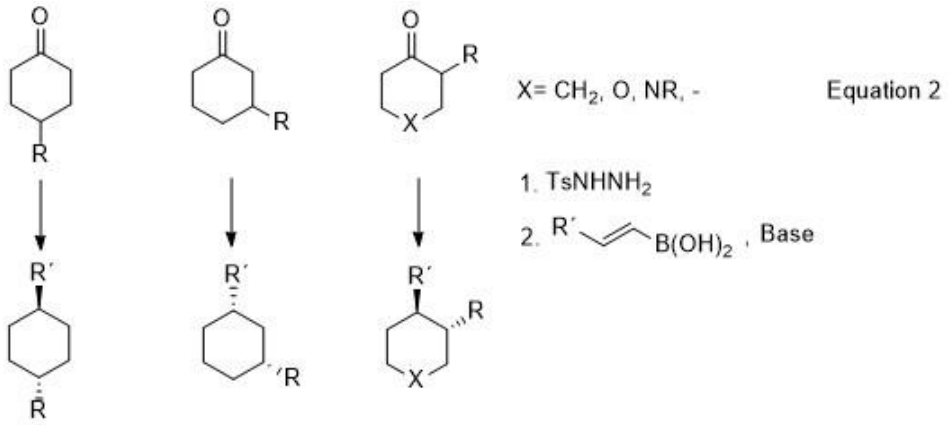
One versatile method for the modification of carbonyl compounds is the reductive coupling between tosylhydrazones and boronic acids (equation 1).[1,2] The reaction, which does not require the use of any catalyst, features wide scope and functional group tolerance. Moreover, this methodology has already found diverse applications in drug discovery programs[3].



Equation 1

Efficient metal-free reactions feature many advantages associated with simplicity, economy and environmental issues. Nevertheless, in our reaction an important limitation associated with the absence of a metal catalyst is the difficulty to introduce any stereochemical control in the reductive coupling process.

As a part of our interest in the development of stereoselective versions of these reactions, herein we present the first examples of diastereoselective reductive couplings, employing tosylhydrazones derived from substituted cyclic ketones and alkenylboronic acids (equation 2). These reactions represent a rare example of stereoselective reactions based on diazo compounds in the absence of any metal catalyst.



Equation 2

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LIGAND-FREE Cu CLUSTERS CATALYZE C-N, C-C, C-O, C-S, AND C-P BOND-FORMING REACTIONS

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Keywords: *copper, naked clusters, catalysis, coupling reaction, polymer*

Sub-nanometric Cu clusters formed by endogenous reduction of Cu salts and Cu nanoparticles in amide solvents are active and selective catalysts for C-N, C-C, C-O, C-S, and C-P bond-forming reactions.[1,2] In absence of diamine ligands, different copper salts decompose to clusters of 2 to 7 copper atoms and only then the coupling reaction begins.[3]

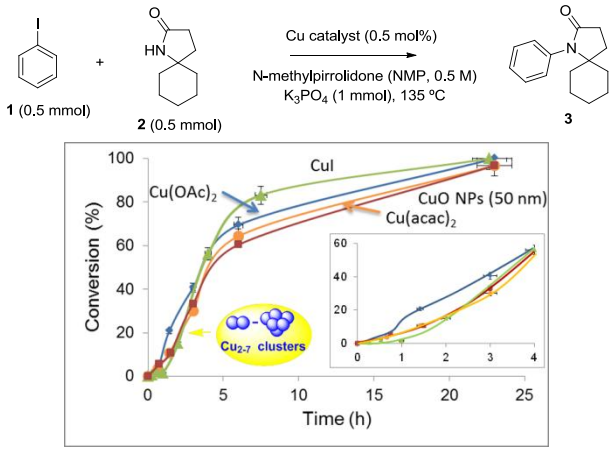

Figure 1.

These sub-nanometric Cu clusters have also been generated within a polymeric film and stored with full stability for months. In this way, they are ready to be used on demand and maintain high activity (TONs up to 10^4) and selectivity for the above reactions. The solvent used is involved in the mechanism of formation of the copper clusters, as we can see below.

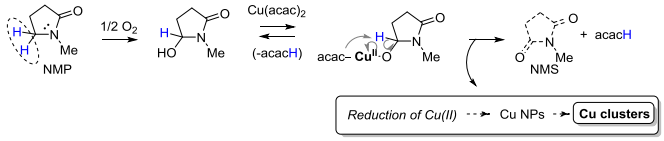

Figure 2.

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Presentaciones Póster (PP)

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E. Aguilar

NUEVA ESTRATEGIA SINTÉTICA PARA LA OBTENCIÓN DE LIGANDOS PIRIDÍNICOS Y SU AUTOENSAMBLAJE MEDIANTE CENTROS METÁLICOS DE Pd (II) Y Pt (II)

C. Alvariño

STEREOCONTROLLED CONSTRUCTION OF PENTACYCLIC YOHIMBINE-TYPE DERIVATIVES

C. Are

SYNTHESIS OF BERKELIC ACID ANALOGUES AND BIOACTIVITY STUDIES

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HIDROSILILACIÓN DE ALQUINOS MARKOVNIKOV CATALIZADA POR PARTES POR MILLÓN DE PLATINO

M. Rivero-Crespo

DIMERIZATION OF A HIGHLY PYRAMIDALIZED ALKENE TO A HYDROCARBON FEATURING FOUR CYCLOHEXANE RINGS IN BOAT CONFORMATIONS

Santiago Vázquez

S7: *Metodología Sintética y Síntesis Total*

SÍNTESIS DE DERIVADOS DE 1-AZAQUINOLIZINIO POR REACCIÓN DE METÁTESIS DE CIERRE DE ANILLO

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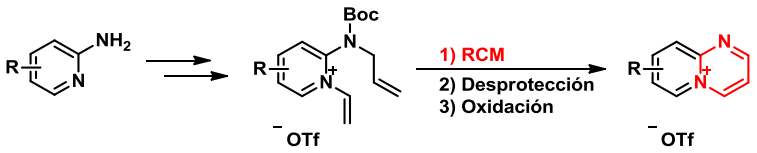
Palabras Clave: *cationes azaquinolizinio, azadienos de piridinio, metátesis de cierre de anillo (Ring Closing Metathesis, RCM).*

El catión quinolizinio y sus sistemas relacionados están presentes en una gran variedad de alcaloides relevantes, como la coralina y la familia de las berberinas, y muestran distintas actividades biológicas de interés (propiedades intercalantes de ADN, actividad antiproliferativa). Además, compuestos altamente fluorescentes basados en derivados de quinolizinio se han utilizado con éxito como sondas fluorescentes en la detección de biomoléculas.[1]

La reacción de metátesis de cierre de anillo (RCM) ha emergido como una metodología muy útil para la síntesis de heterociclos nitrogenados.[2] Utilizando esta reacción como paso clave, hemos desarrollado un novedoso método para obtener el sistema azaquinolizinio a partir de sales de piridinio bajo condiciones de reacción suaves. En este trabajo hemos explorado el alcance de esta metodología y hemos obtenido diversos derivados del sistema 1-azaquinolizinio con buenos rendimientos globales.



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S7: *Metodología Sintética y Síntesis Total*

ALKYNYLCYCLOPROPANECARBONITRILES FROM FISCHER CARBENE COMPLEXES: DIASTEREOSELECTIVITY AND MECHANISM

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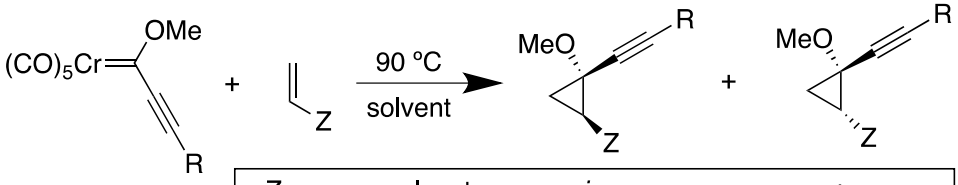
Keywords: *alkynyl cyclopropanes, carbenes, diastereoselectivity, DFT calculations*

Alkynyl cyclopropanes have been recently used as substrates for gold-catalyzed cycloisomerization reactions.[1] They can be readily synthesized by direct thermal cyclopropanation of electron-deficient olefins with chromium alkoxy alkynylcarbene complexes. The diastereoselectivity of this reaction depends on the solvent employed and usually good dr are reached in THF, being the isomer with a *cis*-relationship between the electron-withdrawing group (Z) and the alkynyl substituent the major one.[2] However, some results in gold-catalyzed cycloisomerization reactions suggested that when Z is a cyano group, the major diastereomer displays a *trans*-relationship between CN and alkynyl group. A reinvestigation of such reaction was carried out, and its results are presented in this communication.



Z	solvent	*cis*	*trans*
CO_2Me	THF	major	
CN	THF		major
CN	-	major	

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S7: *Metodología Sintética y Síntesis Total*

NUEVA ESTRATEGIA SINTÉTICA PARA LA OBTENCIÓN DE LIGANDOS PIRIDÍNICOS Y SU AUTOENSAMBLAJE MEDIANTE CENTROS METÁLICOS DE Pd (II) Y Pt (II)

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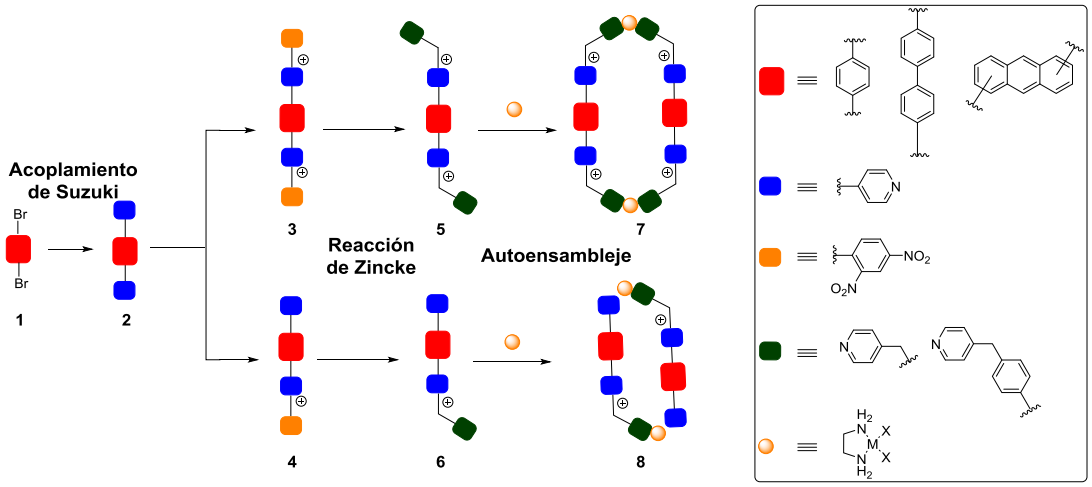
Palabras Clave: *acoplamiento C-C, reacción de Zincke, química supramolecular, autoensamblaje, metalociclo, receptores moleculares.*

La reacción de Suzuki [1], permite la preparación de una amplia variedad de ligandos piridínicos mediante el acoplamiento de un arilo halogenado (**1**) y el éster pinacolínico del ácido 4-piridinilborónico [2]. Siguiendo esta metodología, se han diseñado y preparado una serie de ligandos piridínicos bidentados de tipo **2** basados en un esqueleto fenilénico o antracénico. Estos ligandos pueden ser activados a sales de Zincke (**3**, **4**) mediante S_NAr con 1-cloro-2,4-dinitrobenceno, dando lugar la reacción de éstas con aminas bencílicas o arílicas a la formación de ligandos bidentados derivados de *N*-alquilbipiridinio (**5**) o *N*,*N*'-dialquilbipiridinio (**6**). Los compuestos así obtenidos, fueron sometidos a estudios de autoensamblaje en presencia de complejos metálicos de Pd(II) y Pt(II), en medio acuoso y orgánico, dando lugar a la formación de especies metalocíclicas dinucleares (**7**, **8**).



Los metalociclos preparados destacan por su capacidad como receptores moleculares [3], y su potencial aplicación en diversos campos como mejora en la distribución y transporte de fármacos, seguimiento y eliminación de contaminantes, reconocimiento biomolecular, catálisis supramolecular, etc.

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S7: *Metodología Sintética y Síntesis Total*

STEREOCONTROLLED CONSTRUCTION OF PENTACYCLIC YOHIMBINE-TYPE DERIVATIVES

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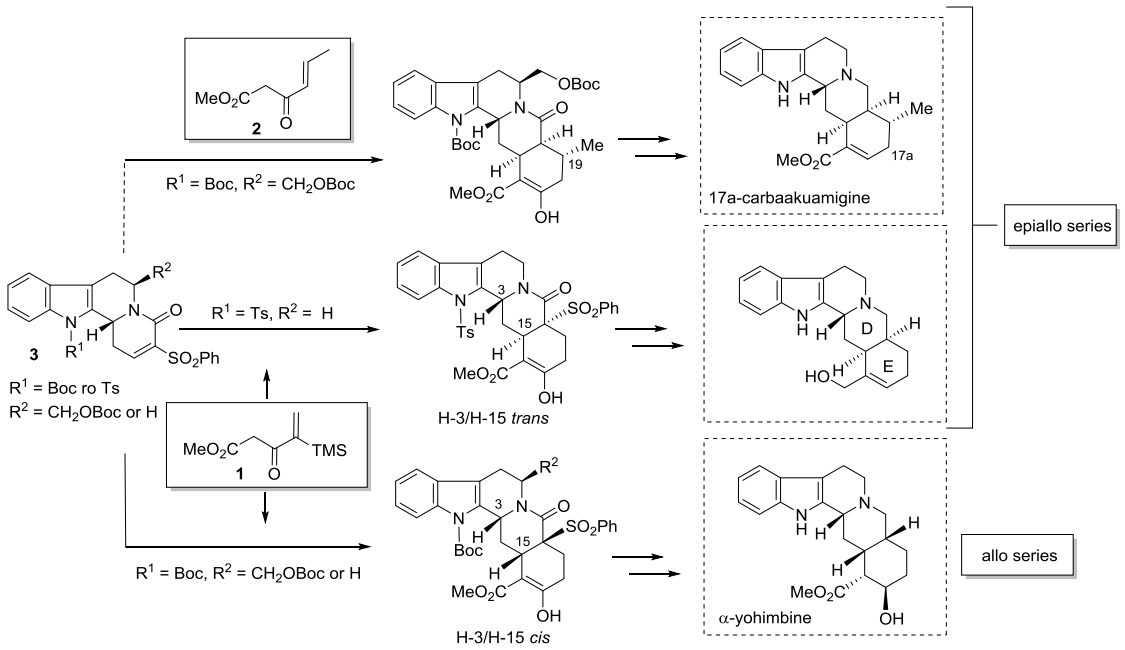
Keywords: *Indole alkaloids, Nazarov's reagent, double Michael reaction*

Tryptophanol-derived oxazolopiperidone lactams, easily accessible by a stereoselective cyclocondensation reaction between a δ-oxoacid derivative and (*S*)-tryptophanol, are versatile building blocks for the enantioselective synthesis of indolo[2,3-*a*]quinolizidine alkaloids. We present here a straightforward procedure for the stereocontrolled access to pentacyclic yohimbine-type derivatives. Our approach involves, as the key step, the generation of the E ring by a double Michael addition of Nazarov's reagents **1** and **2** to a tetracyclic unsaturated lactam **3**. The synthetic usefulness of the pentacyclic Nazarov-derived adducts is demonstrated by their conversion to allo and epiallo yohimbine-type targets, both in the racemic series and in enantiopure form.[1]



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S7: *Metodología Sintética y Síntesis Total*

SYNTHESIS OF BERKELIC ACID ANALOGUES AND BIOACTIVITY STUDIES

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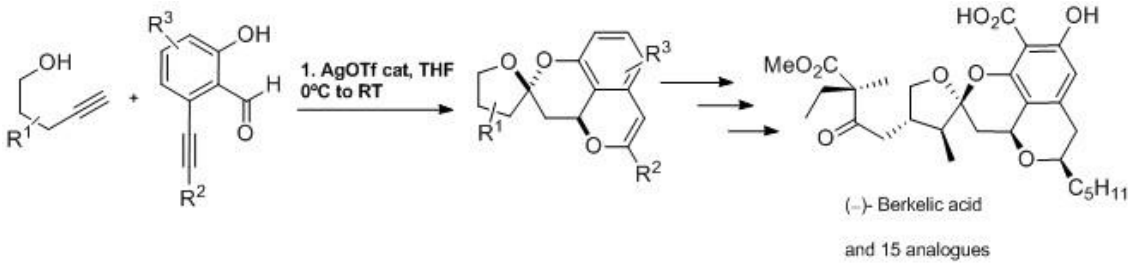
Keywords: *berkelic acid, natural products, antitumoral activity, cancer*

Berkelic acid, discovered by Stierle and coworkers on 2006, is a second metabolite isolated from an extremophile *Penicillium* species found in the extreme environment (highly acidic conditions (pH=2.5) and elevated concentrations of heavy metals) of Berkeley Pit Lake in Montana, (USA).[1] Berkelic acid has a lot of interest due to its complex structure and its promising biological properties. Specifically, the isolation team reported selective activity towards the human ovarian cancer cell line OVCAR-3 and also was found to inhibit matrix metalloproteinase MMP-3 and caspase-1. However, studies with a synthetic berkelic acid simple run by Snider show no antitumoral activity.[2]



We have recently developed a practical total synthesis for this natural product based on a strategy in which the polycyclic skeleton of the compound was directly constructed in just one step with high control of the stereoselectivity and starting from simple materials.[3] following this highly modular and stereoconvergent strategy several structural analogues of berkelic acid have been synthetized. Furthermore, antitumoral activity of some of this compounds as well as berkelic acid itself, against ovarian cancer cell line OVCAR-3 and head and neck adenocarcinoma line SCC38PWZL has been studied.

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S7: *Metodología Sintética y Síntesis Total*

NUEVA ESTRATEGIA SINTÉTICA PARA LA OBTENCIÓN DE METALOCICLOS MONONUCLEARES FUNCIONALIZADOS DE Pd(II) Y Pt(II)

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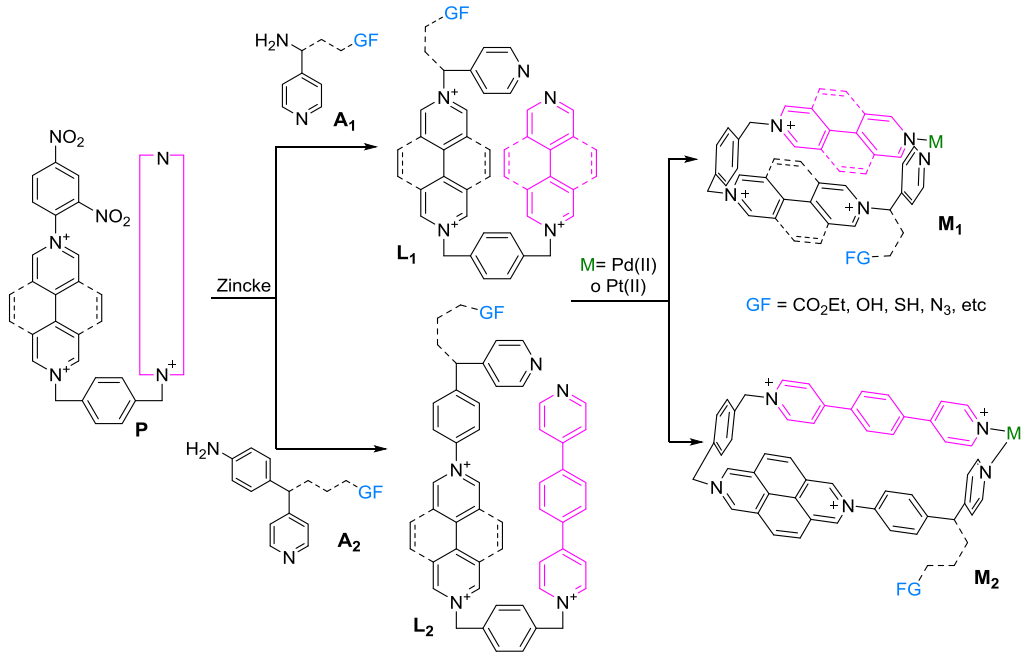
Palabras Clave: *autoensamblaje, reacción de Zincke, funcionalización, química supramolecular, reconocimiento molecular.*

Uno de los principales objetivos de la química supramolecular es el diseño de receptores moleculares para el reconocimiento selectivo de substancias de interés. Así, actualmente, tiene especial relevancia el uso para tal propósito de metalociclos autoensamblados, por la versatilidad sintética con la que pueden ser preparados receptores de distintos tamaños y naturaleza.[1] En la presente comunicación se muestra una nueva metodología para la síntesis de metalociclos mononucleares de tipo **M_1/M_2**, que presentan diferentes tamaños de cavidad y funcionalización. Dichas supramoléculas son sintetizadas mediante autoensamblaje en torno a centros metálicos de Pd(II) y Pt(II) de ligandos derivados de bipiridinio/diazapirenio de tipo **L_1/L_2**, preparados a su vez mediante reacciones de Zincke entre aminas quirales de tipo **A_1/A_2** y el precursor de tipo **P**.



Los campos en los que estos receptores presentan potencial aplicabilidad son múltiples, como por ejemplo el transporte de fármacos, reconocimiento de secuencias específicas de ADN [2], eliminación de contaminantes, etc.

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S7: *Metodología Sintética y Síntesis Total*

SYNTHESIS OF FUSED POLYCYCLIC INDOLES BY BRØNSTED ACID-CATALYZED INTRAMOLECULAR ALKYLATION OF INDOLES WITH ALCOHOLS

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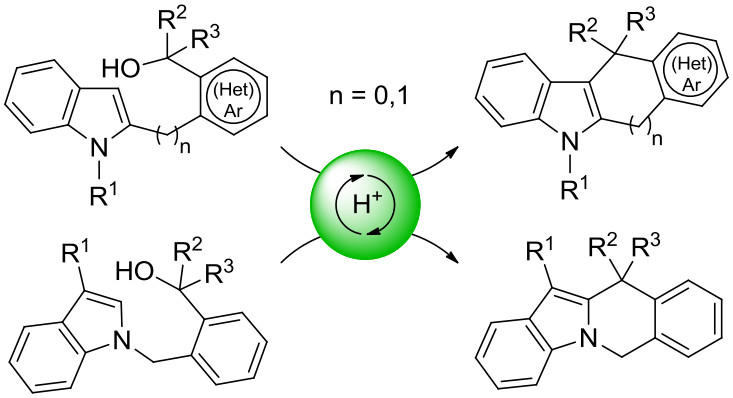
Keywords: *Brønsted acid catalysis; fused-ring systems; nitrogen heterocycles*

The indole nucleus is one of the most ubiquitous heterocyclic structures found in nature, and it is a fundamental constituent of numerous natural or synthetic bioactive compounds [1]. Accordingly, the development of sustainable and chemically efficient methodologies for the functionalization of indoles as well as for the preparation of new indole-derived scaffolds has been a major area of focus for synthetic organic chemists. In this regard, our group has described the direct C-3 alkylation of indoles with alcohols [2] and the straightforward synthesis of benzo[*b*]carbazoles from indoles and *ortho*-[α-(hydroxy)benzyl]benzaldehyde acetals [3], both under metal-free Brønsted acid-catalyis.

In this context, we considered that Brønsted acid-catalyzed alkylation of indole derivatives bearing an alcohol in their structure could be a feasible methodology to obtain diverse polycyclic frameworks. In this communication we report our achievements in this area which encompass the synthesis of C- and N-fused tetracyclic indoles with elusive substitution patterns as well as unknown thieno or indole fused cyclopenta[1,2-*b*]indole scaffolds (Scheme 1).



Scheme 1

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S7: *Metodología Sintética y Síntesis Total*

SÍNTESIS DE 2-AMINO(ARILAZO)PIRIDINAS Y PIRAZINAS A PARTIR DE AMINIDAS DE PIRIDINIO

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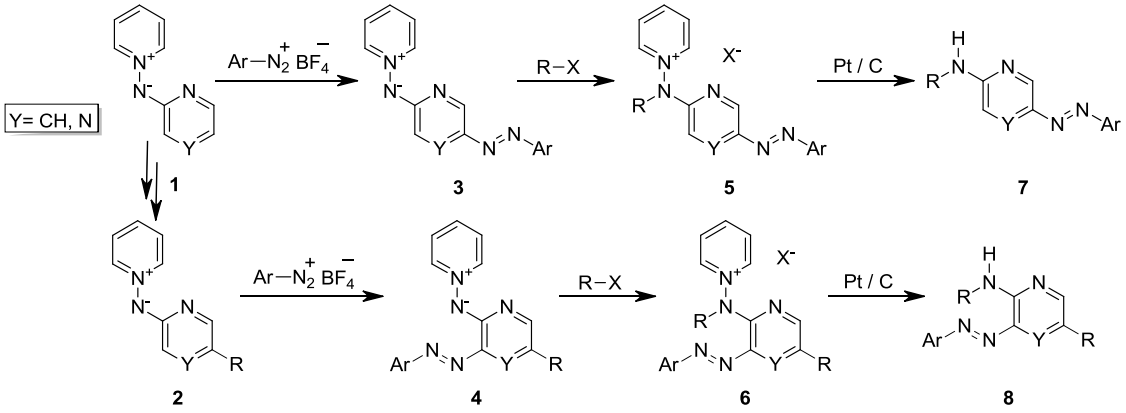
Palabras Clave: *Aminidas de piridinio, Azoderivados.*

Los compuestos tipo azoico se emplean como tintes en numerosos campos debido a su coloración intensa. Su preparación se suele llevar a cabo mediante acoplamiento entre una sal de diazonio y un sustrato aromático activado con grupos electrodadores.

Desde hace años, una parte de nuestra investigación se centra en el estudio de las *N*-heteroarilaminidas de piridinio **1** como intermedios sintéticos de heterociclos más complejos. [1] Estas aminidas reaccionan con electrófilos débiles como sales de diazonio, [2] para dar los productos **3** y **4**, que se han empleado como sustratos de partida para la síntesis de las amino(arilazo)piridinas y pirazinas **7** y **8**.



En esta comunicación, presentamos los resultados obtenidos en la síntesis de los compuestos mostrados en el esquema: Partiendo de las aminidas **1** y **2**, se obtuvieron los productos **3** y **4** mediante reacción con sales de arildiazonio en condiciones básicas. La alquilación regioselectiva con haluros de alquilo sobre el nitrógeno exocíclico dio lugar a las sales **5** y **6**. Finalmente, las aminas finales **7** y **8** se sintetizaron por ruptura selectiva del enlace *N-N* en condiciones reductoras.

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S7: *Metodología Sintética y Síntesis Total*

SÍNTESIS Y CARACTERIZACIÓN DE NUEVOS AZABORINOS POLICÍCLICOS

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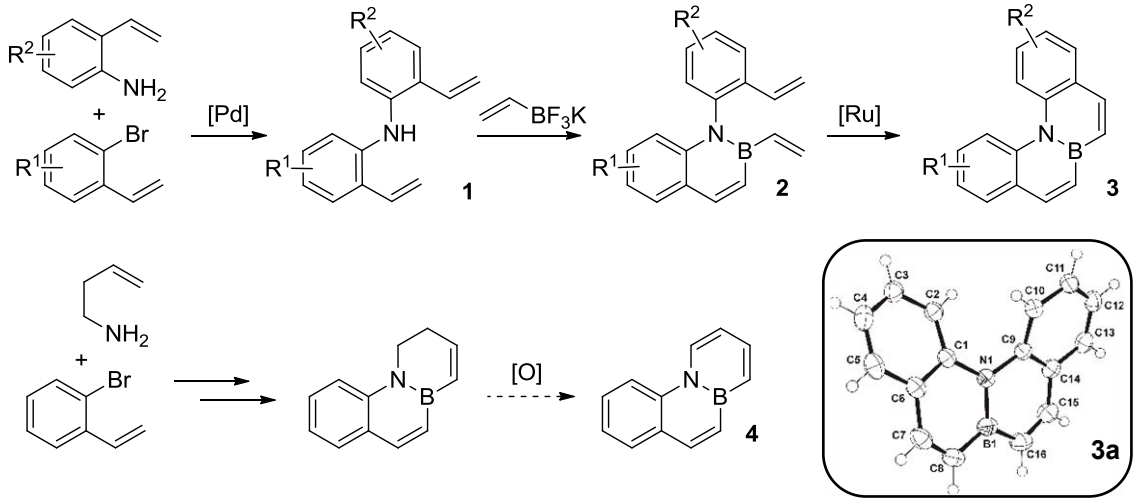
Palabras Clave: *azaborino, acoplamiento, trifluoroborato, metátesis*

Los azaborinos son compuestos aromáticos en los que un enlace C=C se ha sustituido con el isoelectrónico B-N. [1] De este modo es posible acceder a nuevos compuestos estructuralmente semejantes a sus análogos carbonados pero con propiedades muy diferentes, principalmente desde un punto de vista fotofísico, lo que presenta un gran interés en el diseño y producción de nuevos materiales. No obstante el número de azaborinos conocidos es todavía limitado y la mayor parte de procedimientos para su síntesis carecen de la eficiencia o generalidad deseadas.

En este contexto, hemos desarrollado una síntesis para la obtención de los azaborinos tetracíclicos **3**, previamente desconocidos. Las aminas **1**, obtenidas por acoplamiento tipo Buchwald-Hartwig entre los bromoestirenos y aminoestirenos correspondientes, experimentan una ciclación con viniltrifluoroborato de potasio generando el azaborino bicíclico **2**, [2] que mediante una reacción de metátesis conduce a los azaborinos tetracíclicos **3**. De este modo se ha podido acceder al azaborino **3a** (R^1= R^2= H), que ha sido caracterizado mediante experimentos de difracción de rayos X. Además, actualmente están en vías de preparación otros azaborinos **3** dotados de grupos de diferente naturaleza en distintas posiciones, así como el azaborino tricíclico **4**, accesible mediante una ruta análoga seguida de una etapa de oxidación. De este modo se dispondrá de una familia de azaborinos de los cuales se estudiarán sus propiedades. En particular, se evaluará la fluorescencia de estas moléculas, campo en el que se esperan obtener resultados de interés.



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S7: *Metodología Sintética y Síntesis Total*

ACCESS TO ENANTIOPURE 1,5-AMINOALCOHOLS: SYNTHESIS OF *HALICLONA* ALKALOIDS

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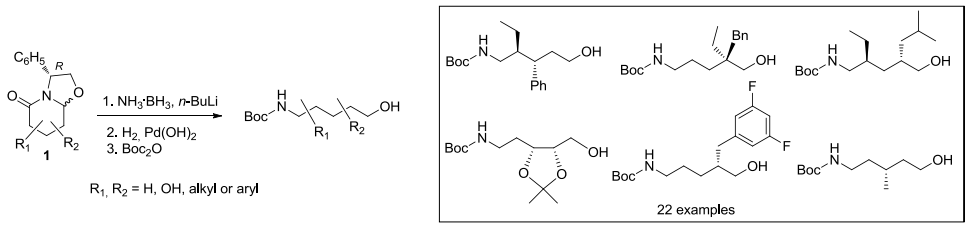
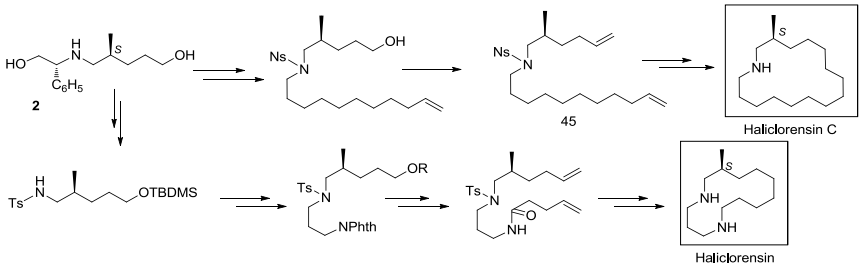
Keywords: *alkaloids, enantioselective synthesis, aminoalcohols, phenylglycinol-derived lactams*

The preparation of a variety of enantiopure 2-, 3-, 4-, 2,2-, 2,3-, 2,4-, and 3,4-substituted 5-aminoalcohols from phenylglycinol-derived oxazolopiperidone lactams **1** under $LiNH_2BH_3$ reduction conditions, in an unprecedented process featuring the reductive opening of both oxazolidine and lactam rings, will be presented.



The synthetic usefulness of these enantiopure scaffolds is illustrated with the total synthesis of the *Haliclona* alkaloids haliclorensin C (first total synthesis) and haliclorensin (only two previous synthesis) starting from (*S*)-4-methyl-5-aminopentanol **2**.[1]



These results significantly expand the potential of phenylglycinol-derived δ-lactams,[2] opening new perspectives in the enantioselective synthesis of nitrogen-containing natural products.

We acknowledge financial support from MINECO (projecte CTQ2012-35250) and the AGAUR, Generalitat de Catalunya (Grant 2014-SGR-0155).

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S7: *Metodología Sintética y Síntesis Total*

MULTICOMPONENT REACTION OF ARYNES, IMINES AND NITRILES

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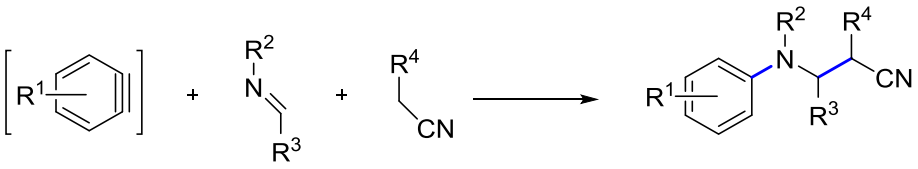
Keywords: *arynes, multicomponent reaction, nitriles.*

Aryne-based synthetic methodology has become a powerful tool to prepare natural products and molecular materials.[1] In particular, multicomponent reactions, in which three or more molecules react in one-step to form complex molecular structures, are specially interesting.[2]

Here we describe a multicomponent reaction between arynes, imines and nitriles to prepare chiral β-aminonitriles.[3] It should be mentioned that two new bonds are formed (C-C and C-N) in one-step without the use of metal catalysts, showing the great potencial of this transformation.



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S7: *Metodología Sintética y Síntesis Total*

SÍNTESIS ESTEREOSELECTIVA DE TETRAHIDROPIRANOS PENTASUSTITUIDOS

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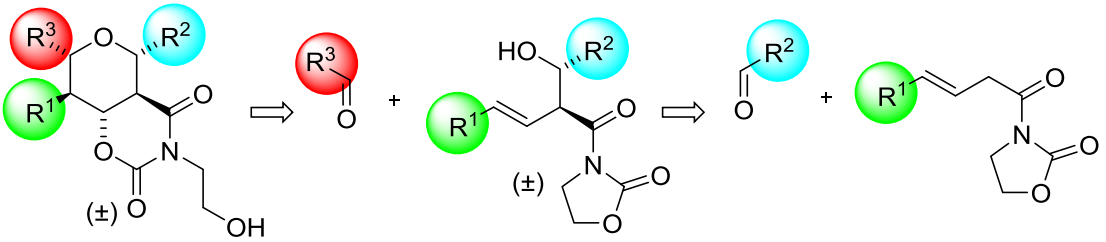
Palabras Clave: *tetrahidropirano, síntesis diastereoselectiva, reacción aldólica de Evans, reacción de Prins*

La reacción de Prins fue descubierta en 1919 por Hendrik Jacobus Prins [1]. Posteriormente, Stapp llevó a cabo dicha reacción observando la generación de tetrahidropiranos (THPs) a partir de alcoholes homoalílicos [2]. Debido al descubrimiento de nuevos productos naturales bioactivos portadores de este tipo de éteres cíclicos, a finales de los años 90 la reacción de Prins se estableció como una poderosa herramienta para la síntesis de estas estructuras.

En el trabajo que se presenta en esta comunicación se podrá analizar cómo, ahondando en las posibilidades que ofrece la reacción de Prins, se pueden sintetizar, de forma diastereoselectiva y utilizando una gran variedad de sustituyentes, estructuras bicíclicas portadoras de un anillo de THP totalmente sustituido e inéditas en la bibliografía. Para ello se emplearán alcoholes secundarios homoalílicos portadores de un grupo *N*-aciloxazolidona, accesibles a través de una reacción aldólica de Evans [3].



Agradecimientos

Este proyecto ha sido cofinanciado por el Ministerio de Economía y Competitividad (MINECO, CTQ2011-28417-C02-01), el Fondo Europeo de Desarrollo Regional (FEDER), el Ministerio de Educación, Cultura y Deporte (MECyD, Programa Campus de Excelencia Internacional CEI10/00018) y por EU ResearchPotential (FP7-REGPOT-2012-CT2012-31637-IMBRAIN). S.J.A.-M. agradece al MECyD por la beca FPU concedida.

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S7: *Metodología Sintética y Síntesis Total*

REACTION OF ARYNES WITH THIOUREAS: SYNTHESIS OF THIOXANTHONES

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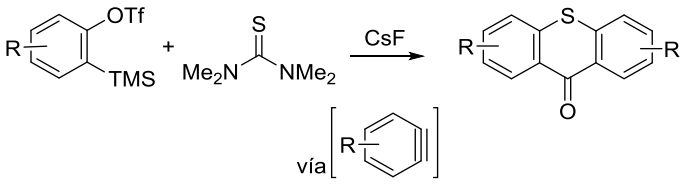
Keywords: *arynes, thioureas, thioxanthones*

In recent years, aryne chemistry has shown to be extremely useful for the preparation of natural products and molecular materials.[1] One of the most interesting reactions in this field is the formal insertion of arynes into σ or π bonds.[2] For example, in 2011 Greaney and Biswas reported the insertion of arynes into thioureas to obtain amidines.[3] Here we describe that by varying certain reaction conditions, the intermediates of this process can evolve to form thioxanthones, an interesting family of bioactive compounds.[4]



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S7: *Metodología Sintética y Síntesis Total*

DESARROLLO DE UNA RUTA SINTÉTICA PARA LA OBTENCIÓN DE LA FEROMONA SEXUAL DEL PIOJO BLANCO DEL LIMÓN (*Aspidiotus nerii*)

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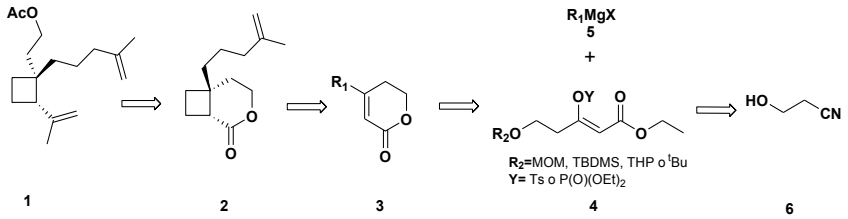
Palabras Clave: *Síntesis total; 4-alquil-5,6-dihidro-2H-piran-2-ona; Cicloadición [2+2]; Feromona sexual; Aspidiotus nerii*.

La feromona sexual de *Aspidiotus nerii* ha sido indentificada,[1] como acetato de 2-[(1*R*,2*S*)-*cis*-2-isopropenil-1-(4´-metil-4´-pentenil)-ciclobutano]etilo **1**, las rutas sintéticas descritas para obtenerla presentan un elevado número de etapas y un rendimiento global bajo.[1,2] Se ha propuesto una ruta sintética a escala multigramo, usando un menor número de etapas y productos de partida de bajo coste para obtener el derivado 4-alquil-5,6-dihidro-2H-piran-2-ona **3** como intermedio clave (esquema 1).



Esquema 1. Esquema retrosintético de la síntesis de la feromona sexual de A. nerii, a partir de 3-hidroxipropanonitrilo **6**.

El intermedio clave **3** puede obtenerse a partir de una reacción de lactonización del alquil ester α,β insaturado resultante de la reacción de acoplamiento del enoltosilato o fosfato **4** con el reactivo de Grignard adecuado **5** para la introducir la cadena lateral (R_1) necesaria. La inversión de estas etapas de lactonización y acoplamiento también permiten obtener buenos rendimientos. El enoltosilato o fosfato **4** puede obtenerse a partir del -hidroxipropanonitrilo **6** convenientemente protegido y el zincato derivado de etilbromoacetato medinte una reacción de Blaise. Actualmente se está trabajando en la optimización de la conversión del intermedio **3** en el intermedio con el anillo ciclobutano **2**, bien de manera racémica o estereoselectiva. Resultados preliminares de reacciones fotoquímicas de la lactona **3** con vinilacetato muestran la viabilidad de la transformación de este intermedio con buenos rendimientos.

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S7: *Metodología Sintética y Síntesis Total*

DIVERGENT ACCESS TO CARBOCYCLIC SKELETONS BY GOLD(I) AND PLATINUM(II) CATALYZED CYCLOADDITIONS OF ALLENEDIENES

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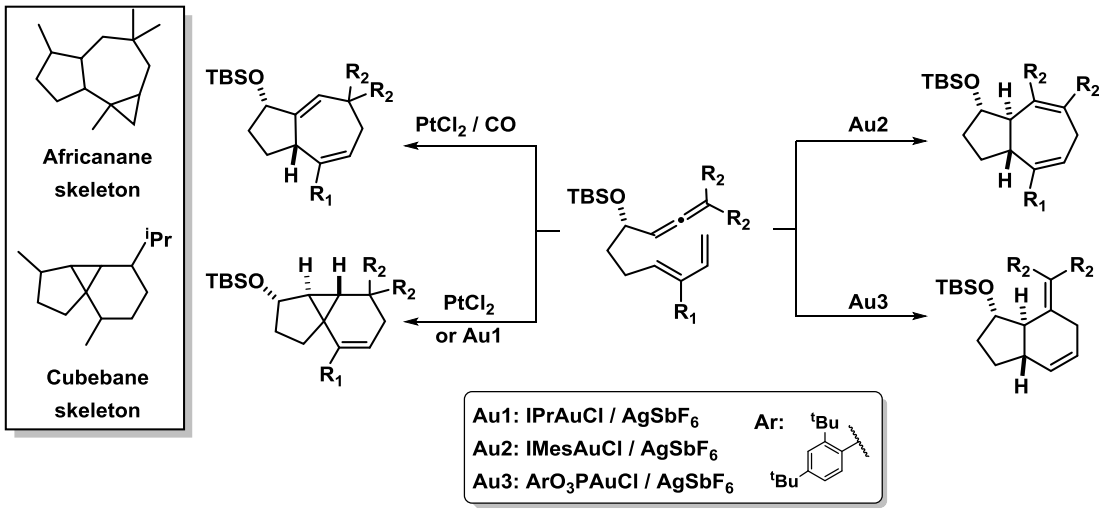
Keywords: *Gold catalyzed, Platinum catalyzed, Cycloadditions, Terpenoids.*

Cycloaddition reactions are among the most practical and efficient methods to construct cyclic products from relatively simple, acyclic starting materials.[1] Our group has developed intramolecular [4C+3C] cycloadditions of allenedienes promoted by $PtCl_2$ or *N*-heterocyclic carbene-gold (I) complexes,[2] and [4C+2C] cycloadditions promoted by phosphite-gold (I) complexes.[3] We show herein further details of the scope of this process and demonstrate that subtle modifications in the catalyst change the outcome of the reaction. Some of the transformations allow the assembly of different carbocyclic skeletons that form the basic core of natural sesquiterpenes.



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S7: *Metodología Sintética y Síntesis Total*

FRIEDEL-CRAFTS REACTIONS OF *p*-QUINOLS

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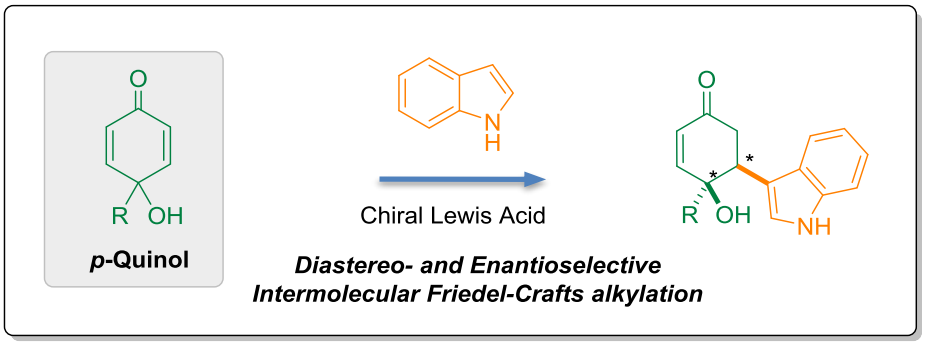
Palabras Clave: *p-Quinol,Indole, Friedel-Crafts, enantioselective conjugated additions.*

The *p*-quinol (4-alkyl-4-hydroxy-2,5-cyclohexadienone) moiety is frequently present in a great number of natural products with simple or complex structures. Some of them show a wide range of interesting biological properties such as antitumoral and trypanocides. From the synthetic point of view, the 2,5-cyclohexadienone framework is a very interesting organic motif because it can undergo a large array of useful transformations en route to highly functionalized cyclohexane derivatives.[1] Despite the importance and abundance of indoles[2] in nature and their excellent role as nucleophiles in Friedel-Crafts-type addition reactions, there are no studies of the intermolecular Michael addition reaction with *p*-quinols. We have studied the study of the behavior of *p*-quinols as electrophile in Friedel-Crafts alkylation reactions of π-excedent heteroaromatic derivatives (Scheme1). The incorporation of heteroaromatic fragments into the *p*-quinol skeleton via 1,4-addition of the π-excedent system to the enone moeity, is of huge interest due to the high synthetic potential of the resulting structures. Moreover, we have developed an asymmetric version of the Friedel-Crafts reaction using enantiopure phosphoric acids.



Scheme1

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S7: *Metodología Sintética y Síntesis Total*

ENANTIOSELECTIVE TOTAL SYNTHESIS OF (-)-LEPADIN A-C AND (+)-LEPADIN D

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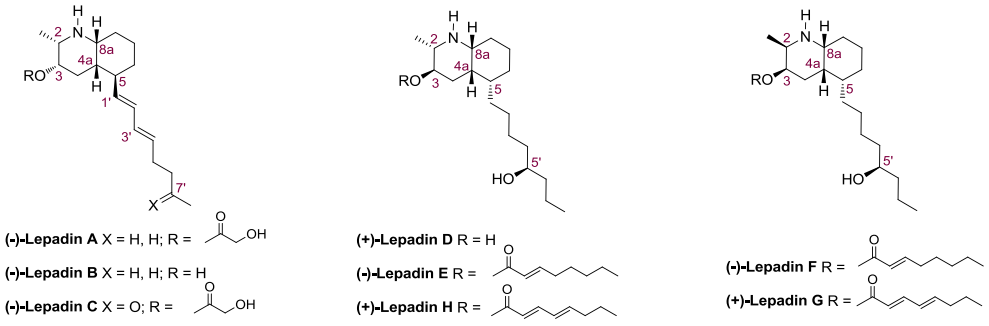
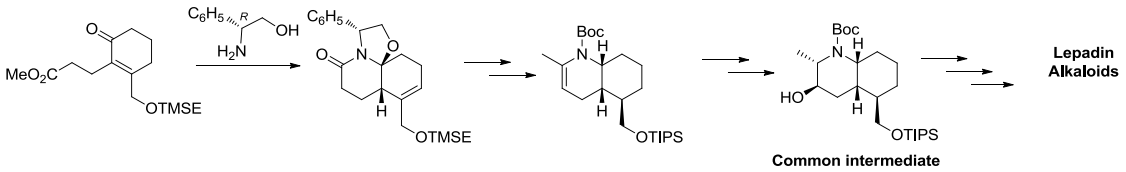
Keywords: *total synthesis, cis-decahydroquinolines, chiral lactams, alkaloids*

The lepadin alkaloids, comprising eight *cis*-decahydroquinoline members, were identified from 1991 to 2002 from different marine sources such as the tunicate *Clavelina lepadiformis*, flatworm *Prosthececeraeus villatus*, tropical marine tunicate *Didemnum* sp., and Australian Great Barrier Reef ascidian *Aplidium tabascum*.[1] Lepadins A and B have been shown to exhibit significant *in vitro* cytotoxicity against several human cancer cell lines.[1a,b] In addition, lepadin B is a potent blocker for neuronal nicotinic acetylcholine receptors (nAChR's). Lepadins D-F have low cytotoxicity but significant and selective antiplasmodial and antitrypanosomal activity.[1c]



In the context of our studies[2] on the use of phenylglycinol-derived chiral tricyclic lactams for the enantioselective synthesis of alkaloids, we will present our studies on the synthesis of the lepadin family of alkaloids, which have culminated in the syntheses of (-)-lepadins A-C[3] and (+)-lepadin D.



Acknowledgment: Financial support from the MICINN, Spain (CTQ 2012-35250), and the AGAUR, Generalitat de Catalunya (2014-SGR-0155).

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S7: *Metodología Sintética y Síntesis Total*

1,7-NAPHTHODIYNE: NEW PLATFORM FOR THE SYNTHESIS OF STERICALLY CONGESTED PAHs

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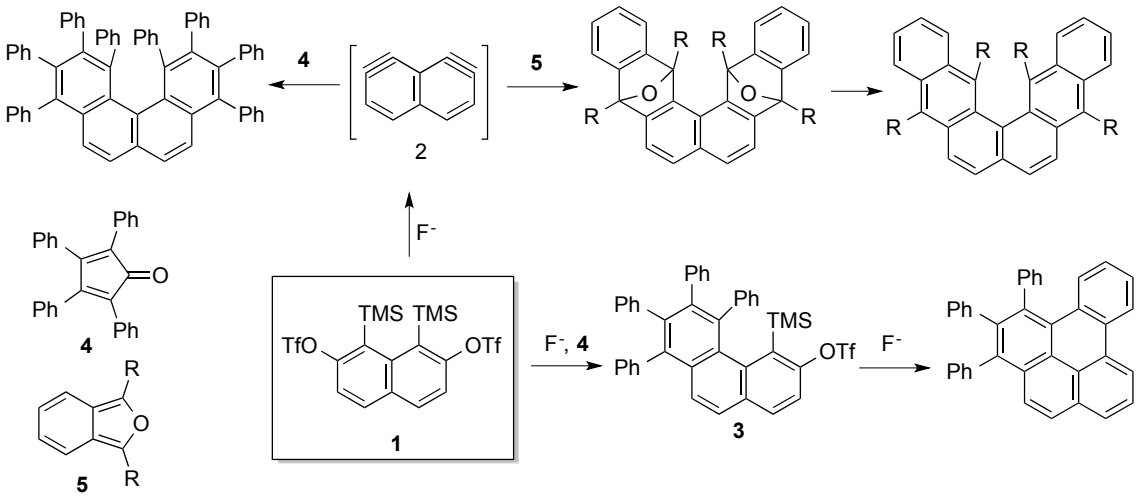
Bisaryne synthons are useful building blocks for the construction of large, extended HPAs. Generation of these reactive species in the presence of a diene leads to two sequential cycloaddition reactions in a single synthetic operation [1], while the selective generation of one triple bond and subsequent reaction with an adequate partner, allows the straightforward access to new structurally complex aryne precursors [2,3]. Here we report the synthesis and reactivity of 1,8-bis(trimethylsilyl)naphthalene-2,7-diyl bistriflate (**1**), an efficient precursor of the novel 1,7-naphthodiyne synthon **2**. Preliminary experiments demonstrate the usefulness of this platform for the synthesis of novel, sterically congested PAHs, such as helicenes and angularly fused acene derivatives. Furthermore, a novel intramolecular aryne trapping reaction will be described.



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S7: *Metodología Sintética y Síntesis Total*

SÍNTESIS DE METALOCICLOS DE Pd (II) Y Pt (II) FUNCIONALIZADOS

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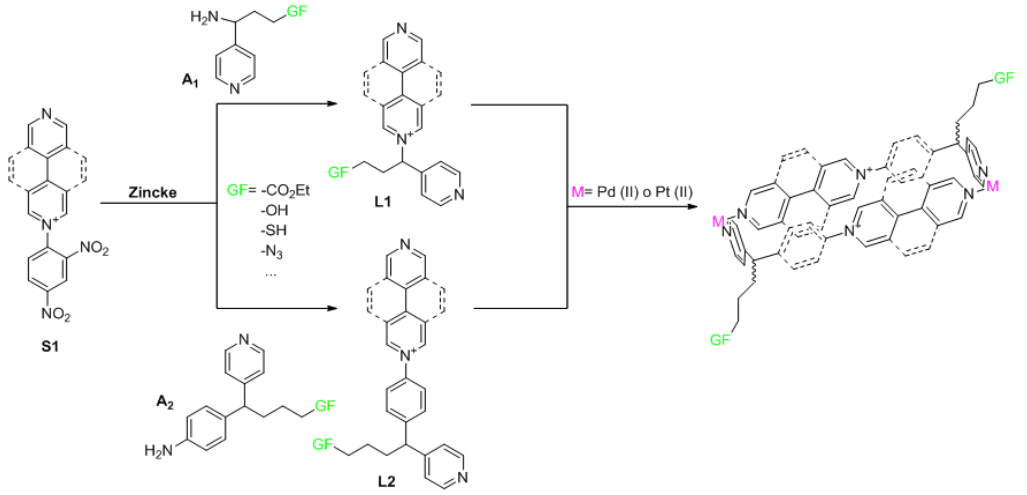
Palabras Clave: *reacción de Zincke, química supramolecular, autoensamblaje, metalociclos, receptores moleculares.*

Actualmente, una de las áreas más activas en el campo de la Química Supramolecular, y en particular en el campo del autoensamblaje dirigido por centros metálicos, consiste en el desarrollo de sistemas supramoleculares funcionalizados basados en estructuras metalocíclicas [1]. En este contexto, se presenta aquí el diseño y síntesis de los ligandos bidentados de tipo **L1** y **L2**, basados en sales de monoalquil-4,4'-bipiridinio/2,7-diazapireno y que presentan funcionalización en posición α al nitrógeno alquilado del heterociclo. La síntesis de estos ligandos quirales se lleva a cabo mediante una estrategia convergente, que utiliza como etapa clave la reacción de Zincke entre sales del tipo **S1** y aminas de tipo **A1** y **A2**.



El autoensamblaje de los ligandos con centros metálicos de Pd (II) y Pt (II), conduce a receptores que presentan funcionalización fácilmente modulable en α al nitrógeno alquilado, y que poseen la capacidad de reconocer sustratos a partir del efecto hidrofóbico, apilamiento π-π y aquellas interacciones adicionales resultantes de la funcionalización introducida. Además, la presencia de quiralidad en estos receptores abre un amplio abanico de posibilidades en el reconocimiento de sustratos enantioméricamente puros, lo que presenta un gran interés en diversas áreas, como por ejemplo, en la biomédica.

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S7: *Metodología Sintética y Síntesis Total*

TRUNCATED POLYCYCLIZATIONS AND UNEXPECTED STEREOSELECTIVITIES IN Ti (III)-CATALYZED CYCLIZATIONS OF KETOEPOXYPOLYPRENES

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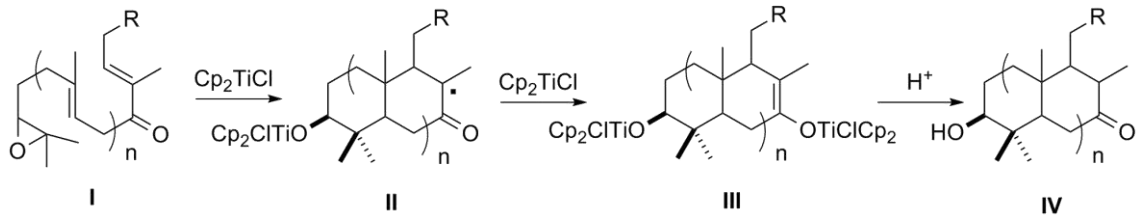
In recent years, the radical cyclization of epoxypolyprenes catalyzed by titanocene(III) complex Cp_2TiCl has emerged as a powerful tool for the synthesis of terpenic structures. This bioinspired protocol has been used for the cyclization, under smooth reaction conditions, of different polyprenes with high diastereoselectivity. [1] However, the preparation of compounds from incomplete cyclizations was not possible using this method.

In the present communication, we describe a new strategy to control the number of cyclization steps in bioinspired radical (poly)-cyclizations involving epoxypolyenes containing keto units positioned along the polyene chain. This approach provides an unprecedentedly straightforward access to natural terpenoids with pendant unsaturated side chains. Additionally, in the case of bi- and tricyclizations, decalins with cis stereochemistry have been obtained because of the presence of the ketone. The preferential formation of cis-fused adducts was rationalized using DFT calculations. This result is unprecedented in biomimetic cyclizations and permits the access to natural terpenoids with this stereochemistry, as well as to non-natural analogues. [2]



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S7: *Metodología Sintética y Síntesis Total*

SYNTHESIS OF POLYENES BY HIYAMA-DENMARK CROSS-COUPLING

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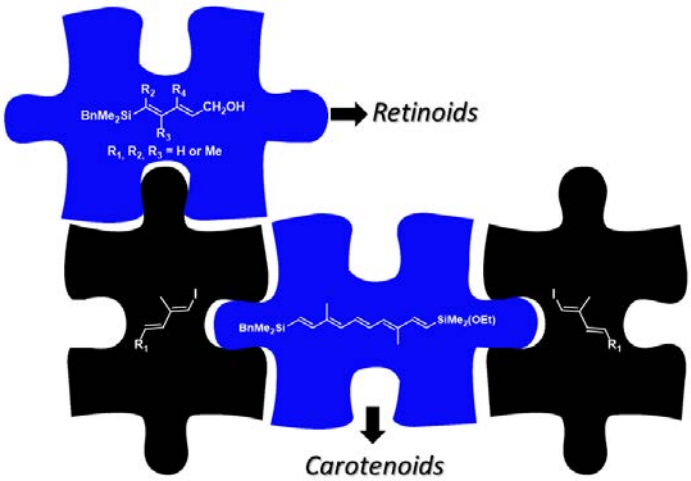
Keywords: *polyenes, Hiyama-Denmark, palladium, cross-coupling, heterobis-silanes*

A large number of compounds contain polyene chains in their structure, such as retinoids or carotenoids and this conjugated system is mainly responsible for their important biological activities.[1] A general method for the synthesis of these polyene moieties on based in the use of Pd-catalyzed cross-coupling reactions, such as Negishi, Stille-Migita-Kozugi or Suzuki-Miyaura.[2] Despite their selectivity and versatility, these reactions are not free of limitations, among them the toxicity or the stability of the nucleophilic organometallic component (i.e. stannane and organoboron compounds, respectively).

Alternatively, organosilanes developed by Hiyama and Denmark are stable, easy to prepare and use, and respectful with the environment. As a consequence the Hiyama-Denmark cross-coupling reaction has lately been considered as a useful tool in the synthesis of conjugated compounds.[3] We will present our recent contributions to the scope of the Hiyama-Denmark reaction in the synthesis of biologically active polyenes.



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S7: *Metodología Sintética y Síntesis Total*

HIDROSILILACIÓN DE ALQUINOS MARKOVNIKOV CATALIZADA POR PARTES POR MILLÓN DE PLATINO

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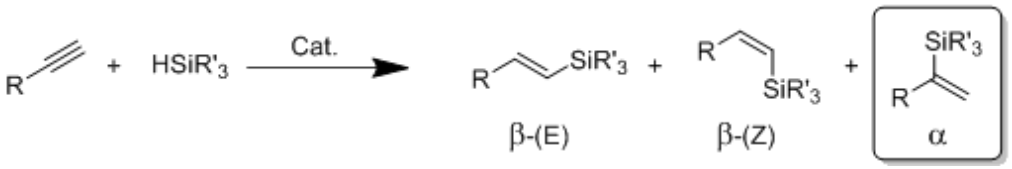
Palabras Clave: *Catálisis, Platino, Vinilsilanos, Hidrosililación, Alquinos*

La hidrosililación de alquinos es el método más sencillo de obtener vinilsilanos, que son intermedios de interés en síntesis orgánica para acoplamientos C-C [1] y oxidaciones[2]. En alquinos terminales existen tres posibles isómeros (Figura): β-(E) (el termodinámicamente más estable), β-(Z) y α. Existen numerosas metodologías sintéticas para obtener regioselectivamente los dos isómeros β [3,4], sin embargo el producto Markovnikov solo se ha obtenido hasta la fecha con un complejo de rutenio catalítico (1mol%) que produce selectivamente el compuesto α para alquinos oxigenados [5].



Los catalizadores de platino son tradicionalmente empleados en la síntesis del isómero β-(E) y en nuestro grupo hemos observado que al disminuir la cantidad de platino significativamente (2-3 órdenes de magnitud) e independientemente de la especie de platino empleada se obtiene preferentemente el isómero α, con una elevada actividad (TOF superiores a 10^5) y cantidad de catalizador menor a 50ppm respecto a los reactivos. Esto nos lleva a pensar que las especies de platino añadidas a la reacción son precatalizadores y que las especies activas se forman *in situ* en el medio de reacción, de modo que determinando la especie de Pt que cataliza a cada regioisómero, aislándola y poniéndola directamente en reacción nos permitirá tener catalizadores altamente eficientes y regioselectivos. Esto se cumple para un amplio rango de sustratos (50 alquinos y 8 silanos diferentes) de distinta naturaleza: alifáticos, aromáticos y con diversos grupos funcionales. La cantidad obtenida de los regioisómeros depende de la naturaleza estérica y electrónica de los alquinos de partida y no de la especie de platino puesta en la reacción y varía entre 1:1 y >15:1.

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S7: *Metodología Sintética y Síntesis Total*

DIMERIZATION OF A HIGHLY PYRAMIDALIZED ALKENE TO A HYDROCARBON FEATURING FOUR CYCLOHEXANE RINGS IN BOAT CONFORMATIONS

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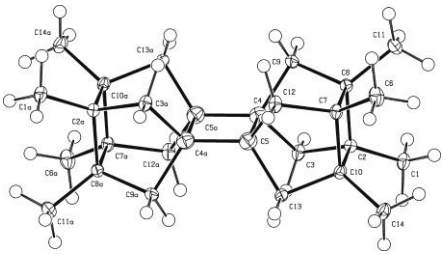
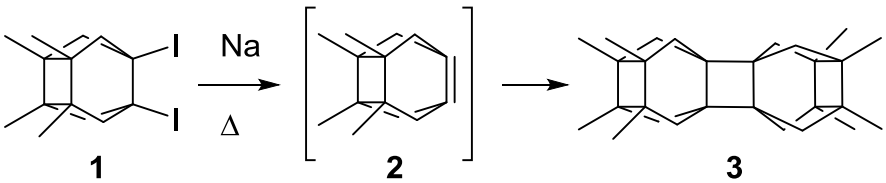
Keywords: *dimerization, hydrocarbons, pyramidalized alkenes, strained compounds*

Pyramidalized alkenes are compounds containing carbon-carbon double bonds in which one or both of the sp^2-carbon atoms do not lie in the same plane as the attached atoms. [1] We have previously reported the generation, trapping, and dimerization of several highly pyramidalized alkenes and the first cross-coupling of two different pyramidalized alkenes. [1-2] Herein, we report the generation of **2**, a novel highly pyramidalized alkene, its trapping with 1,3-diphenylisobenzofuran, and its dimerization to a unique polycyclic hydrocarbon, **3**. [3]

X-Ray diffraction analysis unequivocally established the structure of **3** and revealed several interesting features: three planar cyclobutanes, four cyclopentane rings in a "frozen" envelope conformation, and four cyclohexane rings in a boat conformation with the distances between the flagpole hydrogen atoms and the flagpole carbon



atoms smaller than the sum of the van der Waals radius of the involved atoms. Rather surprisingly, in spite of the three cyclobutane rings, nonacyclo **3** is thermally stable up to 500 °C.



1 **2** **3**

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S8. Química Sostenible (QS) / Green Chemistry

Este Simposio está llamado a servir de punto de encuentro de los investigadores que trabajan en este campo. Orientado haciaconceptos clásicos como la catálisis, la economía atómica y la utilización de materias primas renovables, también se abordarán otros aspectos como el desarrollo de procesos en condiciones no clásicas, la utilización de medios no convencionales y otros relacionados con la sostenibilidad en los procesos químicos. Los conferenciantes invitados darán perspectiva actual del tema.

This symposium is intended to be a meeting point for researchers working in this field. Oriented toward classical concepts such as catalysis, atom economy and usage of renewable feedstock, it will also pay attention to other aspects: development of processes under non-classical conditions, usage of non-conventional media and other aspects related to sustainability in chemical processes. The invited speakers will give an up-to-date perspective of the topic.

Organizadores:

Luis Sarandeses (UDC)

José Pérez Sestelo (UDC)

e-mail de contacto: luis.sarandeses@udc.es

Simposio patrocinado por los Grupos Especializados de Química Orgánica, Química Organometálica y Fotoquímica

Martes 21 de Julio 2015

08:40 – 09:40	**PL-3**	***Conferencia Plenaria*** (Común a todos los simposios) **Samuel I. Stupp** *"Supramolecular Materials Chemistry"*

Chairman: José Pérez Sestelo

10:00 – 10:30	**S8-IL-01**	**Robert E. Maleczka, Jr.** *"Advancing C-H Borylations and Green Chemistry through Academic-Industrial Collaborations"*
10:30 – 11:00	**S8-IL-02**	**Rubén Martín** *" Metal-Catalyzed Functionalization of C-O Bonds and CO_2"*
11:00 – 11:30		Pausa Café

Chairman: Moisés Canle López

11:30 – 12:00	**S8-IL-03**	**Sixto Malato** *"Descontaminación de Aguas Utilizando Radiación Solar: Un Proceso Doblemente Sostenible"*
12:00 – 12:15	**S8-OC-01**	**Víctor de la Peña O'Shea** *"Nuevos Avances en la Producción de Combustibles Solares mediante Fotosíntesis Artificial"*
12:15 – 12:30	**S8-OC-02**	**Rebeca Martínez-Haya** *"Photocatalytic Oxidation of Cork Wastewater Pollutants Using Triphenyl(thia)pyrylium Salts"*
12:30 – 12:45	**S8-OC-03**	**Armelle Ouali** *"Design and Preparation of Eco-Compatible Catalysts"*
12:45 – 13:00	**S8-OC-04**	**Joaquín García Álvarez** *"New Synthetic Applications for Deep Eutectic Solvents: Green Reaction Media for Au(I)-Catalyzed Cycloisomerizations"*
13:00 – 13:15	**S8-OC-05**	**Eduardo García-Verdugo** *"ILS-Based Materials as Enabling Tool for the Design of Chemical Processes"*
13:30 – 15:30		Comida

Martes 21 de Julio 2015

Chairman: Luis Sarandeses

15:30 – 16:00	**S8-IL-04**	**Marc Taillefer** *"Metal Catalyzed Arylation of Nucleophiles: Recent Progress and Mechanistic Insight"*
16:00 – 16:15	**S8-OC-07**	**Rodrigo García-Loma** *"Recyclable Polymer-Supported Tin Hydrides for Clean Radical Dehalogenation Reactions"*
16:15 – 16:30	**S8-OC-08**	**Miguel Peña-López** *"Ruthenium-Catalyzed Synthesis of Heterocycles Using Hydrogen Autotransfer Methodology"*
16:30 – 17:00		Pausa Café

Chairwoman: Teresa Rodríguez-Blas

17:00 – 17:30	**S8-IL-05**	**Miquel Costas** *"Selective Oxidation Reactions with Bioinspired Catalysts"*
17:30 – 17:45	**S8-OC-09**	**Julio Lloret-Fillol** *"Aminopyridine Ligands as Platforms for Well-Defined Light-Driven Cobalt Reduction and Iron Water Oxidation Catalysts"*
17:45 – 18:00	**S8-OC-10**	**Ana Pereira** *"Detección de Intermedios Metalocarbénicos de Cobre en la Reacción de Funcionalización del Enlace O-H del H_2O"*
18:00 – 18:05	**S8-FC-01**	**Sonia Abás** *"A Green Access to (2-imidazolin-4-yl)phosphonates"*
18:05 – 18:10	**S8-FC-02**	**Larisha Cisneros** *"Acoplamiento Reductivo de Nitrocompuestos, Aldehidos e Hidrógeno para Formación de Nitronas Usando Nanopartículas de Platino sobre Carbón Activo"*
18:10 – 18:15	**S8-FC-03**	**M. Pilar Gay** *"Nuevos Sistemas Os-NHC para el Estudio de Procesos Sostenibles"*
18:15 – 18:20	**S8-FC-04**	**Sergio Mata** *"Funcionalización del Enlace Si-H mediante un Proceso Multicomponente Catalizado por Cloruro de Zinc"*
18:20 – 18:25	**S8-FC-05**	**José R. Ochoa-Gómez** *"Hydrolisis Lignin Valorisation: Simultaneous Synthesis of Lactic Acid and Phenolics"*
18:25 – 18:30	**S8-FC-06**	**Ruth Sánchez-Hernández** *"Síntesis a Escala Piloto de NaP1 a Partir de un Residuo Peligroso y su Utilización como Adsorbente de Mercurio"*
18:30		***Sesión de Pósteres***

Comunicaciones Invitadas (IL)

S8: *Química Sostenible*

ADVANCING C-H BORYLATIONS AND GREEN CHEMISTRY THROUGH ACADEMIC-INDUSTRIAL COLLABORATIONS

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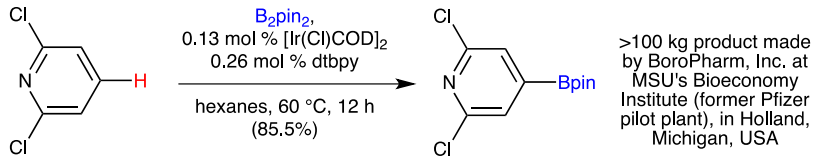
Keywords: *green chemistry, cross-couplings, CH activation, borylation*

Ir-catalyzed C–H borylations can eliminate the need for halogens, alkyllithiums, and/or cryogenic conditions for the syntheses of cross-coupling partners. [1,2] Given the prominent role cross-couplings play in the preparation of pharmaceuticals, agrochemicals, and organic electronic materials, industry has shown considerable interest in such C–H activation processes. Indeed, the Pharmaceutical Roundtable of the American Chemical Society's Green Chemistry Institute deemed cross-couplings that avoid haloaromatics as one of their top aspirational reactions. [3]



With this in mind, we teamed up with Merck [4,5,6] to advance Ir-catalyzed C–H borylations and eliminate the need for halogens in both electrophilic and nucleophilic cross-coupling partners. We are also working with Dow [7] to overcome other barriers to this chemistry being broadly adopted by industry. This talk will describe the research that led to these collaborations and how working to make C–H borylations industrially viable is helping advance our "academic" understanding of the chemistry.

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S8: *Química Sostenible*

METAL-CATALYZED FUNCTIONALIZATION OF C-O BONDS AND CO_2

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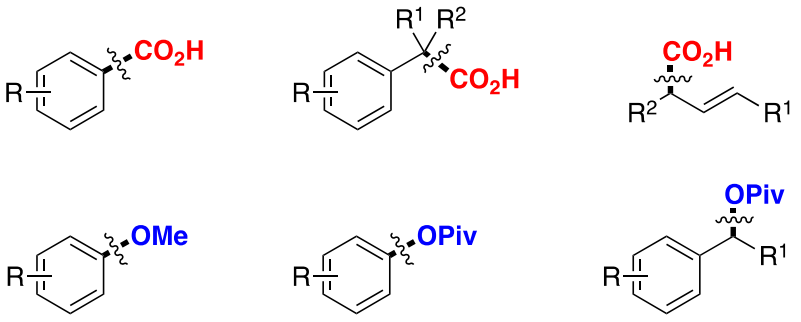
Keywords: *C-O Bonds, Carbon Dioxide, Nickel, Cross-Coupling, Reductive Couplings*

Activation of inert entities has been and continues to be of extreme interest to any organic chemist.[1] This is especially true with activation of atmospheric molecules such as CO_2[2] or the activation of relatively inert C- O bonds.[3] The development of operationally-simple and practical catalytic methods for the activation of the above-mentioned entities would be highly desirable, as many of the current methods involve the use of stoichiometric amounts or air-sensitive organometallic reagents. In the last years, our research group has reported some progress directed towards the catalytic activation of C-O bonds and CO_2 fixation (Scheme 1).[4] These methods are characterized by their simplicity, wide substrate scope, including challenging substrate combinations with particularly sensitive functional groups.



Scheme 1. *Metal-catalyzed functionalization of C-O bonds and CO_2 at Martin´s laboratories*

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S8: *Química Sostenible*

DESCONTAMINACIÓN DE AGUAS UTILIZANDO RADIACIÓN SOLAR: UN PROCESO DOBLEMENTE SOSTENIBLE

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Palabras Clave: *fotocatálisis, foto-Fenton, fotoreactores solares*

Los Procesos Avanzados de Oxidación pueden definirse de como técnicas de tratamiento basados en la acción de especies altamente reactivas, los radicales hidroxilo, que conducen a la oxidación completa de los contaminantes. En los últimos 30 años, se ha desarrollado mucho conocimiento sobre los PAOs debido a la variedad de tecnologías disponibles y el amplio campo de aplicaciones posibles. Entre los PAOs se incluyen, entre otros, la fotocatálisis homogénea y heterogénea en presencia de radiación solar ultravioleta (UV) o radiación visible [1]. Los PAOs tienes como principal aplicación el tratamiento de aguas residuales industriales conteniendo contaminantes tóxicos o no biodegradables pero también se pueden aplicar en aguas subterráneas o bien como tratamiento terciario en EDARs, producción de agua ultrapura, tratamiento de compuestos orgánicos volátiles, etc [2]. La instalación y operación de los PAOs supone un coste relativamente alto y por tanto se considera el uso de energía solar como una de las principales características que los pueden hacer sostenibles. Los primeros fotorreactores solares utilizados para aplicaciones fotocatalíticas se desarrollaron alrededor de 1990 y desde entonces se ha impulsado el diseño de fotorreactores capaces de emplear no sólo radiación solar directa sino también la difusa, y de elevada eficiencia óptica y cuántica.

Es evidente que cada agua real precisa de un estudio completo y siempre es interesante ensayar varios procesos o combinaciones de los mismos para tratar un mismo tipo de agua con el fin de escoger la opción más apropiada. Para determinar la opción de diseño es preciso fijar objetivos de calidad final del efluente, incluir estudios económicos y evaluar los impactos ambientales de cada proceso. Asimismo, es necesario realizar experimentos previos a escala de laboratorio o planta piloto en los que se encuentren las condiciones de operación más favorables. Otro campo interesante es la integración de varios procesos con el fin de aunar de manera sinérgica las ventajas de cada etapa. Un análisis completo de un efluente real que conduzca a un resultado concluyente incluiría pues la evaluación de varios procesos o combinaciones de los mismos y un seguimiento no sólo de la desaparición de los contaminantes sino también de otras variables importantes como la toxicidad y biodegradabilidad, evolución de intermedios de reacción, análisis económico y de impacto ambiental, etc. Esta conferencia versará sobre todos estos aspectos, mostrando el estado actual de la técnica de descontaminación de aguas utilizando radiación solar.

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S8: *Química Sostenible*

METAL CATALYZED ARYLATION OF NUCLEOPHILES: RECENT PROGRESS AND MECHANISTIC INSIGHT

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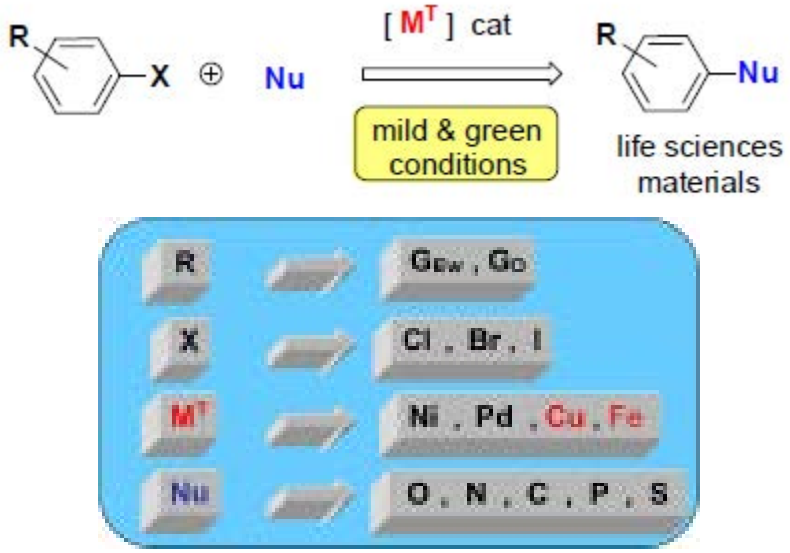
Keywords: *copper, iron, nucleophile, arylation, mechanism, industrial applications*

N-, O-, C- or S-arylation of nucleophiles from aromatic halides occurs with high yields using original Copper and/or Iron - based catalytic systems.[1] [2] Mildness, low cost and simplicity are features of our methodologies, which make them particularly well suited for industrial scale syntheses where financial and environmental issues are of greater concern. Within only ten years a lot of companies adopted this copper technology, which will probably assert its position in the industry over the next decades. Investigations concerning the mechanism will be also presented.[3]



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S8 *Química Sostenible*

SELECTIVE OXIDATION REACTIONS WITH BIOINSPIRED CATALYSTS

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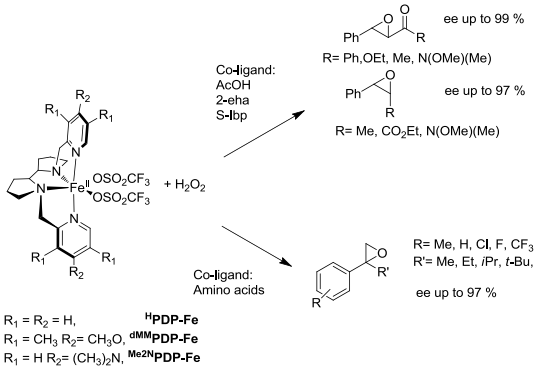
Keywords: *Iron, Manganese, C-H Oxidation, C=C Oxidation, Stereoseletivity, Hydrogen peroxide*

Biologically inspired catalysts are currently explored with the aim to produce selective oxidation reactions. The quest for catalytic methodologies that provide novel reactivities and selectivities that could complement those attained with traditional oxidants, or that could represent a more efficient alternative constitute major reasons of interest for this approach.[1-3] Towards this end, iron coordination complexes ligated to amine and oxygen containing functionalities, and that could be viewed as a minimalistic model of iron coordination sites in non heme iron dependent oxygenases, are employed as catalysts for the oxidation of organic substrates. By control of their structure and electronic properties, catalysts have been designed by our research team that engage in controlled O-O lysis of H_2O_2 to form highly electrophilic high valent metal-oxo species that are finally responsible for enzyme-like selective oxidation chemistry.[4] Principles of catalyst design and use of these catalysts in selective C-H and C=C oxidation reactions will be discussed in this contribution.



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Comunicaciones Orales (OC)

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NUEVOS AVANCES EN LA PRODUCCIÓN DE COMBUSTIBLES SOLARES MEDIANTE FOTOSÍNTESIS ARTIFICIAL

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Fotosíntesis Artificial, resonancia Plasmon superficial, Caracterización in-situ

El diseño y desarrollo de sistemas fotocatalíticos activos para la producción de combustibles solares es un campo de gran interés científico enmarcado en los procesos de conversión de energía. En este sentido, la Fotosíntesis Artificial basada en la conversión fotocatalítica de CO_2 y H_2O, en hidrocarburos y otros productos de valor añadido. La fotorreducción de CO_2 conlleva un complejo mecanismo de transferencias multielectrónicas, en la catalizador juega un papel fundamental tanto en la absorción de luz, como en la generación de pares electrón-hueco [1].
La presente investigación tiene como objetivo profundizar en el entendimiento de los procesos estructurales, superficiales y opto-electrónicos que influyen en el mecanismo fotorreducción de CO_2. Para ello se han seleccionado una serie de catalizadores basados en TiO_2 y modificados con diferentes co-catalizadores metálicos que presentan resonancia de plasmon superficial.
Los experimentos de fotorreducción de CO_2 realizados con TiO_2 bajo irradiación UV dieron lugar a la formación mayoritaria de H_2, CO y CH_4. Por el contrario, la deposición de nanoparticulas (NPs) de Ag o Au causó un aumento significativo de la producción de CH_4. Asimismo, las producciones de CO e H_2 mostraron un claro descenso. Estas observaciones sugirieron la formación preferente de productos de mayor demanda electrónica debido al efecto sinérgico de las NPs metalicas y el semiconductor.

La utilización de diferetenes tecnicas de caracterización in-situ, como RMN y XPS en condiciones cercanas al ambiente (NAP-XPS), han mostado que la formción de especies carbonato como estados intermedios de reacción tiene una gran influencia tanto en los proceoss de foto-activacoión como de deasctivación de los catalizadores.
Por otra parte, las evaluación de las propiedades opto-lectronicas por medio de medidas absorción de transientes (TAS) demostraron que las NPs de Ag mejoran los procesos de separación de cargas y reducen los fenómenos de recombinación. Esto indica que bajo irradiación UV, las NPs de Ag actúan como colectores de los electrones fotogenerados en el TiO_2. En consecuencia, esto da lugar a una separación espacial de las cargas y por tanto, una disminución de los procesos de recombinación [2-3].

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PHOTOCATALYTIC OXIDATION OF CORK WASTEWATER POLLUTANTS USING TRIPHENYL(THIA)PYRYLIUM SALTS

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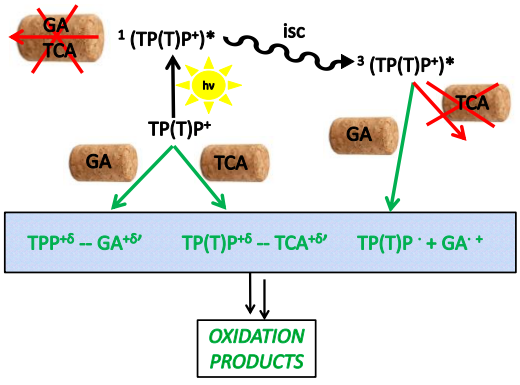
Keywords: *Complex formation, electron transfer, fluorescence, laser flash photolysis, triplet*

The production of wine in Spain involves a parallel cork stoppers industry to guarantee the proper conservation of the product. However, production of cork stoppers includes a post-harvesting treatment that results in wastewaters containing phenolic derivatives, among the most representative pollutants. In the present contribution, photocatalytic degradation of gallic acid (GA) and 2,4,6-trichloroanisole (TCA), using triphenylpyrylium (TPP^+) and triphenylthiapyrylium ($TPTP^+$) salts as organic photocatalysts, has been investigated. Upon visible light irradiation, removal of GA was fast, while degradation of TCA resulted to be slow although efficient. Photophysical measurements were undertaken to identify the nature of the transient species involved in the photodegradation. Involvement of singlet excited states of $TP(T)P^+$ were disregarded since lifetimes of both photocatalysts remained constant upon addition of the pollutants. However, formation of photoactive ground state complexes was observed; the values of the corresponding complexation constants were estimated as $K_{TPP\text{-}GA}$= 468.4 M^{-1}, $K_{TPP\text{-}TCA}$ = 528.0 M^{-1} and $K_{TPTP\text{-}TCA}$ = 657.1 M^{-1}. Besides, triplet excited state of both photocatalysts efficiently participated in the electron transfer oxidation of GA. The absence of triplet quenching in the case of TCA was supported by a thermodynamically disfavored process. Overall from the photophysical results, in the case of GA, oxidative electron transfer occurs mainly from the triplet excited state, while for TCA, formation of ground state complexes constitutes the only mechanistic alternative, see Scheme 1.



Scheme 1: Mechanistic proposal

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DESIGN AND PREPARATION OF ECO-COMPATIBLE CATALYSTS

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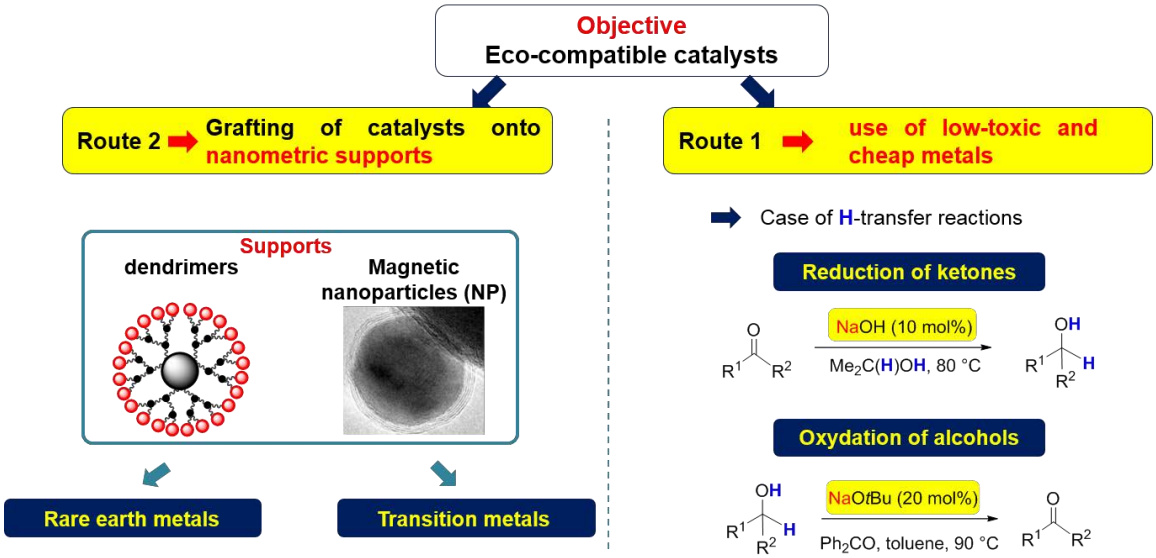
Keywords: *recyclable catalysts, dendrimers, magnetic nanoparticles, alkali metals, hydrogen transfer reactions*

The development of efficient and eco-compatible catalytic systems enabling the preparation of organic compounds is of great concern. We report two approaches to reach this objective. The first one consists in grafting catalysts onto nanometric supports,[1-3] either dendrimers [4] (hyperbranched and perfectly defined nano-sized polymers) or magnetic nanoparticles. The second route, more particularly illustrated in the case of H-transfer processes, consists in using non-toxic and cheap metals.[5-7] In both cases, very competitive catalytic systems could be proposed.



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NEW SYNTHETIC APPLICATIONS FOR DEEP EUTECTIC SOLVENTS: GREEN REACTION MEDIA FOR Au(I)-CATALYZED CYCLOISOMERIZATIONS

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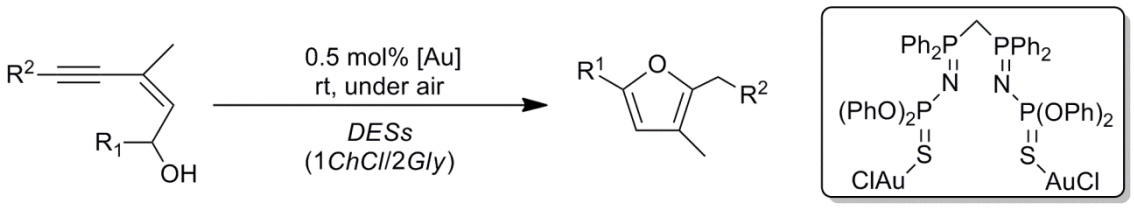
Keywords: *Deep Eutectic Solvents; Homogeneous Catalysis; Gold(I); (Z)-enynols.*

One of the largest areas of consumption of petroleum-based chemicals, in a conventional metal-catalyzed organic reaction, is the solvent used as reaction media. Despite that the problems associated with conventional volatile organic solvents (*VOCs*) are well established, the use of green and biorenewable solvents still remains a lasting challenge. In this sense, the advantages of using Deep Eutectic Solvents (*DESs*) as reaction media are highlighted from the fact that they are biodegradable, non-toxic, recyclable and could be easily prepared using inexpensive raw materials [mixture of a hydrogen bond donor (*i.e.*, glycerol (*Gly*) or urea) with a simple halide salt (choline chloride, *ChCl*)] [1]. Although *DESs* have been explored in a variety of applications including metal deposition, purification of biodiesel, biotransformations and different synthetic processes, their application in metal-mediated organic reactions has been barely noticed [2,3].

In this communication, we will present the use of different *DESs* as green and biorenewable solvents for the Au(I)-catalyzed cycloisomerization of (*Z*)-enynols into furans, proceeding with efficiency, selectivity, atom economy, at room temperature, under air and in short reactions times. It is important to note that the catalyst could be recycled up to 10 consecutive times. Application of this methodology to the tandem cycloisomerization/Diels-Alder reaction will be also discussed.



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ILs-BASED MATERIALS AS ENABLING TOOL FOR THE DESIGN OF CHEMICAL PROCESSES

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Keywords: *Ionic liquid, supported ionic liquid, supercritical fluid, (bio)catalysis, polymeric ionic liquid, continuous flow processes, multicatalytic cascade reactions.*

Sustainability is not just a challenge, but an opportunity to obtain breakthroughs in the synthesis of organic compounds. Thus, the development of innovative synthetic methodologies can be achieved the integration of multicatalytic systems with other enabling techniques. In the last few years, we have intensively explored combine used of (bio)catalysis and the design of advanced multifunctional materials based on the properties of Ionic Liquids (ILs) to design greener reactions and processes. SILLPs and PILs can be applied for catalytic processes in an analogous way to bulk ILs but simplifying product isolation and recycling of the catalyst-IL-phase. [1] the related bulk ILs but also to provide an addition design vector to optimize the final characteristics and performance of the related supported ionic liquids-catalyst composites. An additional factor increased the sustainability of our developments is the use flow chemistry allowing the full integration of reaction and separation steps. Here, we will reported our recent achievements to design synthetic platforms integrating multicatalytic systems, which are able to process sequentially and controllably multiple synthetic operations in a mutually compatible manner. Such systems allow complex syntheses to occur with minimal external intervention and environmental impact. [2-5].

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RECYCLABLE POLYMER-SUPPORTED TIN HYDRIDES FOR CLEAN RADICAL DEHALOGENATION REACTIONS

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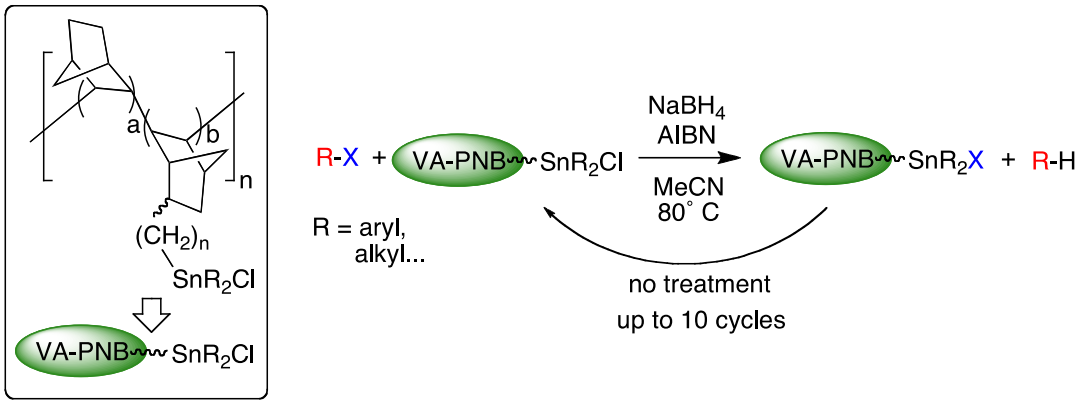
Keywords: *polynorbornene, green chemistry, recyclable catalyst, tin, dehalogenation, radical.*

Tin radicals have been widely used to catalyze different radical organic transformations (i.e. dehalogenations, cyclizations, intermolecular coupling…) and they have major advantages [1]. However their application is declining, mainly because an important drawback of these reactions is the difficult separation of the products from the potentially toxic tin byproducts (a harmful waste). If this can be overcome, the use of these reactions could be brought to its full potential.

We have developed stannylated vinylic-addition polynorbornenes (VA-PNB, see Scheme) that have been applied in the Stille reaction and have shown their advantages as far as easy separation from the target products and recyclability [2]. The VA-PNB skeleton is completely aliphatic and lacks other reactive sites such as double bonds, i.e. ROMP polymers, or benzylic positions, as in the common polystyrene resins. This is specially important in radical processes.

Here we present the use of VA-PNB supported tin hydrides, either preformed or generated in situ, as recyclable catalyst in dehalogenation reactions. A variety of organic halides were reduced in this way. The polymeric tin byproducts were easily separated by simple filtration and reused up to ten times without any significant loss of reactivity.



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S8: *Química Sostenible*

RUTHENIUM-CATALYZED SYNTHESIS OF HETEROCYCLES USING HYDROGEN AUTOTRANSFER METHODOLOGY

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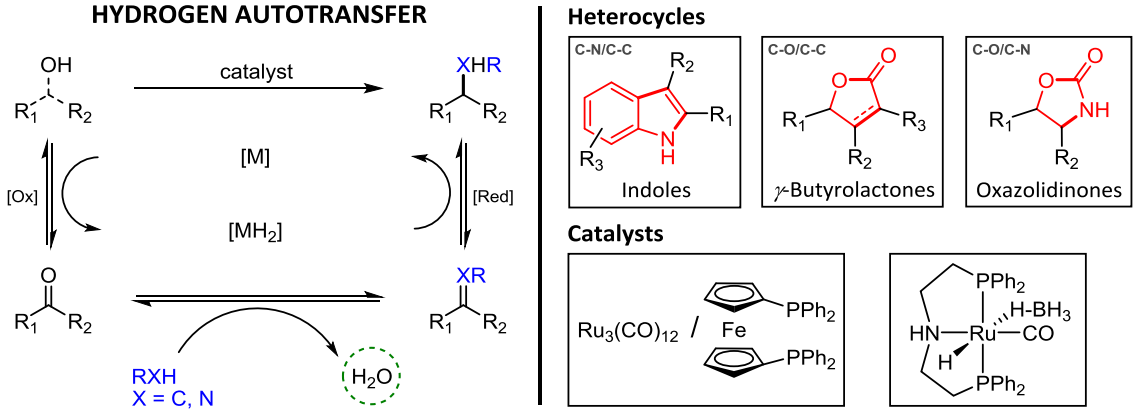
Keywords: *catalysis, heterocycle synthesis, hydrogen autotransfer, atom economy*

Heterocyclic compounds are present in a wide variety of natural products and pharmaceutical agents. With the increasing demand for more sustainable chemical transformations, the development of new and efficient catalytic reactions for the synthesis of valuable heterocycles from cheap and abundant feedstock is still a field of great interest. In this regard, the so called hydrogen autotransfer process has become a powerful alternative for the benign construction of new C-C and C-N bonds using simple alcohols as coupling partners.[1] This strategy, which constitutes a very atom economic process as H_2O is formed as the only by-product, can be efficiently applied to heterocycle synthesis through the use of suitable domino transformations.



On that basis, we here describe the ruthenium-catalyzed synthesis of three different heterocyclic compounds such as indoles, γ-butyrolactones and oxazolidinones using hydrogen autotransfer methodology.[2] More specifically, indoles were obtained from readily accessible anilines and epoxides, whereas the synthesis of γ-butyrolactones and oxazolidinones was accomplished by reaction of the corresponding vicinal diols with malonates and urea, respectively. Our results show that ruthenium-based catalysts are effective for the synthesis of heterocycles from easily available substrates through atom economic metal-catalyzed reactions.

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S8: *Química Sostenible*

AMINOPYRIDINE LIGANDS AS PLATFORMS FOR WELL-DEFINED LIGHT-DRIVEN COBALT REDUCTION AND IRON WATER OXIDATION CATALYSTS

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Keywords: *Light driven reductive reactions, Water Oxidation*

One of the most appealing research areas is the mechanism understanding of multi-electron multi-proton processes, being central in the activation of small molecules such as the water oxidation to O_2 (WO) or reduction to H_2 (WR) processes.[1] In this line, we have discovered that readily available iron coordination complexes based on aminopyridine ligands are highly efficient homogeneous WO but also WR catalysts.[2-5] We present here one of the few examples of homogeneous and well-defined WO catalysts based on 1st row transition metals, which allows for a mechanistic studies. To gain insight into the mechanism of the Fe-catalyzed WO catalysis, we carried out a detailed study through kinetics, spectroscopic monitoring of intermediates, isotopic effects, isotopic labeling, electronic effects and DFT calculations.[3-5] The roles of the high oxidation state oxo-iron (IV) and (V) and new Fe-O-Ce species in the O-O forming event as well as possible intermediates in the oxidation of organic substrates[5] will be discussed.

Likewise, cobalt complexes based on aminopyridine ligands form robust homogeneous catalytic systems for light-driven reductions, in which their electronic and structural properties can be easily tuned.[6] By a combination of experimental and computational studies we have obtained key information about intermediate species and the mechanism for the photochemical reduction of water to H_2, ketones, aldehydes and olefins. The mechanism aspects will be discussed in this basis.

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S8: *Química Sostenible*

DETECCIÓN DE INTERMEDIOS METALOCARBÉNICOS DE COBRE EN LA REACCIÓN DE FUNCIONALIZACIÓN DEL ENLACE O-H DEL H_2O

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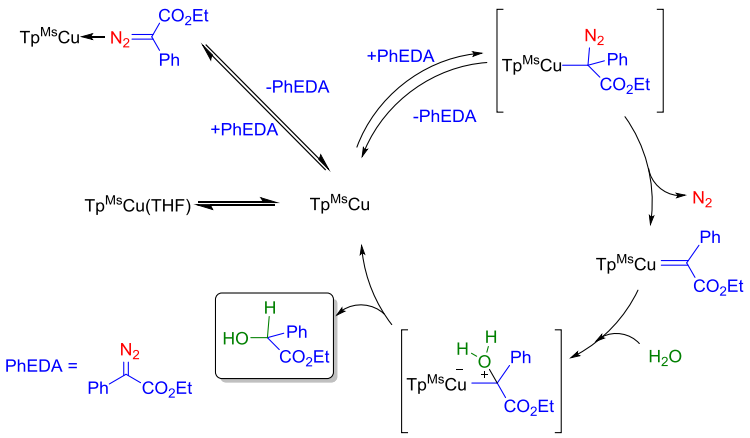
Palabras Clave: *transferencia de carbeno, catálisis con Cu, especies metalocarbénicas.*

El proceso de transferencia de grupos carbeno, procedentes de diazocompuestos, en presencia de un complejo de un metal de transición constituye uno de los métodos más empleados en la formación de un nuevo enlace C–X (siendo X = C, N, O, S, Si).[1] Aunque los sistemas catalíticos basados en cobre han sido ampliamente empleados en este tipo de transformaciones, el número de especies metalocarbénicas de cobre detectadas y/o aisladas es, a dia de hoy, escaso.

Durante los últimos años, nuestro grupo de investigación ha desarrollado catalizadores de Cu(I) con ligandos hidrotrispirazolilborato del tipo Tp^xCuL, muy eficientes en este tipo de reacciones.[2] En esta comunicación se describe la detección de varios aductos de diazocompuesto de fórmula $Tp^xCu[\eta^1\text{-}N_2C(Ph)(CO_2Et)]$ así como la de las correspondientes especies metalocarbénicas, $Tp^xCu{=}C(Ph)(CO_2Et)$, mediante la reacción de los diferentes complejos Tp^xCuL con 2-fenildiazoacetato de etilo (PhEDA). Asimismo, se han llevado a cabo estudios cinéticos mediante la medición de la evolución de N_2 de la reacción de funcionalización del enlace O–H del H_2O catalizada por el complejo $Tp^{Ms}Cu(THF)$. Estos estudios han permitido realizar una propuesta mecanística para dicha transformación.



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S8: *Química Sostenible*

A GREEN ACCESS TO (2-IMIDAZOLIN-4-YL)PHOSPHONATES

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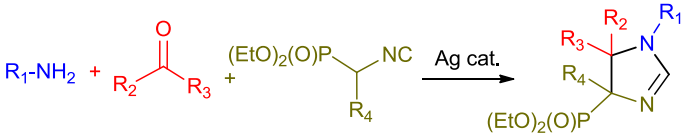
Keywords: *(2-imidazolin-4-yl)phosphonate, microwave, multicomponent reaction, theoretical calculations, diethyl isocyanomethylphosphonate*

2-Imidazoline-containing compounds constitute a valuable class of agents that modulate the α2-adrenergic receptors, and often show a high affinity for imidazoline binding sites (IBS). The biological profile of these IBSs has been examined in pharmacological studies due to their involvement in the control of blood pressure, depression, insuline secretion, neurodegenerative disorders, and tolerance and dependence on opioids. Moreover, 2-imidazolines are an important class of heterocyclic scaffolds that can be found in natural product chemistry, organic synthesis, coordination chemistry and homogeneous catalysis.

Inspired by a previous study by Orru [1] and seeking new applications of isocyano derivatives, we envisaged the possibility of performing a multicomponent reaction between diethyl isocyanomethylphosphonate (PhosMic) or α-substituted PhosMic derivatives, ketones and amines (Scheme 1). Notably, although isocyano derivatives can be found extensively in the literature as reactants in multicomponent reactions, the use of PhosMic in IMCRs has received less attention. It is worth noting that the proposed reaction would give direct access to (2-imidazolin-4-yl)phosphonate compounds. The potential biological interest of these new azaheterocyclic phosphonates is mostly associated with the tetrahedral structure of the phosphonyl group, which may act as a "transition state analogue" in enzymatic peptide hydrolysis.



Scheme 1. Proposed reaction to access (2-imidazolin-4-yl)phosphonates.

This work addresses the synthesis of 2-(imidazolin-4-yl)phosphonates through an environmentally friendly multicomponent heterocyclic reaction following green chemistry considerations. To this end, we envisioned the use of microwave irradiation, which is an outstanding tool for sustainable organic chemistry, maximizing synthetic efficiency, diversity and complexity.

In particular, we disclose a general microwave protocol for a silver-catalysed three-component reaction towards the synthesis of (2-imidazolin-4-yl)phosphonates. The reactivity outcome is rationalized by theoretical calculations.

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S8: *Química Sostenible*

ACOPLAMIENTO REDUCTIVO DE NITROCOMPUESTOS, ALDEHÍDOS E HIDRÓGENO PARA FORMACIÓN DE NITRONAS USANDO NANOPARTÍCULAS DE PLATINO SOBRE CARBON ACTIVO

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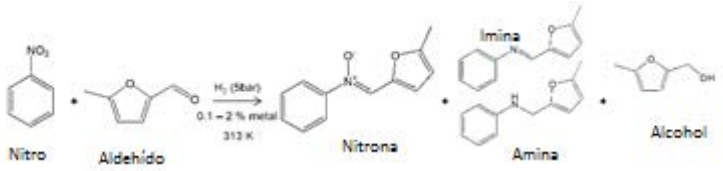
Palabras Clave*: Nitronas, nanopartículas, platino*

En este trabajo se logró sintetizar nitronas con altos rendimientos a partir del acoplamiento reductivo de nitrocompuestos, aldehídos e hidrógeno usando nanopartículas de platino soportadas en carbón activo. La alta selectividad a la nitrona **(97%)** contrasta con la obtenida con los catalizadores comunes (6%) debido a las características del soporte y al control estructural de los sitios activos. Las nitronas son importantes bloques de construcción en química orgánica para la obtención de isoxazolidinas, isoxazolinas y beta aminoalcoholes, y son ampliamente utilizados como atrapadores de radicales, antioxidantes e inhibidores de enzimas y otros procesos biológicos**.[1]** En la actualidad su preparación se realiza a través de rutas sintéticas multietapa, donde a menudo intervienen agentes estequiométricos que generan grandes cantidades de residuos en el proceso. En este contexto, el descubrimiento de un catalizador sólido que proporcione altos rendimientos a nitronas directamente desde compuestos nitro, aldehídos e hidrógeno en una única etapa de reacción sería de gran interés desde un punto de vista fundamental, económico y medioambiental. Para lograr esto se requiere la formación *in situ* de hidroxilamina por reducción parcial del grupo nitro y una condensación entre la ésta y el aldehído para dar la nitrona. El catalizador diseñado deberá evitar: a) una reducción completa del grupo -NO_2 a -NH_2; b) una hidrogenación simultánea del aldehído y c)una degradación de la nitrona a través de rutas de reacción secundarias .

Con este fin, la reacción modelo fue el acoplamiento reductivo entre el nitrobenceno y 5-metil furfural para dar nitrona como producto principal (Esquema 1).



Esquema 1. Acoplamiento selectivo para formación de Nitronas

De todos ellos sólo aquel constituido por pequeñas nanopartículas de platino sobre un carbón activo de alta área proporciona una alta selectividad para la formación de nitrona, porque se logra al limitar la accesibilidad del reactivo al platino en posiciones terraza de las nanopartículas; asi como la reducción completa del grupo nitro. Se comparó la actividad catalítica del Pt/C con otros catalizadores disponibles comercialmente empleados en hidrogenaciones como Pt/Al_2O_3 (6%), Pt/TiO_2(57%) y Pd/C (82%) y, en todos los casos, los resultados fueron significativamente mejor con el Pt/C sintetizado que nos permite obtener un 97% de selectividad.

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S8: *Química Sostenible*

NUEVOS SISTEMAS Os-NHC PARA EL ESTUDIO DE PROCESOS SOSTENIBLES

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Palabras Clave: *osmio, carbenos N-heterocíclicos, ligandos cooperativos*

El complejo $OsH_6(P^iPr_3)_2$ presenta una gran capacidad para activar enlaces σ de multitud de moléculas orgánicas.[1] Este derivado hexahidruro, mediante metalación directa de sales de imidazol, ha permitido la obtención de un amplio abanico de complejos Os–NHC.[2] Por otra parte, es conocido que los ligandos de tipo carbeno *N*-heterocíclico son de fácil acceso y altamente modulables. Esto posibilita la modificación de las propiedades electrónicas de los sistemas metálicos a los que se coordinen. Por ese motivo, los ligandos NHC han experimentado un enorme desarrollo en los últimos años y se han convertido en herramientas muy valiosas en catálisis homogénea, síntesis organometálica y ciencia de los materiales.

En este trabajo se muestra la síntesis de nuevos compuestos Os–NHC basados en ligandos cooperativos para el estudio de procesos químicos de interés. Para acceder a sistemas de este tipo partimos del derivado $OsH_6(P^iPr_3)_2$ y lo hacemos reaccionar con sales de imidazolio que incorporan funcionalidades éster en uno de los nitrógenos del anillo heterocíclico. La ruptura del enlace OC–OR del sustituyente éster durante el transcurso de la reacción provoca la coordinación del grupo acilo al ión osmio en el compuesto final $OsCl\{CN(CH_3)CHCHNCH_2CO\}(P^iPr_3)_2$. Además, se presenta un estudio de cómo esta coordinación acilo del sustituyente N del ligando carbeno afecta a su reactividad y posibles aplicaciones.

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S8: *Química Sostenible*

FUNCIONALIZACIÓN DEL ENLACE Si-H MEDIANTE UN PROCESO MULTICOMPONENTE CATALIZADO POR CLORURO DE ZINC

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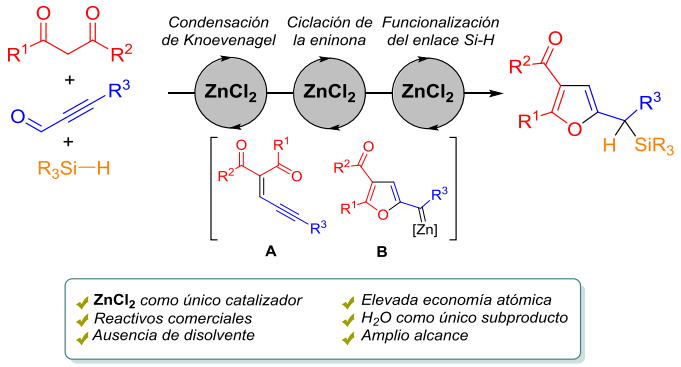
Palabras Clave: *reacción multicomponente, catálisis, zinc, silano, funcionalización Si-H.*

En la actualidad existe un extendido consenso acerca de la necesidad de desarrollar metodologías sintéticas más sostenibles. En este sentido, la sustitución de metales preciosos (escasos, caros y tóxicos) por metales abundantes y de baja toxicidad representa un campo de investigación especialmente activo. Por otra parte, las reacciones multicomponente resultan claramente ventajosas frente a aproximaciones secuenciales más tradicionales ya que suponen un ahorro de esfuerzo y de recursos y una notable reducción de los residuos generados.
Nuestro grupo de investigación ha iniciado recientemente una línea de investigación orientada al desarrollo de nuevas metodologías basadas en el empleo de sales de zinc como catalizadores.[1] En este contexto, en esta comunicación se describe la síntesis de furanos funcionalizados a través de un proceso multicomponente catalizado por cloruro de zinc. La secuencia implicada supone una condensación de Knoevenagel inicial entre la 1,3-diona y el correspondiente alquinal que originaría la eninona intermedia **A**, que mediante una ciclación 5-exo-*dig* generaría el furilcarbeno de zinc **B**. Finalmente, la inserción en el enlace Si-H conduciría a los productos de reacción. Esta metodología ha permitido la preparación de furanos estructuralmente muy diversos. Igualmente, este protocolo se ha extendido a la funcionalización de oligosiloxanos.[2]



Agradecimientos: S.M. agradece al Principado de Asturias la concesión de una beca predoctoral (Programa Severo Ochoa).

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S8: *Química Sostenible*

HYDROLYSIS LIGNIN VALORISATION: SIMULTANEOUS SYNTHESIS OF LACTIC ACID AND PHENOLICS

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Keywords: *Hydrolysis lignin, Lactic acid, Phenolics, Alkaline hydrothermal conversion*

Hydrolysis lignin (HL) is formed during enzymatic hydrolysis of lignocellulosics to produce fermentable monosaccharides for manufacturing 2G bioethanol. HL can contain up to 50% of polysaccharides, and its availability will grow drastically with 2G bioethanol production. The valorisation of polysaccharide-containing HL has not been deeply studied. HL cannot be dissolved in typical lignin solvents (as NaOH solutions) which makes its processing more difficult. However, its heterogeneous nature offers opportunities for simultaneous manufacturing of valuable phenolics from the lignin fraction [1] and organic acids [2] from the cellulose fraction. Herein, the valorisation of a HL by batchwise alkaline hydrothermal conversion under autogenous pressure leading to simultaneous formation of phenolics and lactic acid is reported.

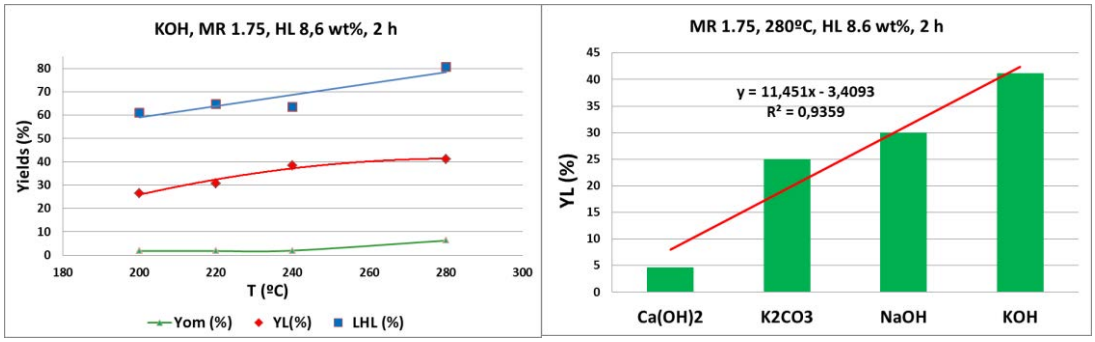

Fig. 1. Left: Effect of temperature. Right: LA yield as a function of base nature.

Influence of molar ratio base/HL (MR), base nature, temperature (T) and co-catalysts addition on HL liquefaction degree (L_{HL}), lactic acid yield (Y_L), phenolics yield (Yom, on a mass basis), phenolics distribution and cellulose-derived chemicals distribution was studied. A peak Y_L of 46% was obtained at 280ºC using KOH and a MR of 1.75. Vanillin is the prevalent phenolic below 220ºC while guaiacol is the predominant one above 260ºC. L_{HL} and Y_L increase with both T (Fig. 1-left) and base strength (Fig. 1-right).

Acknowledgments

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S8: *Química Sostenible*

SINTESIS A ESCALA PILOTO DE NaP1 A PARTIR DE UN RESIDUO PELIGROSO Y SU UTILIZACION COMO ADSORBENTE DE MERCURIO

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Palabras Clave: *zeolitas, residuo peligroso de aluminio, adsorción, mercurio*

Una de las zeolitas con mayor capacidad de intercambio iónico es la NaP1 utilizada ampliamente en el tratamiento de aguas residuales. Su obtención a partir de residuos como las cenizas volantes ha sido estudiada en detalle, no siendo éste el caso cuando se utilizan residuos de aluminio como materia prima [1]. Realizados los primeros ensayos de síntesis de la zeolita NaP1 a partir de un residuo peligroso de aluminio a escala de laboratorio, el objetivo de este trabajo se centra en estudiar su síntesis en un prototipo piloto, para obtener los parámetros necesarios para su escalado. La síntesis se realiza en una única etapa, mediante tratamiento hidrotermal en un reactor de 5 L, a presión y temperatura controladas, con recirculación de aguas madres para minimizar los consumos, y reducir el impacto ambiental del proceso disminuyendo la generación de efluentes. Se estudia la influencia de la recirculación en el rendimiento de la reacción y especialmente en las características morfológicas y superficiales de la zeolita.

De entre los metales pesados considerados como disruptores endocrinos, el mercurio es uno de los que están sometidos a legislaciones más restrictivas, en cuanto a su concentración en aguas de bebida (<1ppb) y aguas continentales (<50ppb), por lo que en este trabajo se estudia la utilización de la zeolita en procesos de adsorción de Hg^{2+}. Los resultados de DRX y MEB indican que en las condiciones de síntesis ensayadas, se obtiene NaP1 como fase cristalina de elevada pureza, no presentando variaciones significativas con el reciclado de las aguas madres (Fig. 1). La optimización del proceso, mediante reducción del consumo de agua y NaOH permite obtener ~1kg de zeolita en una única etapa de reacción. El proceso no genera otros residuos sólidos, ya que todo el residuo se transforma en zeolita. En cuanto a la eliminación de Hg^{2+} (C_i=0,2ppm, pH 2), se obtuvieron valores de eficiencia de adsorción cercanos al 100%.

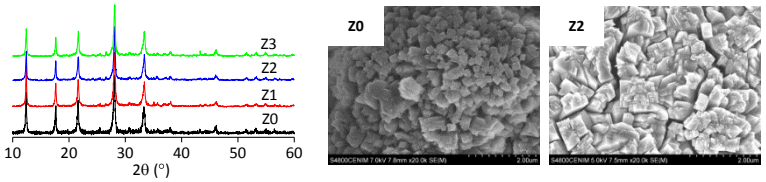

Fig. 1: Difractogramas (DRX) y morfologías (MEB) de NaP1, obtenida en diferentes condiciones experimentales. Z0-3: Número de recirculaciones de aguas madres.

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S8: *Química Sostenible*

POSIBLE FORMACIÓN DE FORMIATO A PARTIR DE LA FUNCIONALIZACIÓN DE CO_2 EMPLEANDO UN COMPLEJO DE COBRE

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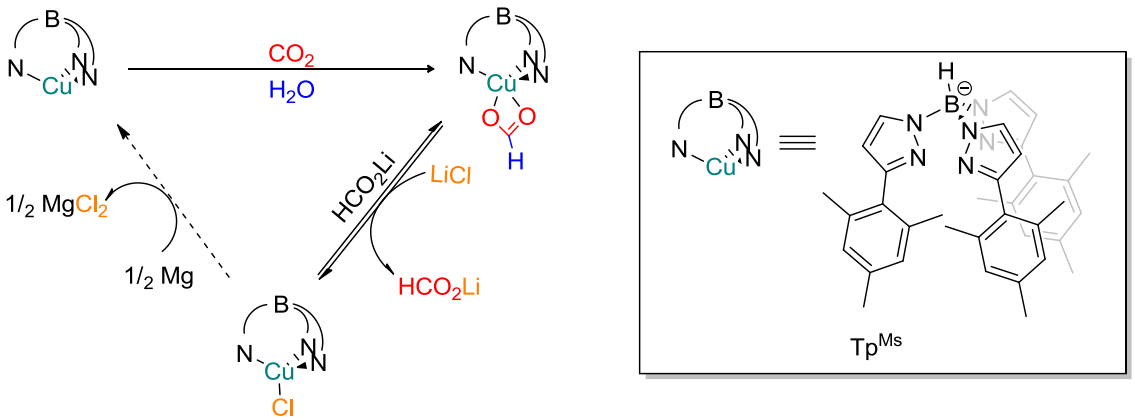
Palabras Clave: *Activación de CO_2, formiato, cobre, dióxido de carbono*

El uso del dióxido de carbono como materia prima en síntesis constituye uno de los retos actuales de la química. El empleo de metales de transición para su activación como primer paso para una posterior funcionalización ha sido descrito hasta el momento en un reducido número de ejemplos.[1] Nuestro grupo de investigación ha descrito la formación de complejos de cobre con moléculas pequeñas (etileno, monóxido de carbono o amoniaco) empleando Tp^{Ms} como ligando.[2] Como contribución de estos trabajos se ha estudiado la reactividad del complejo $Tp^{Ms}Cu$ con dióxido de carbono. No obstante, al tratar dicho complejo con CO_2 no se ha aislado aducto alguno, pero se obtiene un complejo con ligando formiato.

En esta comunicación se presenta los resultados derivados de esta transformación así como la reactividad del complejo de formiato para liberar dicho ligando.



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S8: *Química Sostenible*

SÍNTESIS DE NUEVOS LIGANDOS TRIPODALES CON USO POTENCIAL EN CATÁLISIS

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Palabras Clave: *ligandos tripodales, catálisis, diazocompuestos, carbenos.*

Los ligandos tripodales constituyen una de las familias de ligandos más estudiados en química de coordinación y organometálica. En nuestro grupo de investigación, este tipo de ligandos, concretamente los denominados trispirazolilboratos (Figura 1a), han sido ampliamente estudiados y empleados junto a Cu y Ag en la funcionalización catalítica de alcanos ligeros.[1-2] Son ligandos de naturaleza aniónica que presentan una gran versatilidad en cuanto a sus propiedades estéricas y electrónicas como consecuencia de los diferentes sustituyentes que podemos encontrar en su estructura.[3]

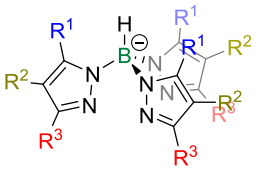


Figura 1a. Ligando tris(pirazolil)borato

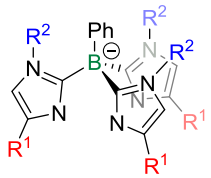
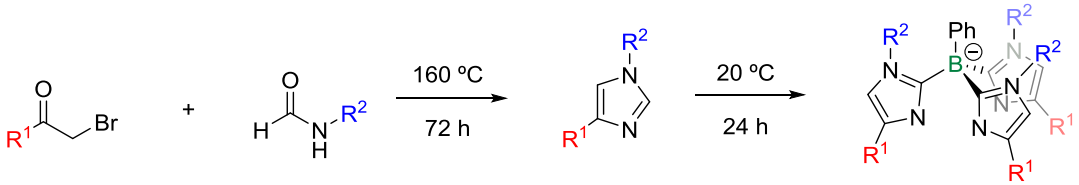


Figura 1b. Ligando tris(imidazolil)borato

En esta comunicación se describe la síntesis y aplicaciones catalíticas de nuevos ligandos tripodales, similares a los trispirazolilboratos pero que contienen anillos de imidazol. Éstos poseen una mayor conjugación de la densidad electrónica y permiten la inserción de un mayor número de sustituyentes. Como consecuencia, las propiedades electrónicas y estéricas pueden variar de forma amplia dependiendo de los mismos.



Esquema 1. Síntesis del ligando trisimidazolilborato

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S8: *Química Sostenible*

FOTOCATALISIS SOLAR PARA LA ELIMINACION DE CONTAMINANTES DE LA INDUSTRIA ALIMENTARIA

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Palabras Clave: *foto-Fenton solar, compuestos fenólicos, Dohelert*

La industria alimentaria (vino, aceite, procesado del corcho…) genera efluentes altamente contaminados, con azucares, taninos, sustancias fenólicas simples y polifenoles. Estudios previos [1] han demostrado que el agua residual generada en el proceso de cocido del corcho posee baja biodegradabilidad y altas concentraciones de polifenoles (1300 mg/L). Los procesos de oxidación avanzada (PAO) se han mostrado como potenciales tratamientos para estas aguas [2].

El proceso foto-Fenton se aplicó sobre una mezcla de 8 contaminantes habituales en estas aguas: ácido galico, ácido protocatecuico, ácido vanílico, ácido siríngico, ácido sinápico, 2,4-dinitrofenol, ácido elágico y ácido tánico, (1 mg/L de cada uno). Las muestras se irradiaron durante 120 minutos con un simulador solar. Se parte de un Diseño experimental tipo Dohelert con tres factores (pH, concentración de peróxido de hidrógeno y concentración de hierro) y tres puntos centrales. Con los resultados de estos 15 experimentos, se calculó el tiempo necesario para degradar el 80% de la suma de los contaminantes y se realizó en análisis estadístico de los resultados que muestran como a medida que aumentamos la concentración de Fe^{2+} el óptimo se desplaza hacia valores más elevados de pH y menores concentraciones de peróxido de hidrógeno.

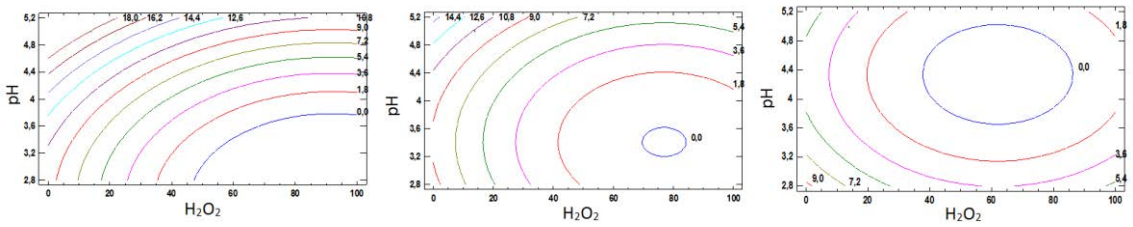

Figura 1 Graficas de contornos de la superficie de repuesta estimada para concentraciones de Fe^{2+} de 1, 3 y 5 mg/L (de izquierda a derecha)

Agradecimientos

Al Ministerio de Economia y Competitividad (Proyecto CTQ2012-38754-C03-02). Sara García le agradece la concesión de la beca FPI (convocatoria 2012, CTQ2012-38754-C03-02)

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COMPETITION STUDIES ON C-H BOND FUNCTIONALIZATION OF HYDROCARBONS: TOWARDS A SCALE OF NUCLEOPHILICITY FOR ALKANES

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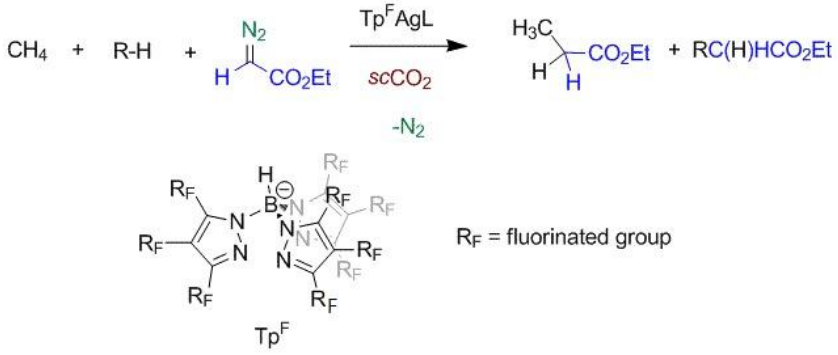
Keywords: *alkanes, C-H bond functionalization, carbene, silver complex, reactivity scale.*

Alkanes are considered as plausible raw materials in chemistry on the basis of their availability. However, their chemical inertness has yet circumvented such use, that is yet restricted to a few examples. Moreover, this family of compounds displays quite different behavior on the basis of the chain length: the lighter members (C_1-C_4) are gaseous at atmospheric pressure, then the alkanes becoming liquid and solid when increasing the number of carbon atoms in the chain. Because of this, the direct comparison of their relative reactivity has been difficult to achieve, avoiding the accessibility to a scale of reactivity for the overall group of C_nH_{2n+2} hydrocarbons.

We have recently discovered the catalytic capabilities of silver-containing catalysts for the functionalization of alkanes upon transfer of the carbene unit $CHCO_2Et$ from ethyl diazoacetate, including the C_1-C_4 members, on the basis of the employment of supercritical carbon dioxide as the reaction medium.[1] We have now taken advantage of such catalytic behavior to carry out a series of competition experiments from which an overall relative reactivity scale from methane to adamantane has been built.



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S8: *Química Sostenible*

MECHANISM OF UV-PHOTOTRANSFORMATION OF THE BENZIMIDAZOLE FUNGICIDE THIABENDAZOLE

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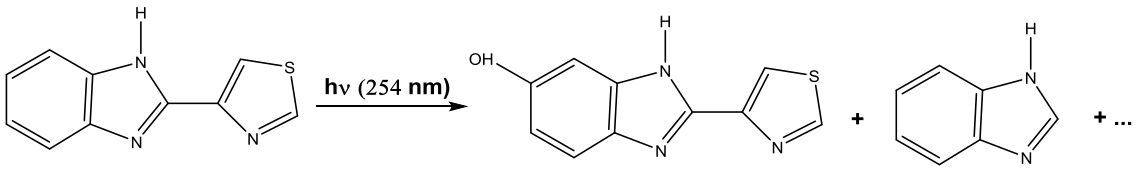
Keywords: *photoreactivity, fungicide, benzimidazole, thiabendazole*

Thiabendazole (TBZ) a systemic benzimidazole fungicide used as post-harvest protection for citrus fruit. [1] The agro-food industry is one of the main European manufacturing activities. The use of water in food businesses is essential to the development of productive activities. This water is used as a cooling agent, for cleaning and disinfecting and in the process itself (Food Drink Europe, 2012). The food processing industry produces large volumes of wastewater that require treatment before being released into the environment. This wastewater usually has a high BOD_5/COD ratio and is therefore suitable for biological treatment. However little information exists concerning the presence and fate of organic contaminants commonly found in agro-food industry wastewater such as pesticides, some of which escape the water treatment. Amongst them, thiabendazole (TBZ) was the most frequently detected compound during the study, with concentrations as high as 3.3 $mg \cdot L^{-1}$, which was considered a consequence of its resistance to the biological treatment applied. [2] There is an urgent need to have alternative treatments available to eliminate or reduce refractory persistent organic micropollutants such as TBZ. We have studied and describe here the mechanism of direct UV-photodegradation of Thiabendazole.



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S8: *Química Sostenible*

SYNTESIS OF 3,5-DISUSTITUTED ISOXAZOLES AND ISOXAZOLINES IN DEEP EUTECTIC SOLVENTS

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Keywords: *DES, 1,3-Dipolar cycloaddition, Recyclability,*

Liquids produce by the mixture of two or more solid compounds having hydrogen bond donor systems with simple halide salts is defined as a Deep Eutectic Solvent (DES).[1] These two components are capable of self-association, often through a strong bond interaction, to form a eutectic mixture with a melting point lower[2] than that of each individual component. The typical green characteristic properties of a solvent, such as conductivity, viscosity, vapor pressure and thermal stability can be fine-tuned by the corrected chosen of the mixture, with the large-scale preparation being feasible. The DES's have notable advantages compare with classical organic solvents, including sustainability, bio-renewability, diversity, price, etc. As most of the components are soluble in water, addition of water to the reaction mixture dissolves the reaction medium and the organic products either form a separate layer or precipitate. Moreover, the DES and the catalyst may be recycled by the adequate quenching of the reaction.

DES's have been used as ideal medium in biocatalysed,[3] organocatalysed[4] reactions, as well as in reactions using homogeneous[5] and heterogeneous[6] catalysts. However, Its use as alternative solvent for multicomponent processes was unknown. In this communication, we introduce the one-pot three-component process for the regioselective synthesis of 3,5-disubstituted isoxazoles and the related 3,5-disubstituted-4,5-dihydroisoxazoles starting from aldehydes, hydroxylamine hydrochloride, NCS, and alkynes or alkenes, using choline chloride (ChCl):urea as renewable DES.

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S8: *Química Sostenible*

GREEN SYNTHESIS OF NEW TRIAZINE DERIVATIVES WITH DONOR-ACCEPTOR PROPERTIES

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Keywords: *Green synthesis. Donor-acceptor s-triazine derivatives.*

1,3,5-Triazine has been described as a remarkable heterocyclic system with application in supramolecular chemistry, which can experience all kinds of interactions[1]. Donor–acceptor (D–A) systems, containing an *s*-triazine unit as acceptor, deserve much attention due to their high potential to be applied in molecular electronics and optoelectronic devices. As an example of its potential in this field, 1,3,5-Triazine, as a π-deficient heterocyclic system, has been used in the preparation of star-shaped derivatives with a D–π–A configuration. [2]

Efficient green procedures were applied for the preparation of triazines **3a-e** with 2,5-dimethoxyaniline as Donor unit, using microwave irradiation in the absence of solvent. This resulted in short reaction time (15 min) and a simple and clean purification procedure (Figure 1).

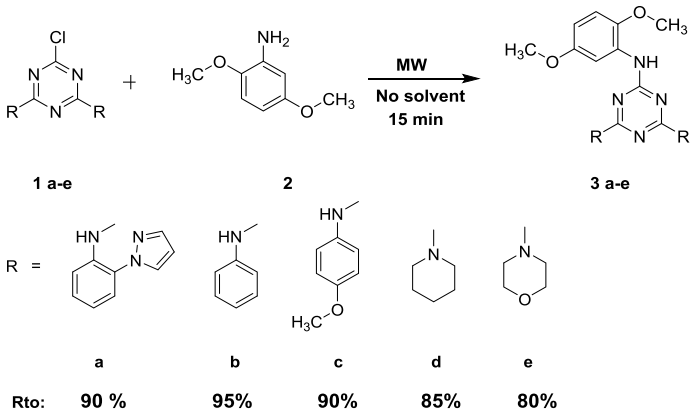

Figure 1. Green Synthesis of *s*-triazines **3a-e**.

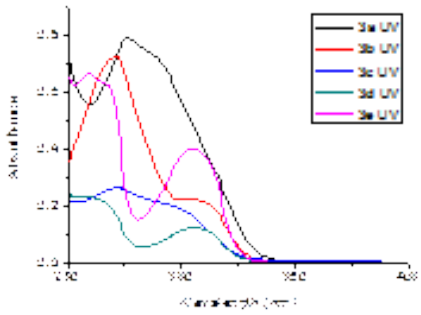

Figure 2. UV spectra of **3a-e** CH_2Cl_2 (10^{-5}M)

The title compounds **3a-e** have been fully characterized and their properties as Donor-Acceptor systems have been studied by UV-vis and fluorescence spectroscopy (Figure 2) and electrochemical studies. The high ability to exhibit supramolecular interactions have been demonstrated in the fluorescence spectra by the detection of excimers and by determination of the hydrodynamic diameter by Dynamic Light Scattering (DLS) experiments.

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S8: *Química Sostenible*

A STUDY IMPROVING THE PRODUCTION OF FURFURAL AND FURFURYL ALCOHOL FROM A SYNTHETIC HEMI-CELLULOSE PART OF BIOMASS

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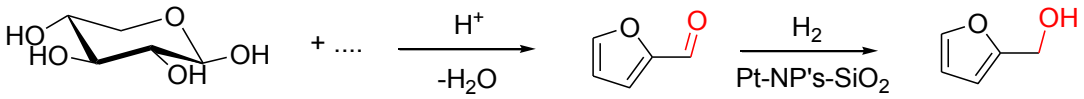
***Keywords**: Furans, biphasic reactions, ionic liquids, platinum nanoparticles, recyclability.*

Furans are one of the 'top 10' high value compounds derived from biorefinery carbohydrates signaled within the strategic goal of the displacement of imported petroleum in favor of renewable domestic raw materials.[1] Indeed the co-production of Furfural from the hemi-cellulose part of biomass could be an important way to improve the design of a biorefinery.[2]

Thermal dehydration of pentoses in acid media is the usual way for furfural production.[3] In this work, we study the furfural obtainment from a synthetic 'hemi-cellulose part of biomass'. Different solvents, including ionic liquids within biphasic systems, catalysts and temperature reactions were analyzed. Furfural yields bigger than 90 % were obtained.



synthetic hemi-cellulose

The reduction of furfural to furfuryl alcohol is carried out in the industry by catalytic hydrogenation.[4] Some of the used catalysts are carcinogenic or lost through wastes. Now we have studied that reduction by hydrogenation on platinum nanoparticles supported in silica. A recyclability up to 6 times was achieved at >98% conversion and selectivity.

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S8: *Química Sostenible*

TANNIC ACID AS HIGHLY EFFICIENT ORGANOCATALYST FOR THE CONVERSION OF OXIRANES AND CO_2 INTO ORGANIC CARBONATES

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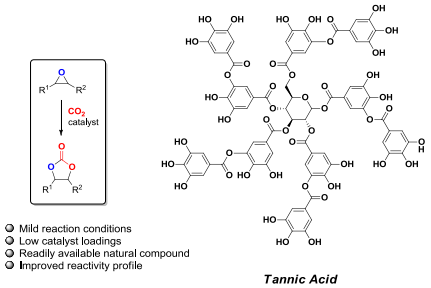
Keywords: *organocatalysis, carbón dioxide, cyclic carbonates, epoxides, renewable based, tannic acid*

The organocatalytic activation of oxiranes[1] through hydrogen-bonding using polyphenolic compounds such as pyrogallol (1,2,3-trihydroxybenzene)[2] has been studied thoroughly by our group, developing a highly efficient organocatalytic system able to mediate the coupling between terminal epoxides and CO_2 under extremely mild reaction conditions (T = 25–45ºC, $p(CO_2)$ = 2-10 bar, 2% mol catalyst). Of particular importance is the cooperative nature of the adjacent phenol groups, allowing the formation of an extended hydrogen-bond network upon activation of the oxirane thereby lowering the activation barrier for its ring-opening by an external nucleophile.[3]



Tannic Acid

Tannic acid is a cheap and commercially available natural compound; the higher local concentration of phenolic sites within the tannic acid structure (when compared to other polyphenolic compounds) seems to exert an advantageous effect on the catalytic turnover. This allows its use at reduced loadings and under comparatively mild reaction conditions (0.03 – 0.5 mol %, T = 80 ºC, $p(CO_2)$ = 10 bar, t = 18 h) for the quantitative formation of cyclic carbonate products [Picture 4]. Therefore, tannic acid stands out as a readily available, powerful organocatalyst active towards the formation of cyclic organic carbonates through direct coupling of CO_2 and a broad range of terminal oxiranes.

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S9. Síntesis, Caracterización y Propiedades de Materiales Emergentes (SCPM) / Synthesis, Chracterization and Properties of Emergent Materials

En este simposio se abordarán diferentes aspectos del estudio de materiales emergentes con aplicaciones en diversos campos tecnológicos como electrónica, fotónica, superconductores, almacenamiento y generación de energía, catálisis, biotecnología, etc. Se abordará el uso de técnicas avanzadas de síntesis, de caracterización estructural y microestructural, propiedades y funcionalidad de nuevos materiales moleculares y no moleculares.

This symposium will be dedicated to different aspect of the study of emergent materials with applications in different technological fields, such as electronics, photonics, superconductors, generation and storing of energy, catalysis, biotechnology, etc. The use of advanced synthetic methods, structural characterization techniques, properties and functionalities of new molecular and non-molecular materials will be dealt with, as well.

Organizadores:

Flaviano García Alvarado (CEU)

Mª Antonia Señarís Rodríguez (UDC)

Susana García Martín (UCM)

Mª Rufina Bastida de la Calle (USC)

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Simposio patrocinado por: Grupo Especializado de Química de Estado Sólido y Grupo Especializado de Química Inorgánica

Lunes 20 de Julio 2015

19:30	**Reunión del Grupo Especializado de** "*Química del Estado Sólido y Materiales*"

Martes 21 de Julio 2015

08:40 – 09:40	**PL-3**	***Conferencia Plenaria*** (Común a todos los simposios) **Samuel I. Stupp** *"Supramolecular Materials Chemistry"*

Chairman: Flaviano García

10:00 – 10:30	**S9-IL-01**	**Montserrat Casas Cabanas** *"Crystal Chemistry of Battery Materials"*
10:30 – 10:45	**S9-OC-01**	**Miguel A. Alario-Franco** *"Incremento en la Temperatura Crítica y Modificaciones en la Estructura Local en la Óxidoreducción de Molibdo-cupratos Superconductores del Tipo: Mo_xCu_1-$xSr_2RECu_2O_y$ (RE=Y, Er, Tm)"*
10:45 – 11:00	**S9-OC-02**	**A. Navarro** ***"Microporous Lignin-derived Carbons for Electric Double-Layer Capacitors"***
11:00 – 11:30		Pausa Café

Chairwomen: M. Antonia Señarís / Rufina Bastida

11:30 – 12:00	**S9-IL-02**	**Florent Boucher** *"Ab initio Calculation for Characterizing Energy Storage Materials: Study of the FePOA Family (A=Li, Na)"*
12:00 – 12:15	**S9-OC-03**	**Rubén Más Ballesté** *"2D/3D COF Nanostructures: From Structural Design to Practical Applications"*
12:15 – 12:30	**S9-OC-04**	**Salomé Delgado** *"Multifunctional Coordination Polymers Based on Organosulfur Ligands"*
12:30 – 12:45	**S9-OC-05**	**Pedro González** *"Efecto de la Grafitización en las Propiedades de Materiales de Carbono Derivados de Complejos Organometálicos"*
12:45 – 13:00	**S9-OC-06**	**Alaina Moragues** *"Improving the Accessibility of Guest Species in Nanoparticulated Bimodal Porous Silicas"*
13:00 – 13:30	**S9-IL-03**	**Jorge Gascón** *"Rational design of structured catalysts and membranes"*
13:30 – 15:30		Comida

Martes 21 de Julio 2015

Chairwoman: Susana García

15:30 – 16:00	**S9-IL-04**	**Amir Abbas Haghighirad** *"Perovskite Material as Light Harvester: Materials Design and Structure"*
16:00 – 16:15	**S9-OC-07**	**Juan Bermúdez García** *"Temperature and Pressure Dependence on Functional Properties in a Novel Multisensitive [TPrA][Mn(dca)$_3$] Perovskite"*
16:15 – 16:30	**S9-OC-08**	**Jordi Cirera** *"Molecular-Level Characterization of the Guest Effect on the Transition Temperature in Spin-Crossover Metal-Organic Frameworks"*
16:30 – 17:00		Pausa Café

Chairman: Regino Sáez

17:00 – 17:30	**S9-IL-05**	**Ulises Amador Elizondo** *"Understanding the Properties of SOFCs Materials through their Composition, Structure and Microstructure"*
17:30 – 17:45	**S9-OC-09**	**Elena Solana** *"Structural Characterization and Magnetic Properties of High Pressure Mn_2MSbO_6 Oxides"*
17:45 – 18:00	**S9-OC-10**	**Mario Llusar** *"Synthesis and Characterization of New Reddish-Brown Pigments Based on Perovxkite Y(Zn, Ti, Fe)O_3 Solid Solutions"*
18:00 – 18:30	**S9-IL-06**	**"Elías Palacios** *"New Materials for Magnetic Refrigeration at Low Temperatures"*

18:30	***Sesión de Pósteres***
19:30	**Reunión de la Junta Directiva del Grupo Especializado de "*Química* Inorgánica"**
20:00	**Asamblea General Directiva del Grupo Especializado de "*Química* Inorgánica"**

Comunicaciones Invitadas (IL)

S9: *Síntesis, Caracterización y Propiedades de Materiales Emergentes*

CRYSTAL CHEMISTRY OF BATTERY MATERIALS

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Keywords: *structure, microstructure, Li-ion, Na-ion, FAULTS program*

Batteries are the leading electric energy storage technology today and the main contender for the large volume of future applications linked to stationary energy storage of renewables and electric transportation fields. These devices store energy in the form of chemical (redox) reactions and the amount of energy stored as well as their cycling ability is strongly dependent on the physico-chemical properties of the constituent electrode materials. These include mainly the composition, the structure, the microstructure (i.e. size, morphology, amount and location of defects) and the electronic and ionic conductivities.

In this talk different battery chemistries will be reviewed with a special focus on the crystal chemistry properties of electrode materials and their advanced characterization using diffraction techniques (X-ray, neutron and electron diffraction). Examples of structural transformations occurring upon battery cycling or the impact of the initial structure of the electrode material on the electrochemical properties will be shown [1-4]. These and other examples will illustrate the capabilities of diffraction techniques, from which quantitative information regarding microstructural features such as anti-phase domains, stacking faults, twinning or intergrowths can now be extracted in order to establish correlations with materials' properties. The FAULTS refinement program [5-7], now available within the FullProf suite of programs [8], is a powerful tool that has been developed with this purpose and will be presented here as well.

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Available at http://www.ill.eu/sites/fullprof/php/downloads.html

S9: *Síntesis, Caracterización y Propiedades de Materiales Emergentes*

"Ab INITIO CALCULATIONS FOR CHARACTERIZING ENERGY STORAGE MATERIALS: STUDY OF THE $FePO_4$ FAMILY (A=Li, Na)"

F. Boucher,[1] J. Gaubicher,[1] M. Cuisinier,[1] D. Guyomard,[1] and P. Moreau[1]

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Keywords: *DFT, Olivine, EELS, charge ordering, Mössbauer, X-Ray synchrotron*

Sodium-ion batteries (SIB) are considered as an attractive alternative to lithium-ion batteries (LIB) as they could potentially be much less expensive, safer, and sustainable.[1] Clearly, one of the major concerns that we currently face consists in determining to what extent the results gathered over the past twenty years in the Li battery field, can be transferred to the Na one.

In the case of the olivine $FePO_4$ family, the Na intercalation process is significantly different from the Li one with the existence of a stable intermediate $Na_{2/3}FePO_4$ phase.[2] By combining electronic diffraction, X-Ray synchrotron radiation diffraction as well as Mössbauer and NMR spectroscopies, we identified the intermediate phase as a fully ordered $Na_{2/3}FePO_4$ composition. Thanks to *ab initio* DFT calculations, a very good agreement between all analytical methods was found, which definitely confirms the good assignment of the superstructure showing a vacancy ordering along the channels coupled with a Fe^{II}/Fe^{III} charge ordering in a monoclinic three-fold supercell.[3] From our DFT calculations, we also propose a structural model for the intermediate $Li_{2/3}FePO_4$ which is very similar to the sodium one.

Formation energies and electrochemical potential calculations confirm that $Na_{2/3}FePO_4$ and $Li_{2/3}FePO_4$ are stable and metastable, respectively, and that they yield insertion potentials in fair agreement with experimental values. Quite surprisingly, the threefold ordering mechanism we describe for $Na_{2/3}FePO_4$ and $Li_{2/3}FePO_4$ seems to be quite general as it can also explain the NMR data experimentally observed for ^{7}Li and ^{31}P in $Li_{2/3}CoPO_4$.[4]

Ab initio DFT calculations have been also used to help at the interpretation of electron energy loss spectra obtained on different Li_xFePO_4 crystals. A specific signature for lithiated and non lithiated particles was evidenced and used afterwards for a very fast identification procedure using energy filtered TEM images.[5,6]

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S9: *Síntesis, Caracterización y Propiedades de Materiales Emergentes*

RATIONAL DESIGN OF STRUCTURED CATALYSTS AND MEMBRANES

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Palabras Clave: *metal organic frameworks, catalysis, membrane separation*

The worldwide primary energy consumption, although decelerated due to the economic global crisis, continues growing year by year, with an increase of 2.5% in 2011. The current energy system is mostly based on fossil fuels, which have led to an increase in global warming gas emissions. As a result, the concentration of CO_2 in the atmosphere and in the oceans keeps increasing, leading to a global temperature rise and to water acidification, respectively. Most of the global warming over the past 50 years is very likely to have been caused by emissions of carbon dioxide (CO_2) and other greenhouse gases (GHG) derived from human activities. Without any action to reduce these emissions, the global average temperature is likely to rise further by 1.8-4 °C this century, and by up to 6.4 °C in the worst case scenario. These are the greatest environmental, social and economic threats mankind is facing nowadays.

Combating climate change is a key priority for the European Commission who has agreed on three common objectives for tackling today's energy and climate challenges, the so-called "3x20": reduce greenhouse gas emissions and energy use both by 20%, and achieve a 20% of renewable energy in the supply chain by 2020 [1]. These efforts are aimed to facilitate the transition to sustainable energy sources and to mitigate global warming associated with the massive utilization of fossil fuels. In order to address these challenges, new nano-structured materials are going to play a pivotal role, especially in the fields of catalysis and gas separation, the main topics of this lecture. [2-4]

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S9: *Síntesis, Caracterización y Propiedades de Materiales Emergentes*

PEROVSKITE MATERIALS AS LIGHT HARVESTER: MATERIALS DESIGN AND STRUCTURE

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Keywords: *Organic-inorganic hybrid materials, perovskites, materials synthesis, crystallography*

In recent years there has been an increasing interest in hybrid organic-inorganic perovskites and perovskite-related materials, due to their unique structures of alternate stacking sheets of organic and inorganic components. These materials enabling the design of insulators, semiconductors and metals offer the potential for a wide range of electronic, magnetic and structural properties. Prominent example of recent discoveries in this family of compounds has been the development of solution processed photovoltaic metal halide perovskites, i.e. $CH_3NH_3PbI_3$ as light absorber achieving efficiencies up to 20%. However, surprisingly little is known about the structural and the mechanism that makes them so successful for optoelectronic and solar cell applications. $CH_3NH_3PbI_3$ adopts a variant of the well-known perovskite structure ABX_3, with Pb and I forming the BX_3 framework and the methyl-ammonium molecule occupying the *A* site. $CH_3NH_3PbI_3$ is cubic (SG) at high temperatures, and is known to undergo two phase transitions on cooling – from cubic (or pseudo-cubic) to tetragonal at ~327K and from tetragonal to orthorhombic at ~162K [2]. However, there has been a longstanding and still unresolved controversy about the exact symmetry, due to disordered arrangement of CH_3NH_3 molecules in the lattice [1,2,3,4]. I will give an overview of the single crystal diffraction study of $CH_3NH_3PbI_3$ and $CH_3NH_3SnI_3$ to address this by having a closer look into the subtle structural features.

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S9: *Síntesis, Caracterización y Propiedades de Materiales Emergentes*

UNDERSTANDING THE PROPERTIES OF SOFCS MATERIALS THROUGH THEIR COMPOSITION, STRUCUTRE AND MICROSTRUCTURE

Alejandro Gómez-Pérez[1], M.Teresa Azcondo-Sánchez[1], Mercedes Yuste[1], Juan Carlos Pérez-Flores[1], Khalid Boulahya[2], Susana García-Martín[2], Julio Romero de Paz[3], Glenn Mather[4], Domingo Pérez-Coll[4], Jesús Canales-Vázquez[5], Clemens Ritter[6], Nikolaos Bonanos[7], Florence *Porcher*[8], Alvaro Muñoz-Noval[9], Markus Hoelze[10], Flaviano García-Alvarado[1] and Ulises Amador[1]

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Keywords: *SOFC, perovskite, cathode, oxygen vacancies, defect chemistry, electrical properties, phase transitions, nanomaterials, combustion synthesis*

The so-called “double perovskites” with general formula $A_2B'B''O_6$ with transition-metal cations on the B sites of different sizes and electronic structures provide a huge range of compositions and properties due to their ability to support mixed oxidation states and high concentrations of oxygen vacancies. Excellent electrical and electrocatalytic properties can be engendered, which find application in numerous high-temperature electrochemical applications

In this research field, perovskite-like compounds have been extensively considered in the development of new materials potentially useful as electrodes in SOFCs. Aliovalent substitution in the A or B position may produce oxygen vacancies and hence an enhancement of ionic conductivity. On the other hand, when B is occupied by an adequate transition metal, different average oxidation states at different oxygen partial pressure can be stabilized and it may change the both nature and magnitude of the electronic conductivity. Therefore, mixed ionic-electronic conductivity (MIECs) and high catalytic activity can be found.

In this contribution we present some results on materials with general formulae $(LnLn'Sr\square)_{2-x}MTiO_{6-\delta}$ (Ln=La, Ln’=Ce, □=vacancy, M=Ni, Co) studied by different techniques to stablish the relationships between composition, structure, microstrucuture and electrical and electrochemical properties.

S9: *Síntesis, Caracterización y Propiedades de Materiales Emergentes*

NEW MATERIALS FOR MAGNETIC REFRIGERATION AT LOW TEMPERATURES

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Keywords: *Magnetocaloric effect, Molecular group, Low temperature.*

Recently the refrigeration by adiabatic demagnetization, or more generally, by different magnetic processes, became again a competitive procedure (due to the huge increasing price of ^{3}He) to liquefy gases as He, H_2, natural gas, and so on [1]. For this purpose compounds with high magnetic density are adequate, and with magnetic ordering (Curie, T_C, or Néel, T_N, point) near the working temperatures, like RCo_2 (R = rare earth). In addition to T_C, T_N, the most important properties are the entropy decrement $-\Delta S_T$ under a given isothermal magnetic field increase ΔB, and the temperature increment ΔT_S when the field is adiabatically changed.
We present here the properties of some RXO_4 (R = Gd, Tb, Ho, X = P, V, Cr) and $Gd(HCOO)_3$. Gd is are the most interesting rare earth due to its extremely low magnetic anisotropy, being an spin-only (s = 7/2) magnetic atom, in spite of its magnetic moment, lower than that of Tb and Ho. In this sense the Gd formate has the highest $|\Delta S_T|$= 53 J/kg·K observed [2] at 2 K, for ΔB = 7 T, until the ortho-phosphate was studied, with $|\Delta S_T|$= 62 J/kg·K for the same ΔB [3].

Another strategy is to use molecular, high spin compounds. The intra-molecular interaction produces crossing of magnetic energy levels depending on the field B, which results in larger entropy changes for some given B values, and in general a normal, $(dS/dB)_T$ <0, or inverse $(dS/dB)_T$ > 0 magnetocaloric effect depending on B. Some cases of the molecular groups Fe_{14}, Gd_2, or Gd_7 will be presented. As just an example, Gd_2 showed $|\Delta S_T| \cong$ 30 J/Kg.K for a very moderate ΔB = 1 T, never reached before with a molecular group [4].

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Comunicaciones Orales (OC)

***S9:** Síntesis, Caracterización y Propiedades de Materiales Emergentes*

INCREMENTO EN LA TEMPERATURA CRÍTICA Y MODIFICACIONES EN LA ESTRUCTURA LOCAL EN LA OXIDOREDUCCIÓN DE MOLIBDO-CUPRATOS SUPERCONDUCTORES DEL TIPO: Mo_xCu_{1-x} $Sr_2RECu_2O_y$ (RE = Y, Er AND Tm)

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Palabras Clave: *Cupratos superconductores,desplazamientos atómicos, Tc*

El estudio por medio de difracción de R-X y neutrones del proceso de oxidación de los materiales citados a elevadas presiones de oxígeno (P ≈ 1bar-90 kbar) y altas temperaturas (≤ 1273 K), modifica la estructura local de las pirámides [Cu-O_5], cuyas bases constituyen los planos superconductores en los cupratos: El oxígeno apical se aproxima progresivamente al cobre del cuadrado plano [Cu-O_4] y el ángulo basal O1-Cu2-O1 se incrementa con el contenido en oxígeno.

En el curso de ese proceso Red-Ox, el molibdeno se oxide y el cobre se reduce. Al mismo tiempo, la temperatura crítica se incrementa de manera notable.

Este comportamiento resulta anómalo en relación a la tendencia habitual de los procesos de oxidación de superconductores análogos como los de la familia de los denominados *cupratos de mercurio*. Estos resultados serán descritos y comentados en la presente comunicación.

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MICROPOROUS LIGNIN-DERIVED CARBONS FOR ELECTRIC DOUBLE-LAYER CAPACITORS

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Key words: *supercapacitors, lignin, carbons*

Electrical double–layer capacitors (EDLCs) store charge at the electrode/electrolyte interface by ion adsorption on the surface of a porous carbon electrode. Scarce progress on the development of carbons with controlled porosity has restricted further advances in the energy density of EDLCs, especially in the volumetric terms, with most recent improvements being rather connected to the use of more stable electrolytes and the design of hybrid systems. [1] Importantly, an adequate pore size is crucial to improving EDLC performance as evidenced for nanoporous carbons with an average pore size smaller than 1 nm and specific surface areas lower (~ 1500 m^2/g) than for a great number of activated porous carbon materials. [2,3] Thus, advancing the synthesis of nanoporous carbons appears to be crucial among the approaches to adapting EDLCs to high energy-demanding applications.

The synthesis of high surface activated nanoporous carbons as electrode material for supercapacitors from renewable natural precursors seems to be a suitable approach because of their extremely large capacitance values, their relative low price, and the easy route of preparation of these materials in large quantities. [4]

Nanoporous carbons with narrow and tuneable pore size (~ 1 nm) and surface area (800-1600 m^2/g) have been produced by activation of lignin with KOH. For different carbonization and activation temperatures, the pore size and specific surface area were analysed by adsorption/desorption of N_2 gas at 77 K and SAXS. Studies related to the material properties of the most adapted pore size and the electrolyte characteristics as well as their effect on its capacitive properties in symmetric double–layer capacitors were assessed. Capacitances up to 200 F/g and 100 F/g in aqueous and organic electrolytes respectively were achieved.

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2D/3D COF NANOSTRUCTURES: FROM STRUCTURAL DESIGN TO PRACTICAL APPLICATIONS

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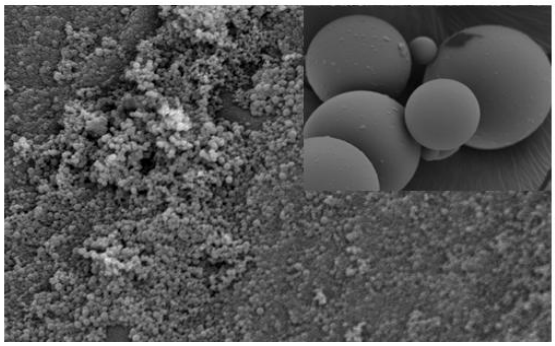
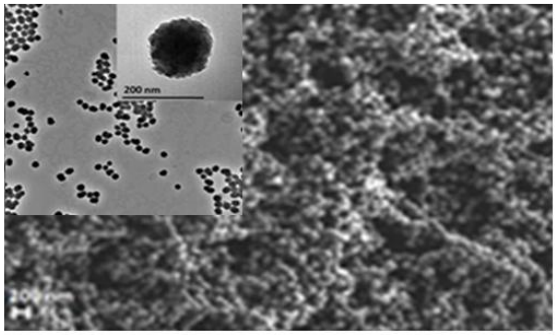
Keywords: *Covalent Organic Frameworks, nanoparticles, catalysis*

In this communication we will demonstrate how not only structural design of building blocks, but also fine tuning of reaction conditions, allow to control the nanostructures found by condensation of Covalent Organic Frameworks (COFs). In particular, first, we will show that, under certain conditions, laminar COFs based on imine bridging groups can collapse into spherical structures. Later, we will report about the obtention of crystalline nanoparticles from 3D COF architectures also based in imine condensation. Encapsulation of relevant molecular species and base-catalyzed organic transformations will be presented as main applications of these materials.

Spherical structures collapsed from a laminar COF



Crystalline nanoparticles from 3D COF architecture



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MULTIFUNCTIONAL COORDINATION POLYMERS BASED ON ORGANOSULFUR LIGANDS

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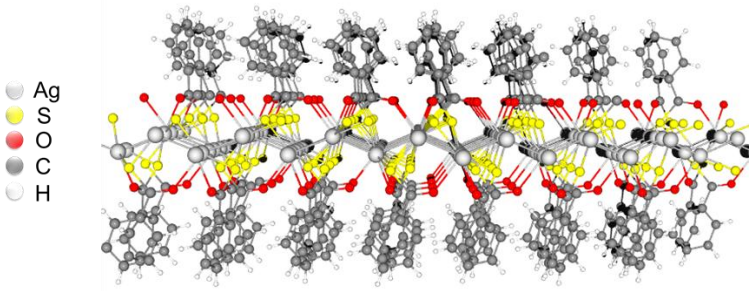
Keywords: *Coordination polymers, physical properties*

The study of coordination polymers (CPs) as materials advanced has gained major attention in recent years as an interface between synthetic chemistry and crystal engineering providing a solid foundation to help in the understanding of how molecules can be organized and how functions can be achieved[1]. The use organosulfur ligands in combination with metal ions is especially suitable for the design of multifunctional materials with electronic properties including electrical, optical and magnetic[2].

The direct reactions between $CuCl_2$ or $AgNO_3$ and thiobenzoic or thioacetic acids have led to three new 2D CPs of formula $[M(R\text{-}C(O)SH]_n$ (M= Cu, Ag, R= Ph, **1**, **2**; M= Ag, R= CH_3, **3**). Their X-ray diffraction structural characterization show a similar layered structure where metal atoms are tetrahedrically coordinated by three sulfur and one oxygen atoms of four different thioacid moieties.



The electrical conductivity at room temperature show values of $\sigma = 1.3\cdot10^{-6}$, $1.1\cdot10^{-7}$and $2.9\cdot10^{-6}$ S/cm for **1**, **2** and **3** respectively, suggesting a semiconductor behavior that was confirmed by DC electrical conductivity measurements at variable temperature. The photoluminescent properties have been studied in solid state at room temperature. Unlike the molecular species, most CPs are insoluble once formed, therefore recrystallization is not a choice for their processability. However, in this case polymers **1** and **2** show an unusual reversible recrystallization process when both are dissolved in acetonitrile or pyridine respectively, and these solutions revert to the starting materials **1** and **2** (characterized by CNHS analyses, IR spectroscopy and X-ray powder diffraction) upon concentration by controlled solvent elimination.

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EFECTO DE LA GRAFITIZACIÓN EN LAS PROPIEDADES DE MATERIALES DE CARBONO DERIVADOS DE COMPLEJOS ORGANOMETÁLICOS

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Palabras Clave: *Grafitización, Nanoestructura, Propiedades texturales, Capacitancia.*

Los materiales de carbono nanoestructurado han recibido especial interés debido a sus potenciales aplicaciones como capacitores electroquímicos, soportes catalíticos, almacenamiento de gases, entre otras. Los complejos organometálicos han sido ampliamente usados como precursores de carbono para producir nanoestructuras de carbono, debido a que su composición química provee el metal catalizador y el carbono precursor [1,2]. El presente trabajo, describe la síntesis y caracterización de materiales de carbono poroso, preparados por reacción de cloro gas con precursores organometálicos. Las muestras se prepararon en un horno tubular a 900 ºC durante 30, 60, 90 y 120 min en un flujo de gas cloro (50 mL/min) de acuerdo con la siguiente reacción:

$Ti(C_5H_5)_2Cl_2 + 6Cl_2 \rightarrow 10C + TiCl_4 + 10HCl$

Los materiales se caracterizaron utilizando difracción de rayos X, espectroscopia de Raman y adsorción/desorción de nitrógeno a 77K. Los patrones de difracción de rayos X sugieren que estas muestras consisten principalmente de carbono desordenado con bajo grado de grafitización (13.5 – 16.5 %). Estos resultados están de acuerdo con los datos obtenidos a partir de los espectros de Raman, donde la presencia de la banda D (≈ 1350 cm^{-1}) indica la presencia de redes de carbono desordenadas. La longitud en el plano de las láminas tipo grafeno de estos materiales varía de 4.04 a 4.70 nm, cuando el tiempo de reacción aumenta de 30 a 120 minutos. Los análisis texturales revelan isotermas de adsorción de Tipo I con H4 histéresis, áreas microporosas tan altas como 855 m^2/g y volumen de poros de 0.56 cm^3/g. El análisis de espectroscopia infrarroja, indica la ausencia de grupos funcionales superficiales oxigenados. Las medidas de voltametría cíclica muestran valores de capacitancia que van desde 185 F/g a 43 F/g en electrolito de KOH. La forma de los diagramas de Nyquist, de los electrodos de carbono fabricados, indica un proceso casi puramente difusivo a tiempos de reacción bajos y una mezcla de los procesos cinéticos y difusivos para los materiales clorados tiempos más largos.

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IMPROVING THE ACCESSIBILITY OF GUEST SPECIES IN NANOPARTICULATED BIMODAL POROUS SILICAS

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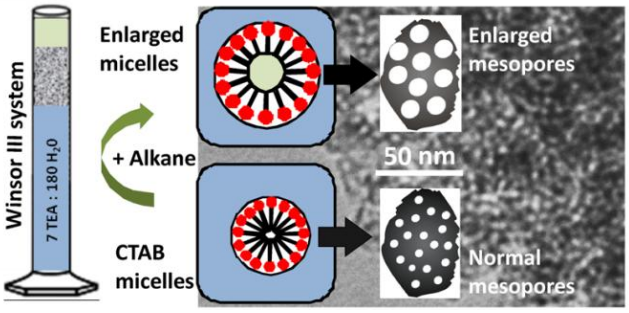
Keywords: *Mesoporous silica, swelling agents, template synthesis*

Mass-transfer kinetics seems to be highly favoured in siliceous supports consisting of aggregates of mesoporous nanoparticles [1]. Nanoparticle aggregation causes large textural voids. Diffusion constrains through the resulting hierarchically structured pore systems are mainly dependent on the features of the intra-particle mesopores [2]. By using alkanes as swelling agents, we have been able to significantly increase the mesopore size in previously well characterized UVM-7-derived materials. Thus, regardless the alkane used, a comparable global swelling effect has been achieved: we have reached intra-particle expanded mesopore sizes up to ca. 4.3 nm starting from the ca. 2.7 nm in the original UVM-7 materials. This expansion really represents an important progress in terms of enabling the incorporation of certain bulky substrates to the silica network. The combination of hierarchical porosity and short-length of the mesopores (showing expanded cross-sections) allows improving accessibility (avoiding undesired phenomena of pore-blocking) and results in an enhanced capability of these supports to host drugs and enzymes. The achieved pore expansion has been possible by judiciously adapting our preparative protocols based on classical concepts of the chemistry of colloids (Winsor III system).



The use of UVM-7-like expanded nanoparticulated silicas as supports entails a significant increase of the total uptake for small drugs (as ibuprofen) and enzymes (lysozyme and trypsin). In addition, when compared to other mesoporous silicas, short contact times are required.

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TEMPERATURE AND PRESSURE DEPENDENCE OF FUNCTIONAL PROPERTIES IN A NOVEL MULTISENSITIVE [TPrA][Mn(dca)$_3$] PEROVSKITE

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Keywords: *hybrid organic-inorganic, multiferroic, thermal expansion, high–pressure, phase transition.*

Hybrid organic-inorganic materials are an emergent family of compounds in modern materials science.[1] In these versatile compounds, the appropriate combination of organic and inorganic units can not only give rise to new and interesting properties, but also afford possible coexistence and/or synergism of multiple functionalities and sensibilities within one material. In this context, recently, hybrid organic-inorganic formate materials with perovskite-like structures and formula [AmineH][M(HCOO)$_3$]$_n$ (where M: divalent transition metal cations, AmineH: mid-sized protonated amines) have been intensively studied as promising type I-multiferroic materials.[2,3]

In the present work, we have focused on another related, but very little explored, family of potentially interesting compounds: the dicyanamide-bridged perovskite-type [TPrA][M(dca)$_3$] materials (where M: divalent transition metal cations, dca: dicyanamide anion, [N(CN)$_2$]$^-$, [TPrA]: tetrapropylammonium cation, [(CH$_3$CH$_2$CH$_2$)$_4$N]$^+$). According to the literature [TPrA][Mn(dca)$_3$] crystallizes in the tetragonal *P*-42$_1$*c* space group (non-centrosymmetric) and retains the same symmetry and space group from room temperature down to 110 K and it exhibits long-range weak-antiferromagnetic ordering below 2.1 K.[4]

Here, and for the first time, we explore the structural characteristics of this compound above room temperature, its dielectric properties and the influence of external hydrostatic pressure and temperature on its behaviour. Very interestingly, we have observed that this compound experiences a sharp first order structural phase transition at $T_t \approx 330$ K (from the room temperature *polymorph I* –non-centrosymmetric, *P*-42$_1$*c*- to the high temperature *polymorph II* –centrosymmetric, *I*4*/mcm*–), that implies order/disorder phenomena, ionic displacements, a large and anisotropic thermal expansion (specially along the c-axis) and gives rise to an associated antiferroelectric (AFE)-paraelectric transition. Additionally, the obtained experimental results reveal that this compound is not only a multiferroic material (exhibiting coexistence of magnetic and electric order) but also a multistimuli-responsive material, with a very large sensitivity towards temperature and applied external pressure, even for low values. For this reason, this material displays a potential interest for technological applications such as temperature/pressure sensing.

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MOLECULAR-LEVEL CHARACTERIZATION OF THE GUEST EFFECT ON THE TRANSITION TEMPERATURE IN SPIN-CROSSOVER METAL-ORGANIC FRAMEWORKS

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Keywords: *Metal-Organic Frameworks (MOFs), Spin-Crossover, Transition Temperature, Electronic Structure, Molecular Mechanics*

Metal-Organic Frameworks (MOF) represent a versatile class of porous materials that have recently attracted much interest due to their broad range of potential technological applications, ranging from gas separation to catalysis and sensing devices.[1,2] The presence of open-shell metal centers, such as Fe(II), in the MOF secondary building unit provide the opportunity to develop multifunctional porous materials in which both surface area and magnetic properties can be rationally tuned for specific applications. In particular, it has been shown that the magnetic properties of the spin-crossover MOFs are tightly bounded to the loading and nature of the guest molecule. In this contribution, we describe our recent work on the molecular modelling of the spin-crossover behaviour of MOF materials using a hybrid Monte Carlo/Molecular Dynamics (MC/MD) methodology. Our results for the $[Fe(pyrazine)_2Pt(CN)_4]$ MOF, for which the spin-crossover properties have been shown to be extremely sensitive to the nature of the guest molecules adsorbed in the pores, are in excellent agreement with the experimentally reported results.[3] We demonstrate that, by expanding the conventional molecular mechanics scheme to account for electronically-driven effects,[4] it is possible to develop molecular models of MOF materials that correctly represent both spin states, thus enabling direct simulations of spin-crossover properties as a function of temperature and guest adsorption.[5] In particular, the effect of water loading in the gradual decrease of the transition temperature will be shown, for which our simulations provide with a molecular level understanding of the interplay between water loading, pore expansion and shift in the transition temperature.

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STRUCTURAL CHARACTERIZATION AND MAGNETIC PROPERTIES OF HIGH PRESSURE Mn_2MSbO_6 OXIDES

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Keywords: *high pressure, double perovskites, magnetic structures*

A large variety of interesting electric and magnetic properties develop in compounds of general formula ABO_3 crystallizing with perovskite structure. The diversity on possible compositions makes them attractive not only for fundamental science but also for their potential applications. Double perovskites, of general formula $A_2BB'O_6$, are obtained when B and B' cations are sufficiently different in charge and/or size, getting rock-salt type ordered [1]. *A* or *B* site Mn containing perovskites show complex orderings due to their different charge and spin degrees of freedom, which induce a wide range of properties, including magnetorresistance and multiferroicity[2].

Here we present a recent study on some Mn_2MSbO_6 double perovskites, high pressure synthesized to stabilize the small Mn^{2+}cation in the highly coordinated *A*-site. Different magnetic properties arise from the substitution of M for different transition metals. For instance, the M = Cr compound shows antiferromagnetic interactions between the Mn^{2+} and Cr^{3+} sublattices, arranged in a simple magnetic structure defined by the propagation vector k = [½ 0 ½][3].The substitution of Cr^{3+} for Fe^{3+} turns the magnetic structure into an elliptical spiral determined by the incommensurate propagation vector k = [0 0.4260]. As a result, ferromagnetic inhomogeneities appear as short range order correlations at low temperatures, originating a hysteretic behavior of the resistivity[4].

The polymorphism of these oxides depending on the pressure synthesis conditions is also presented. Ilmenite modifications of the M = Cr and Fe compounds show complex and different frustated magnetic structures which arise from the competition of antiferro and ferrimagnetic interactions. Interestingly, the substitution of M for Sc^{3+} induces a non-centrosimmetric arrangement of cations in a $LiNbO_3$-type structure allowing a potential multiferroic behavior as that observed for $MnTiO_3$-II [5].

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SYNTHESIS AND CHARACTERIZATION OF NEW REDDISH-BROWN PIGMENTS BASED ON PEROVSKITE $Y(Zn,Ti,Fe)O_3$ SOLID SOLUTIONS

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Keywords: *Perovskite, $YFeO_3$, Red Ceramic Pigments, Iron, Citrate gels*

One of the most prolific research hot topics in the ceramic industry concerns the discovery of new better-performant red ceramic pigments [1]. For instance, $YAl_{1-x}Cr_xO_3$ and related compositions [2,3], chromium-doped $CaTiO_3$ and other alkaline-earth titanate perovskites [4] have been postulated as new reddish pigments. Recently, P. Jiang *et al* smartly reported the feasible modulation from yellow to orange, reddish and to dark brown colors by increasing the Fe content in $YIn_{1-x}Fe_xO_3$ hexagonal phases (related but distinct to common ABO_3 perovskites), in which the coordination for the In/Fe site is trigonal-bipyramidal [5]. These phases could be interesting for paint and pigmenting industries, although their application as pigments or dyes was not tested.
Considering that indium is rather an expensive and scarce element, it thus occurred to us that we could also obtain a nice color gamut from yellowish to brown and red by replacing Fe^{3+} ions by equal amounts of Zn^{2+} and Ti^{+4} (instead of In^{3+}) in $YFeO_3$ hexagonal (metastable) or orthorhombic perovskite phases [6]. With this aim, different $Y(Zn_xTi_x)Fe_{1-2x}O_3$ solid solutions were prepared by solid-state route and also from metalorganic decomposition of nitrate-citrate xerogels [7]. Raw and fired pigments were characterized by XRD, SEM/EDX, BET, ATD/TG, UV-vis-NIR and CIE-L*a*b* (color measurement) techniques. The effect of synthesis route, composition and firing temperature is discussed in terms of stabilization of hexagonal or orthorhombic phases, microstructure, color evolution and performance as new ceramic pigments.

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S9: *Síntesis, Caracterización y Propiedades de Materiales Emergentes*

METAL-ORGANIC FRAMEWORKS BASED ON LANTHANIDE AND CARBOXYLATE LIGANDS: SYNTHESIS, STRUCTURE AND PROPERTIES

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Keywords*: MOFs, Lanthanide, Carboxylate, Porosity, Luminescence*

Metal-organic frameworks (MOFs) are considered nowadays as the most promising class of materials ideal for various relevant applications such as gas storage and separation, catalysis, drug delivery and chemical sensing due to the inherent structural modularity [1]. In particular, lanthanides-organic frameworks (LOFs) in which the intrinsic chemical character, magnetic and optical properties of lanthanides (Ln^{3+}) cations are often not matched by other transition metal cations. Thus, synthesis of LnOFs is an attractive subject of great interest both from a fundamental scientific standpoint and also for different practical applications [2,3]. Carboxylate linkers are of particular interest to design LnOFs due to their structural rigidity, diversity of coordination geometries, possibility of facilitating the formation of porous structures [4], and high affinity toward Ln^{3+} cations.

In this communication, we give an overview of our ongoing research concerning the synthesis of novel LOFs by using rigid carboxylate linkers, such as dianion BDC (1,4-benzenedicarboxylate acid) [5] and PDC (2,5-pyridinedicarboxylic acid), and trianion BTB (1,3,5-benzene(tris)benzoic acid).

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SÍNTESIS Y CARACTERIZACIÓN DE NANOFÓSFOROS Eu^{2+}-$Ca_{0.5}Zr_2(PO_4)_3$

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Palabras Clave: *nanofósforos, estructura tipo NASICON, emisión azul, método sol-gel*

Constituye un reto hoy la obtención de luz blanca basada en fósforos que, dentro del espectro visible, emitan en la zona del rojo, del verde y del azul [1]. Si bien es más conocida la emisión correspondiente al rojo y al verde, menos estudiada ha sido hasta fecha la emisión en la zona azul del espectro. Existe, por este motivo, un interés focalizado hacia la mejora de las prestaciones que puedan ofrecer, de cara al mercado tecnológico, los fósforos que emiten en el azul.

Los fosfatos de estequiometría $M_{0.5}Zr_2(PO_4)_3$ (con M = Ca^{2+}, Sr^{2+}, Ba^{2+}) y dopados con un cierto porcentaje de europio se han investigado por su emisión luminiscente centrada en la zona del azul [2]. Estos compuestos que cristalizan en una estructura tipo NASICON, se han obtenido por reacción en estado sólido a temperaturas elevadas dando origen a polvos constituidos por partículas de un tamaño apreciable [3].

Considerando que, en general, el uso de nanopartículas favorece la intensidad de las emisiones luminiscentes, hemos sintetizado fases del tipo indicado empleado un método sol-gel seguido de un tratamiento en corriente de N_2/H_2 que ha permitido la obtención de nanopartículas de composición $Ca_{0.5}Zr_2(PO_4)_3$ dopadas con un 10% de Eu^{2+}. Se exponen en este trabajo los resultados obtenidos en la preparación y la caracterización de dichas fases.

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MATERIALES RESPETUOSOS CON EL MEDIOAMBIENTE: ÓXIDOS MIXTOS DE Fe Y Mn COMO ÁNODOS PARA BATERÍAS DE IÓN Li

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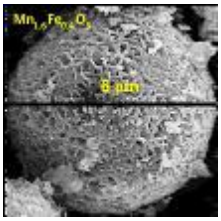
Palabras Clave: *baterías de Li, ánodos, óxidos mixtos de Fe y Mn*

Las baterías de iones litio son dispositivos diseñados para almacenar energía eléctrica y presentan alta densidad de energía y una gran variedad de aplicaciones [1]. Para mejorar sus prestaciones es conveniente aumentar su densidad energética, su potencia específica y su vida útil. En la actualidad, las baterías comerciales han utilizado ánodos de grafito, ya que este material presenta las características idóneas para ser empleado como ánodo [2]; sin embargo, los ánodos de grafito presentan dos inconvenientes relevantes, por una parte su capacidad teórica (372 mA·h/g) que está limitada a la introducción de un átomo de Li por cada 6 átomos de C y por otra su baja reversibilidad en el ciclaje. Una alternativa viable para la sustitución de estos ánodos son los óxidos de metales de transición, en los que tiene lugar una reacción redox o de conversión con Li [3] basada en que la presencia de partículas manométricas de M de transición, pueden descomponer el Li_2O. En este trabajo, se indican los resultados más relevantes de una serie de óxidos mixtos de Mn y Fe, que pueden utilizarse como ánodos en dichas baterías. Los resultados electroquímicos más relevantes de los óxidos mixtos $Mn_{2-x}Fe_xO_3$ (estructura bixbyite) y $Mn_{3-x}Fe_xO_4$ (estructura espinela). Las reacciones implicadas en estos procesos proporcionan capacidades teóricas bastante elevadas 1017 mA·h/g para la estructura Bixbyite y 930 mA·h/g para la estructura espinela. Además, éstos materiales tienen destacadas propiedades electroquímicas, son baratos y no presentan problemas de contaminación ambiental. En este trabajo, se emplean diferentes rutas de síntesis para la obtención materiales nanoestructurados uniformes y porosos que facilitan los caminos de difusión de los iones Li en los óxidos de los M de transición. Todos ellos presentan una forma esférica con una gran cantidad de poros en la superficie (figura 1, $Mn_{1.6}Fe_{0.4}O_3$). Los electrodos utilizados están formados con alginato sódico con agua como disolvente, los electrolitos son una disolución de $LiPF_6$ en (EC)- (DEC) y el ánodo es Li metal.



Todas las pilas se ciclan a diferentes velocidades, analizando los resultados en función de la composición, la estructura y la morfología. Los resultados más destacados corresponden a los materiales con estructura tipo bixbyita (4/1) con una capacidad específica (35 ciclos) del orden de 500 mA·h/g a una

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LOW-COST SYNTHESIS OF BIMODAL MESOPOROUS SILICA-BASED MATERIALS

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Keywords: *Mesoporous silica, sodium silicate, template synthesis*

The interest on mesoporous materials has continued significantly increasing in recent years due to their possible applications in areas such as catalysis, molecular sieving, chemical sensors, environmental and biomedical sciences. In some cases, the performance of mesoporous silicas can be improved if they are prepared in the form of nanoparticles, either isolated or as aggregates [1]. Regardless the particle size, expensive reagents like tetraethyl ortosilicate (TEOS) or related alkoxides are virtually "universal" precursors. When thinking about possible applications, the cost of the Si source may be a significant parameter and the "need" for TEOS a problem for the implementation of large-scale processes. Hence, the design of low-cost synthetic strategies became a stimulating task.

Here we present two reproducible synthetic strategies which allows an independent control of both the intra- and inter-particle pore systems in Nanoparticulated Bimodal porous Silicas (NBS) produced from a low-cost Si reagent as is the sodium silicate; also, the procedure is easily scalable. Depending on the order of addition of the reagents we can differentiate two routes: 1) a "top down" route through which the final silica (UVM-10) is obtained by pseudomorphic transformation of an initial xerogel (without dissolution of the reagents) [2], a route for the isolation of porous materials relatively little explored until now, and 2) a "bottom up" route in which the porous silica (UVM-12) is constructed by self-assembling of micelles and silica oligomers. Both silicas show a similar architecture built up from small mesoporous nanoparticles whose aggregation generates a disordered secondary 3-D pore system (large-meso/macropores) defined by interparticle voids [3]. Moreover, both routes are compatible with the incorporation of heteroelements (Al and Ti).

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PREPARACIÓN, CARACTERIZACIÓN Y ESTUDIO DE NÚCLEOS MAGNÉTICOS QUE SE RECUBREN CON POLÍMEROS BIOCOMPATIBLES

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Palabras Clave: *ferritas, nanocomposite magnético, superparamagnetismo, ferromagnetismo.*

En la actualidad muchos investigadores enfocan sus investigaciones hacia el aislamiento de nanocomposites que combinan las propiedades de los materiales constituyentes. Especial relevancia presentan en biomedicina los denominados polímeros magnéticos. El diseño de esos nanocomposites conlleva la elección de un núcleo con propiedades magnéticas conocidas, y susceptibles de ser modificadas atendiendo al método de preparación, que se recubre por un polímero biocompatible, biodegradable y no toxico. En algunos casos estos recubrimientos poliméricos también pueden aportar cierta facilidad de funcionalización [1].

Se presentan en este trabajo los resultados obtenidos en la preparación, caracterización y estudio de núcleos magnéticos de nanoferritas de composición MFe_2O_4, con M = Fe y Co, que han sido recubiertas con polietilenglicol (PEG), polivinilbutiral (PVB) polivinil alcohol (PVA) y chitosán. Se describen los diferentes ensayos realizados para llevar a cabo todos los recubrimientos. Finalmente, se encuentra un recubrimiento más homogéneo en el caso de núcleos de magnetita que se han encapsulado en chitosán y polietilenglicol. Este hecho afecta al comportamiento magnético de los nanocomposites.

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ELECTRODOS DE CARBÓN NANOPOROSO DECORADOS CON NANOPARTÍCULAS DE ORO PARA SU APLICACIÓN EN SUPERCONDENSADORES

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Palabras Clave: *carbón nanoporoso, nanopartículas de oro, supercondensador, almacenamiento de energía*

Los condensadores electroquímicos de doble capa (Electrical double-layer capacitors-EDLCs) pueden almacenar energía mediante interacción electrostática de la superficie cargada de un electrodo de carbón poroso y los iones presentes en el electrolito [1]. La expansión de la aplicación de los EDLC en vehículos y dispositivos electrónicos portátiles, ha dirigido el foco de investigación en el aumento de su densidad de energía por unidad de volumen.

En este sentido, en esta comunicación se presenta una alternativa sintética sencilla y escalable de electrodos de carbón activo, a partir de residuos de bambú, que contienen una dispersión de nanopartículas de oro AuNps (Figura 1) [2].

La aplicación de este material como electrodo EDLC, muestra una capacidad volumétrica de 47 Fcm^{-3} que duplica la del carbón activo cuando no incorpora AuNPs. Por otra parte, las resistencias electroquímicas en serie de la celda simétrica disminuyeron un orden de magnitud en comparación con el material de carbono activado poroso no modificado. Curiosamente, la incorporación de nanopartículas de oro también supera el almacenamiento de carga irreversible debido a los restos de oxígeno presentes habitualmente en la superficie del electrodo.

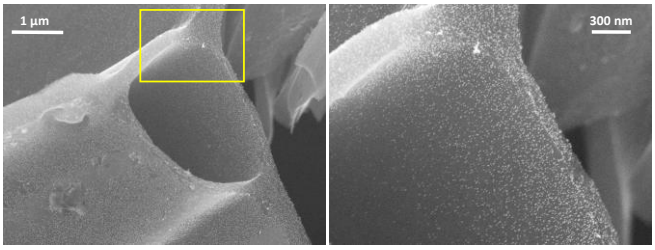

Figura 1: Micrografía SEM de una partícula de carbón activo decorada con AuNps.

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S9: *Síntesis, Caracterización y Propiedades de Materiales Emergentes*

MATERIALES EMERGENTES EFICIENTEMENTE ENERGÉTICOS PARA EL ÁMBITO DE LA EDIFICACIÓN

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Palabras Clave: *Phase Change Materials, Cemento, Eficiencia Energética.*

El ahorro de energía en la construcción y rehabilitación de edificios implica disminuir las emisiones de CO_2 a la atmósfera con el fin de cumplir con los acuerdos internacionales alcanzados, incluido el Protocolo de Kyoto. En este sentido, el aislamiento térmico en los edificios se presenta como un factor clave para alcanzar los objetivos establecidos por las distintas normativas de ahorro energético. Los equipos de aire acondicionado son los principales responsables del consumo de energía en muchos edificios públicos y viviendas. A través del uso de los materiales de construcción adecuados, en los elementos interiores y exteriores, la envolvente térmica de la construcción puede ser mucho mejor. Esta acción permitiría reducir el tiempo de uso del aire acondicionado y, en el mejor de los casos, evitar la instalación de estos equipos.

Por lo tanto, existe un interés creciente por estudiar nuevos materiales de construcción eficiencia energéticas avanzadas [1-3]. Estos materiales, junto con cemento, mortero y hormigón, permiten la preparación de un producto con propiedades térmicas mejoradas. Por lo tanto, la calidad y el confort interior de los edificios se optimizará: minimizando el consumo de energía y maximizando la eficiencia energética de los mismos.

El presente trabajo aborda diferentes simulaciones de laboratorio de los morteros eficientemente energéticos, se estudió la utilización de diferentes aditivos de aislamiento térmico, entre otros: vermiculitas, aerogeles, PCMs... Para cada uno de los diferentes aditivos, la optimización de las características físico-mecánicas y térmicas requiere el uso de una cantidad específica en la formulación del mortero. Las resistencias físicas y mecánicas de los morteros han cumplido con los requisitos de la norma. Las formulaciones seleccionadas presentan buenos valores de resistencia térmica y son propuestas como materiales emergentes de eficiencia energética en el ámbito de la edificación.

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SÍNTESIS Y CARACTERIZACIÓN DE COMPLEJOS DE COBALTO(II) TERMOCRÓMICOS CON UN LIGANDO DERIVADO DE 1,2,4-TRIAZOL

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Palabras Clave: *Termocromismo, Complejos de cobalto(II)*

En compuestos de coordinación con ligandos orgánicos y propiedades termocrómicas el cambio de color es, generalmente, el resultado de cambios en el entorno de coordinación del centro metálico siendo utilizados como materiales termocrómicos [1].

Los complejos termocrómicos tienen hoy en día numerosas e importantes aplicaciones, lo que hace que el estudio de los factores que influyen en los procesos termocrómicos sea un área de investigación muy activa tanto en Química como en Ciencia de los Materiales. Así, en los últimos años han aparecido nuevas aplicaciones de estos materiales tales como recubrimientos sobre ventanas para ahorrar en energía en la climatización en edificios [2], sensores de temperatura [3], o sistemas químicos para almacenar energía [4].

Este trabajo pretende comprobar la influencia del contraión en sales de Co(II) sobre la temperatura en la que se produce el cambio de color. Para ello, se han sintetizado fases sólidas de complejos a partir del ligando 2-(1,2,4-triazol-1-il)-2-tiazolina (TrTn) con sales de Co(II) (cloruro y bromuro). A partir de los resultados obtenidos podemos indicar que el cambio de color reversible de rosa a azul que experimentan los compuestos de partida al ser calentados, es consecuencia de una pérdida de ligandos en la esfera de coordinación del ion metálico. Así, los compuestos que inicialmente presentan índice de coordinación seis y geometría octaédrica pasan a tener, tras el calentamiento, un índice de coordinación cuatro y geometría tetraédrica. De manera que para el complejo cuyo cambio estructural implica rotura de enlaces metal-ligando más estables, la temperatura necesaria para observar el cambio de color es mayor.

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PREPARACIÓN Y CARACTERIZACIÓN DE NUEVOS ÓXIDOS MIEMBROS DE LA SERIE HOMOLOGA $(Nd\text{-}Sr)_{n+1}((Fe/Mn)\text{-}Co)_nO_{3n+1}$

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Palabras Clave: *Pilas de combustible tipo SOFC, perovskitas, Microscopia Electrónica.*

La revolución energética ha remarcado la necesidad de controlar las propiedades físicas así como las características estructurales de los materiales para componentes de nuevos dispositivos avanzados generadores y acumuladores de energía basados en óxidos funcionales.

El $SrCoO_3$ cristaliza en la estructura correspondiente a la perovskita cúbica en la que bloques de octaedros $[CoO_6]$ comparten todos los vértices en las tres direcciones del espacio [1]. Sr_2CoO_4 es el miembro n=1 de la familia de perovskitas laminares de Ruddlesden-Popper (RP) [2]. Su estructura consiste en 1 bloque de la perovskita cúbica que intercrece alternadamente con una capa SrO tipo NaCl. La sustitución de los cationes tanto de las posiciones Sr como Co, debe inducir cambios estructurales y, a su vez, cambios en las propiedades físicas de estos óxidos.

Dentro de nuestras investigaciones, estamos realizando una búsqueda sistemática de nuevos materiales avanzados basados en óxidos funcionales, preparados por diferentes métodos que permiten controlar la estructura atómica y electrónica, con vistas a establecer relaciones con las propiedades físico-químicas de los sistemas. Estos materiales presentan conductividad mixta, por lo que son potenciales electrodos de pilas de combustible tipo SOFC. De acuerdo con estas ideas, se han preparado nuevos óxidos de la serie homóloga RP $(Nd\text{-}Sr)_{n+1}((Fe/Mn)\text{-}Co)_nO_{3n+1}$, cuyo estudio estructural se ha realizado mediante la microscopia electrónica de alta resolución. Además, se ha llevado acabo la caracterización y el análisis de sus propiedades electroquímicas, con objeto de estudiar su comportamiento como cátodos de pilas de combustible tipo IT-SOFC.

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SYNTHESIS OF SILVER NANOPRISMS AT ROOM TEMPERATURE

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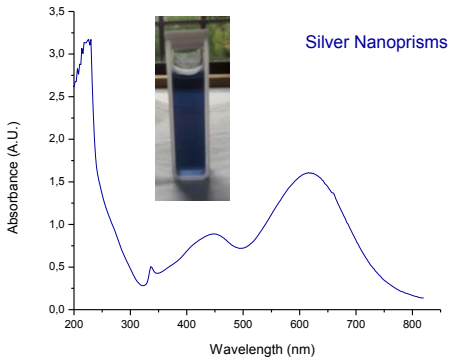
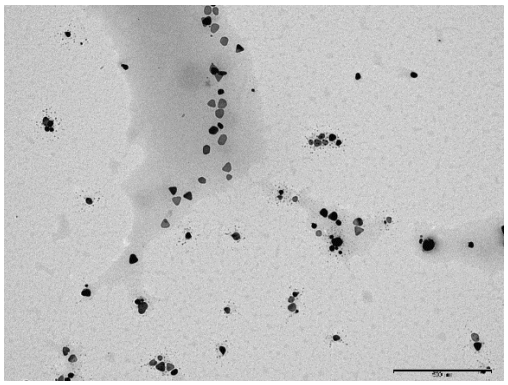
Keywords: *silver nanoprism*

Silver nanoprisms have attracted much attention because of their optical properties and potential applications in catalysis, sensing, and surface-enhanced Raman scattering (SERS) [1]. The degree of enhancement is dependent on a number of factors. One of these is shape. It has been shown by discrete dipole approximation calculations that nanorods and nanoprisms show a much higher degree of enhancement of the local field than spheres [2].

In this study we present a simple and rapid seed-mediated method for the synthesis of silver nanoprisms [2]. The syntheses were performed at room temperature in aqueous solution. By hanging the amount of silver seeds and other synthesis parameters (as silver concentration, amounts of stabilizer, reducing agent…), it was possible to obtain silver nanoprisms of different sizes in coexistence with variable amounts of other silver structures. The samples were characterized by UV- vis absorption spectroscopy, transmission electron microscopy (TEM) and scanning electron microscopy (SEM).



UV-Vis Spectrum of silver nanoprisms



TEM image of silver nanoprism

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OBTENCIÓN DE DIFERENTES ARQUITECTURAS HELICOIDALES DE Zn Y Cu A PARTIR DE UN LIGANDO *BIS*TIOSEMICARBAZONA METIL-SUSTITUIDO

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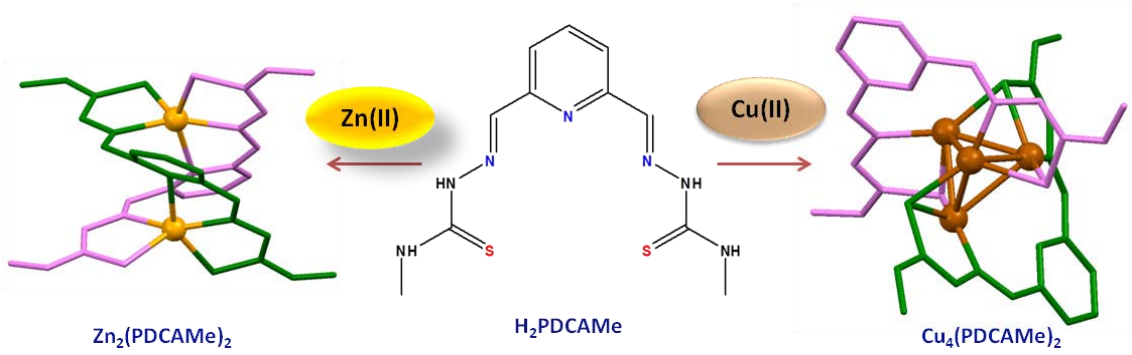
Palabras Clave: *Química supramolecular, Helicatos, Síntesis electroquímica*

El reconocimiento molecular y los procesos de autoensamblaje juegan un papel esencial en la formación y en el funcionamiento de los sistemas biológicos. Inspirándose en este modelo, los procesos artificiales de autoensamblaje dirigidos por metales pueden ser utilizados para obtener compuestos de coordinación multinucleares de una forma fácil y espontánea. Los helicatos supramoleculares son un tipo especial de complejos metálicos en los cuales dos o más ligandos se enrollan alrededor del eje definido por dos o más centros metálicos. En esta linea, ligandos del tipo *bis*tiosemicarbazona han demostrado ser precursores adecuados para generar sistemas supramoleculares autoensamblados.[1]

En este trabajo nos hemos planteado el estudio coordinativo del ligando *bis*(4-metil-3-tiosemicarbazona)-2,6-piridin-dicarboxaldehido (H_2PDCAMe) obtenido a partir de diformilpiridina y 4-N-metil-3-tiosemicarbazida frente a los iones metálicos Zn(II) y Cu(I). Así, empleando un método electroquímico se han sintetizado un dihelicato dinuclear de Zn(II) y un helicato clúster tetranuclear de Cu(I). Los resultados obtenidos demuestran que iones metálicos diferentes permiten obtener diferentes arquitecturas supramoleculares helicoidales con interesantes propiedades.



Agradecimientos: Xunta de Galicia (Proyectos EM2014/018 y 2014-PG097).

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SELF-ASSEMBLY OF Ag_3 ATOMIC QUANTUM CLUSTERS ON CYCLIC PEPTIDE NANOTUBES

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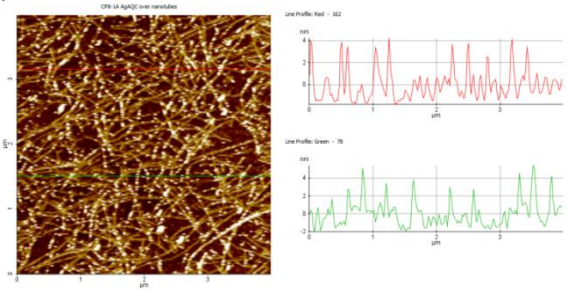
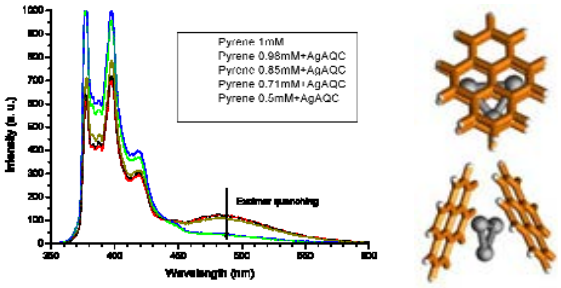
Keywords: *atomic quantum cluster, cyclic peptide, photoluminescence, hybrid nanostructure*

Subnanometric noble metal clusters, composed by only a few atoms, behave like molecular entities and display magnetic, luminescent and catalytic activities. However, non-covalent interactions of molecular metal clusters, lacking of any ligand or surfactant, have not been seen at work. Theoretically attractive and experimentally discernable, van der Waals forces and non-covalent interactions at the metal/organic interfaces will be crucial to understand and develop the next generation hybrid nanomaterials. Atomic force microscopy, fluorescence experiments, circular dichroism and computational simulations present experimental and theoretical evidence of non-covalent interactions between subnanometric metal clusters (Ag_3) and aromatic rings, and their application in the preparation of 1D self-assembled hybrid architectures with ditopic peptide nanotubes, to conclude that induced supramolecular forces are optimal candidates for the precise spatial positioning and properties modulation of purified molecular metal clusters.



AFM topography images of 1D arrangement of silver AQCs on peptide nanotubes deposited on mica. Nanotubes displayed average diameters between 3-4 nm.



Photoluminescence spectra of pyrene in the presence of Ag AQCs and computational simulations of Ag3 clusters with two pyrene molecules

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SYNTHESIS AND SURFACE MODIFICATION OF MAGNETITE NANOPARTICLES

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Keywords: *Magnetite nanoparticles, functionalization, core-shell*

Magnetic nanoparticles are very interesting materials because their wide range of applications that includes magnetic fluids, hyperthermia, MRI contrast agents, drug delivery and purification of waste water. These applications are related to the change in physical and chemical properties of nanoparticles due the possibility of modification and functionalization of their surface.

In this work, magnetite nanoparticles, Fe_3O_4, have been synthesized with acid and amine functional groups at the surface by a co-precipitation method. Fe (II) and Fe (III) chlorides were used as precursors and succinic acid and ethylenediamine were used as acid and amine groups sources respectively. Thiol functionalized nanoparticles and core-shell nanoparticles where synthesized by a two-step process. First, magnetite nanoparticles have been synthesized by thermal decomposition of Fe (III) acetylacetonate and oleic acid and oleylamine as stabilizers in a high boiling point solvent. Particle size is controlled varying the time and temperature reaction. In a second step, magnetite nanoparticles have been coated with 2,3-dimercaptosuccinic acid (DMSA) by a ligand exchange reaction. Core-shell nanoparticles were prepared using pre-synthesized nanoparticles and tetraethyl orthosilicate, TEOS, as silica precursor.

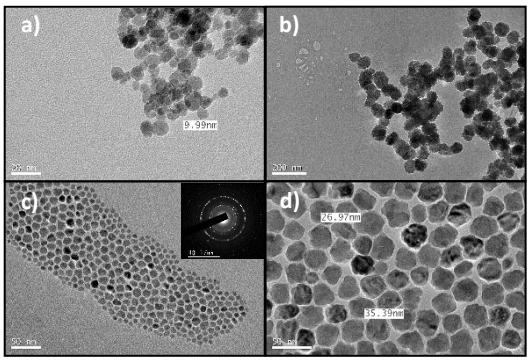

Figure 1. (a) TEM images of acid functionalized magnetite nanoparticles, (b) amine functionalized nanoparticles, (c) and (d) 10 nm and 27 nm sized oleic stabilized magnetite nanoparticles and SAED diagram.

All the samples were characterized by X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM). IR spectroscopy was used to study de functional groups coordinated to the surface of nanoparticles. Thermal analysis was used to obtain the ferrite/organic shell ratio and the functional groups concentration at the surface of nanoparticles.

Magnetic susceptibility versus temperature and magnetization versus applied field measurements were made to study the magnetic properties of the samples.

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POLíMEROS ORGANOMETALICOS DE Ni/K y Pd/K CONTENIENDO FENIL DITIOLENO COMO LIGANDO DADOR σ y π. ESTUDIO DE SUS PROPIEDADES FISICAS

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Palabras Clave: *Ditiolenos, polímeros de coordinación, metales grupo 10*

La química de Metales de Transición con ligandos ditioleno ha atraído la atención de los investigadores desde el punto de vista de Ciencia de Materiales, por las interesantes propiedades físicas que este tipo de compuestos pueden exhibir, así como desde el punto de vista de Ingeniería Cristalina por su riqueza estructural [1]. Recientemente hemos preparado polímeros de coordinación (PCs) bidimensionales heterobimetálicos Ni/K y Pd/K con el ligando ligando $–SC_6H_2Cl_2S–$ que han mostrado interesantes estructuras y propiedades eléctricas [2]. Con fines comparativos, hemos evaluado, en condiciones anaeróbicas, el comportamiento de estos metales frente al ditioleno $–SC_6H_4S–$, que carece de sustituyentes dadores en el anillo aromático. Los resultados de esta investigación confirman la formación de PCs de características marcadamente diferentes a los anteriores, puesto que ahora los átomos de K están coordinados a través de la nube p de los arenos. Adicionalmente, se ha estudiado el comportamiento frente al oxígeno de estos polímeros.

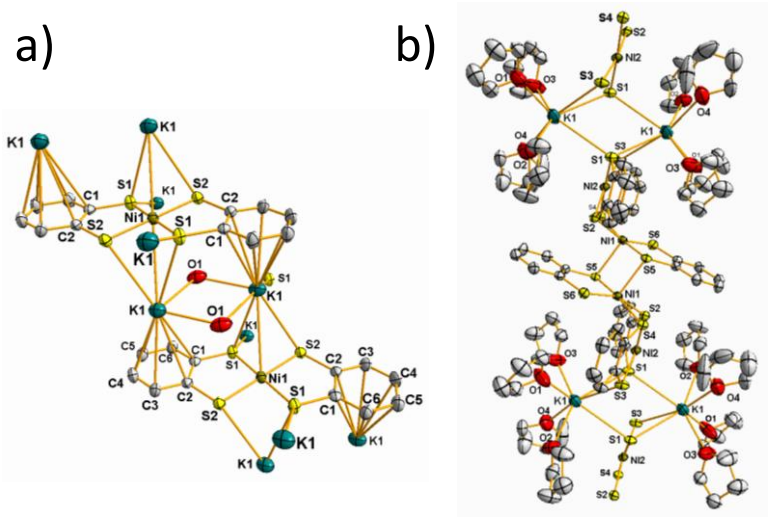

Fig. 1. Estructura de rayos X de los compuestos $[K_2(\mu\text{-}H_2O)_2]_n[Ni(SC_6H_4S)_4]_n$ (a) y $[K_2(THF)_8]_n[Ni_4(SC_6H_4S)_6]_n$ (b).

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STRUCTURE AND PROPERTIES OF $RCrO_4$ (R = RARE EARTH) POLYMORPHS OBTAINED UNDER HIGH PRESSURE CONDITIONS

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Keywords: zircon, scheelite, antiferromagnetism, magnetism, magnetocaloric effect

Rare-earth chromates of general formula $RCrO_4$ (R = rare earth) crystallize in two structural types depending on the size of the trivalent R^{3+} cation. The first member of this family of compounds, $LaCrO_4$, shows a monazite type-structure (S. G. $P2_1/n$); $PrCrO_4$ is a dimorphic compound that yields a mixture of monazite and zircon polymorphs at ambient pressure. The remaining $RCrO_4$ oxides crystallize with the zircon type-structure, (S. G. $I4_1/amd$). Only few studies have been reported on the high-pressure phase transformations in these $RCrO_4$ oxides [1]. It may be due to the high instability of Cr^{5+} cation and its tendency to be reduced giving the most stable perovskite $RCrO_3$ phases. However, it has been reported in our research group that the zircon phase transforms to scheelite polymorph at 4 GPa and 813 K [2-4].

The coexistence of two paramagnetic cations in these oxides (*i.e.* Cr^{5+} and R^{3+}) constitutes an ideal scenario to study the 3d-4f complex magnetic interactions and to explain the changes in the magnetic properties accompanying these structural phase transitions. The zircon-type $RCrO_4$ oxides are ferromagnetic while the scheelite polymorphs behave as antiferromagnets. A detailed study of the magnetic properties from bulk magnetic measurements and neutron diffraction studies has been done in order to determine the magnetic structure and to establish structure-magnetic properties relationship. On the other hand it has been recently reported that some of the zircon $RCrO_4$ phases show a large magnetocaloric effect that make them potential candidates to be used for the hydrogen liquefaction [5]. In this work the study of the magnetocaloric effect, in both, zircon and scheelite RCrO4 polymorphs has been also done from the evaluation of the isothermal entropy change, ΔS_T, upon the application of a magnetic field. In the case of $GdCrO_4$ zircon compound, the maximum ΔS_T under a magnetic field increase up to 9 T is 31 J/KgK.

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S9: *Síntesis, Caracterización y Propiedades de Materiales Emergentes*

SÍNTESIS DE Ni-GEIKIELITA: EFECTO MINERALIZADOR E INMOVILIZADOR DE LA ADICIÓN DE BORATOS

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Keywords: *Níquel, Geikielita, boratos, mineralizador, ecotoxicidad, pigmento.*

La Geikielita ($MgTiO_3$) pertenece al grupo de la ilmenita ($FeTiO_3$) (Grupo Espacial R3). En la literatura se conoce bien la estabilidad y cristalización de la fase Co-ilmenita ($CoTiO_3$) como pigmento cerámico. Relacionados con este sistema, los compuestos Mg_2TiO_4 con estructura espinela y $MgTi_2O_5$ con estructura pseudobrookita se consideran en la literatura como estructuras estabilizadas por entropía: su relativamente alta entropía se asocia con la mezcla en posiciones cristalográficas específicas de diferentes cationes (1): la ilmenita es isoestructural con el corindón con la sustitución formal $2Al^{3+} \rightarrow Mg^{2+} + Ti^{4+}$ de modo que los octaedros de una capa están ocupados por el divalente Mg y la capa sucesiva por Ti. El dopado de la geikielita $MgTiO_3$ con Ni es un nuevo pigmento amarillo (2): la incorporación de Ni^{2+}(0,83 Å coord. VI) substituyendo a Mg^{2+} (0,86 Å coord. VI) relaja el campo cristalino sobre catión, desplazando las bandas de absorción hacia el rojo y refleja en el amarillo en lugar del verde habitual para Ni^{2+} en coordinación octaédrica. En esta comunicación se presenta la síntesis por reacción en estado sólido entre el carbonato de magnesio, óxido de níquel y anatasa a 1000ºC durante 3 horas sin adición y con adiciones de 2, 5 y 10% de dos mineralizadores borato (ácido bórico H_3BO_3 y perborato de sodio tetrahidrato $NaBO_3{\cdot}4H_2O$). Los polvos calcinados se caracterizaron por DRX, colorimetría CIEL*a*b* y espectroscopia UV-Vis-NIR, asimismo se estudió el lixiviado de los polvos en tratamientos de 24 horas en proporción agua:polvo=1:5 (Lavado 1), el rendimiento colorimétrico del esmaltado en vidriados de monococción a 1080ºC y el lixiviado de los polvos procedentes del lavado 1 con tratamientos de 24 horas en proporción agua:polvo=1:16 (Lavado 2) con el test de inhibición de luminiscencia EC50 sobre Photobacter phosphoreum para su evaluación ecotoxicológica. Los resultados indican que el ácido bórico presenta un bajo efecto mineralizador sobre la reactividad, el perborato se muestra más efectivo en este sentido. Sin embargo, la utilización de adiciones bajas de ambos mineralizadores (2%) ejercen un significativo efecto inmovilizador sobre la lixiviación de níquel y magnesio con resultados negativos en el test de ecotoxicidad microtox con Photobacter phosphoreum. La utilización de mayores adiciones de mineralizador, que incrementan ligeramente el tono amarillo del esmaltado, no compensaría el aumento de lixiviación de boro y el coste de la adición de mineralizador.

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SYNTHESIS OF $Nd_{1-x}Ca_xCoO_3$ PEROVSKITE NANOWIRES FOR THERMOELECTRIC APPLICATIONS

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Keywords: *perovskite, thermoelectricicty, nanostructuration, Seebeck*

The thermoelectric devices are a future alternative as a renewable energy resource. Perovskites [1] have interesting properties for thermoelectric applications such as: large Seebeck coefficient, low production costs and high stability at high temperatures. Nanostructuration plays an important role for the efficiency in thermoelectricity, especially the use of nanowire shape because this morphology improves the efficiency of the thermoelectric devices. The present work studies the synthesis and characterization of $Nd_{1-x}Ca_xCoO_3$ perovskite nanowires, where Ca is the dopant element of the perovskite. This kind of perovskite has been synthetized by the hydrothermal method [2] and with propose to them for thermoelectric applications.

The results of our investigation show that the best thermoelectric efficiency has been obtained for perovskites with a content of Ca x=0.1. The electrical conductivity and Seebeck coefficient are strongly related to the calcium content, while the thermal conductivity is clearly lower than that of bulk materials [3].

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HÍBRIDOS ORGÁNICO-INORGÁNICOS [M(dca)$_2$pyz] (M: Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}) CON TRANSICIONES DIELÉCTRICAS A TEMPERATURA AMBIENTE

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Palabras Clave: *Materiales dieléctricos, materiales híbridos, transición estructural.*

Los híbridos orgánico-inorgánicos despiertan gran interés desde hace aproximadamente una década[1] fundamentalmente por sus aplicaciones en almacenamiento de gases, en catálisis o en la separación de moléculas. Más reciente es el interés por sus propiedades funcionales[2], magnéticas, eléctricas, ópticas o dieléctricas, abriendo las puertas a aplicaciones tecnológicas tan variadas como la grabación magnética, las comunicaciones inalámbricas o los dispositivos emisores de luz (LED). En este trabajo nos hemos centrado en los híbridos de formula general [M(dca)$_2$pyz] , donde *M* es un ion metálico divalente (Fe^{2+}, Co^{2+}, Ni^{2+} o Zn^{2+}), *dca* es el ligando dicianoamiduro ((CN)$_2$N)$^-$) y *pyz* es el ligando pirazina (C$_4$H$_4$N$_2$). Su estructura cristalina fue estudiada previamente por Paul Jensen y col. [3]. Describieron una estructura tipo α-Po a temperatura ambiente con dos redes interpenetradas y una transición estructural, próxima a la temperatura ambiente, vease figura 1.

Nosotros hemos estudiado por primera vez sus propiedades dieléctricas, observando que todos ellos presentan una transición dieléctrica próxima a la temperatura ambiente, sumamente interesante de cara a sus posibles aplicaciones tecnológicas, y coincidiendo con la transición estructural. Hemos comprobado que el origen de las dichas propiedades dieléctricas está directamente relacionado con la existencia de dos redes ferroeléctricas interpenetradas antiparalelamente y con fenómenos de orden/desorden de los ligandos.

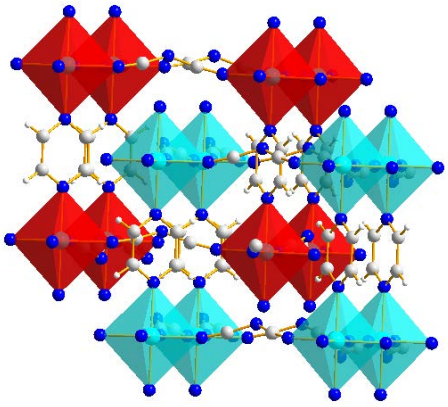

Figura 1.- Estructura cristalina de los compuestos [M(dca)$_2$pyz](M: Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}) formada por dos redes tipo α-Po interpenetradas.

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EFECTOS DEL ORDEN CATIÓNICO EN LA ESTRUCTURA CRISTALINA Y PROPIEDADES FÍSICAS DE $Gd_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}O_{3-\delta}$

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Palabras Clave: *IT-SFOCs, Perovskitas, SAED, HRTEM, ASR*

Las pilas de combustible de óxido sólido de temperatura intermedia (IT-SFOCs) que operan en un rango de temperaturas comprendido entre 500-700 ºC se encuentran entre los dispositivos generadores de energía más interesantes actualmente debido principalmente a su alta eficiencia y al bajo impacto para el medio ambiente [1-2].

Los materiales con estructura tipo perovskita son los más estudiados como electrodos en este tipo de dispositivos y en particular, las perovskitas con orden laminar de los cationes [3,4]. Trabajos recientes han señalado la perovskita $LnBaCo_2O_{5+\delta}$ (Ln= Pr, Gd), que presentan este tipo de ordenamiento, como potencial material para cátodos en pilas de combustible IT-SFOCs. La estructura consiste en capas de Ba-O y Ln-O ordenadas de forma alterna en planos (001) a lo largo del eje c y donde las vacantes aniónicas se colocan en los planos del Ln-O originando planos donde la conductividad iónica es muy elevada [5,6]

Con esta idea de estudiar nuevos materiales con estructura tipo perovskita con orden laminar de cationes como objetivo, presentamos la síntesis y caracterización estructural de la perovskita $Gd_{0.5}Ba_{0.5}Mn_{0.5}Fe0_{3-\delta}$ tanto en su forma desordenada como con los cationes Gd/Ba ordenados en capas. Mediante la combinación de diferentes técnicas microscópicas (SAED, HRTEM, HAADF-STEM, EELS y EWR) estudiaremos como afecta el orden entre el Gd/Ba en la estructura cristalina. Compararemos el rendimiento electroquímico de ambas fases en la aplicación de estos materiales como cátodos en pilas de combustible IT-SFOCs, empleando como electrolito de trabajo $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (CGO).

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PEROVSKITAS DOBLES CON TIERRAS RARAS EN LA POSICIÓN *B*: $Sr_2Nd_{0.5}Y_{0.5}RuO_6$

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Palabras Clave: *perovskita doble, tierras raras, rutenatos, magnetismo*

En el presente trabajo se ha llevado a cabo un estudio de perovskitas dobles de fórmula general Sr_2TRRuO_6introduciendo en la posición B de la red estructural (coordinación octaédrica) el rutenio y dos tierras raras de diferente radio iónico. El interés en estas fases se debe, además de a su estructura cristalina, a sus propiedades magnéticas ampliamente estudiadas en las últimas décadas [1]. Esta familia de compuestos se conoce desde 1977 [2] y desde ese momento han sido numerosos los trabajos en los que se estudian sus estructuras cristalográfica y magnética [3][4] y sus propiedades. El hecho de introducir dos tierras raras de muy diferente tamaño despierta un gran interés en el estudio de la estructura de la solución sólida, así como, el de sus propiedades eléctricas y magnéticas.

La perovskita objeto de este trabajo cuya composición es $Sr_2Nd_{0.5}Y_{0.5}RuO_6$ se ha sintetizado por el método cerámico convencional a partir de los óxidos precursores. Se ha llevado a cabo su caracterización estructural por difracción de Rayos X y refinamiento Rietveld, microscopía electrónica de transmisión y análisis termogravimétrico. En lo referente a la caracterización magnética se ha estudiado el comportamiento de la susceptibilidad magnética frente a la temperatura.

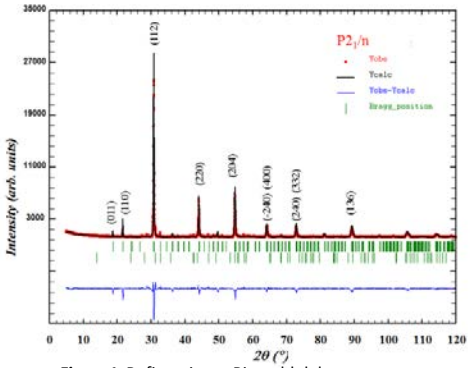

Figura1. Refinamiento Rietveld del $Sr_2Nd_{0.5}Y_{0.5}RuO_6$

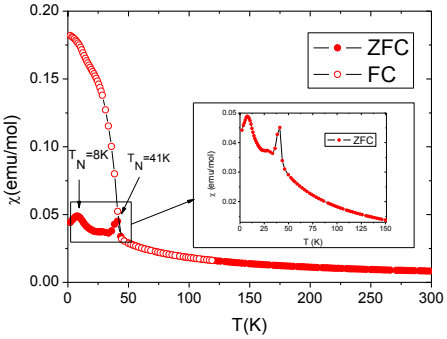

Figura2.Medidas magnéticas del $Sr_2Nd_{0.5}Y_{0.5}RuO_6$

Los resultados obtenidos, que se presentan en las figuras 1 y 2, serán comentados y discutidos en la presente cpmunicación.

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HIGHLY FLUORESCENT COPPER CLUSTERS WITH CYSTEINE

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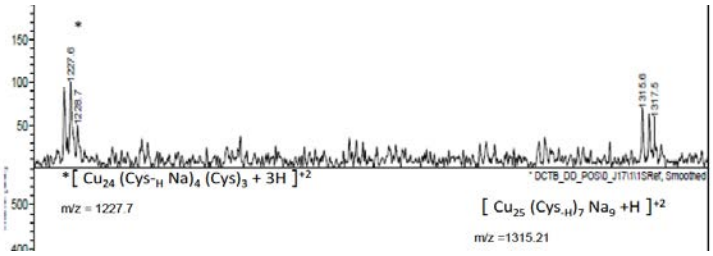
Keywords: *subnanometric metallic clusters, cysteine, photocatalysis*

Subnanometric metallic clusters are getting considerable attention recently due to their properties, which are very different from the bulk or nanoparticle ones, offering exciting possibilities for their use in novel materials or devices and in different fields like medicine, magnetism or catalysis [1]. A subnanometric cluster is a metallic molecule having between 2 and ≈ 100 atoms with a fixed geometry and, due to its reduced size, a bandgap (larger as the cluster is smaller), which appears at the Fermi level of the metal, granting the cluster with an electronic structure that will determine the appearance of completely new properties strictly depending on cluster size. Moreover, changes in one or two atoms will affect the bandgap thus changing completely their properties [2,3]. Therefore, it is clear the importance of designing effective synthesis methods trying to produce monodisperse cluster samples.
Here, we report the synthesis of highly fluorescent Cu clusters protected with cysteine. Clusters were characterized by UV-Vis spectroscopy, Fluorescence Spectroscopy, AFM, XPS and Mass Spectrometry. The developed synthesis opens up different possibilities for their application in different fields (due to the small bandgap and the low energy position of the HOMO), like visible photocatalysis.



Mass spectra of high fluorescent Cu clusters protected with cysteine

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FUNCTIONAL ORGANIC-INORGANIC HYBRIDS WITH UP-CONVERTING PROPERTIES

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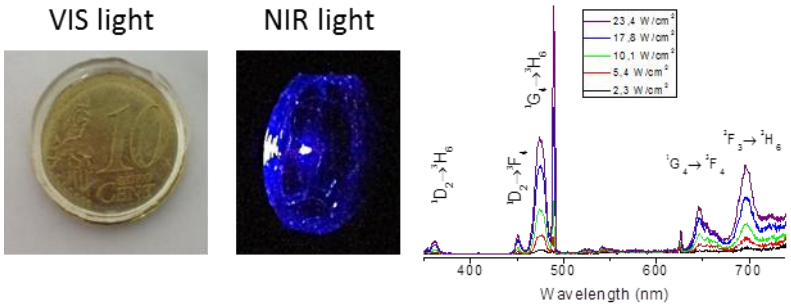
Keywords: *hybrid materials, up-conversion, optical materials*

Up-converting (UC) materials can efficiently convert NIR into visible/UV/NIR light. With the control of different synthetic approaches at the nanoscale level, this phenomenon becomes interesting for new technologies such as photonics, photovoltaics, sensors, biotechnology, etc.[1] Among the UC materials, β-$NaYF_4$ doped with active emitters (Er^{3+}, Tm^{3+}, Yb^{3+}…) is by far the most efficient up-converter due to the low phonon energy of the fluoride host matrix. Metal oxides such as Y_2O_3 or ZrO_2, even being less efficient, are also interesting matrices because of their low toxicity and tunable optical and textural properties.[2]

The main drawback for their technological application is the difficult processability as massive pieces, thin films, etc. required for device fabrication. Thus, their encapsulation into hybrid organic-inorganic materials has emerged as a promising way to obtain a unique functional material, easy to process, which integrates the optical properties of the UC materials together with the tunable properties (mechanics, hydrophobicity…) of the organic components.[3]

We address the development of functional hybrid inorganic-organic materials exhibiting UC properties and their processing as monoliths and films. In particular, we demonstrate that Er^{3+},Tm^{3+},Yb^{3+}-doped nanoparticles of ZrO_2 and β-$NaYF_4$ can be efficiently dispersed into polydimethylsiloxane and diureasils based hybrids leading a transparent material that preserves the structural and optical features of both constituents. The study reveals that these nanocomposites represent a low cost, environmentally friendly, size-controlled, easy-processed and chemically-stable alternative material to be used in photonics (as optical fiber, solar concentrator, etc.), sensors or photovoltaics.



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NANOCOMPOSITES PARA CÁTODOS DE BATERÍAS DE LI-ION BASADOS EN MATERIALES DE TIPO OLIVINO $LiMn_{1-x}M_xPO_4$ (M=Fe, Co, Ni, Cu)

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Palabras Clave: *baterías Li-ion, olivino, nanocomposites, liofilización, EPR*

Los fosfatos $LiMPO_4$ (M=Mn, Fe, Co, Ni) con estructura de tipo Olivino se encuentran entre los materiales catódicos más interesantes para las baterías Li-ion [1]. El $LiFePO_4$ es en principio el material más interesante, pero por su pequeño voltaje de reacción (3.4 V frente al par Li^+/Li) no puede proporcionar la densidad energética que necesitarán los futuros dispositivos de almacenamiento. Los compuestos de Co y Ni presentan voltajes de reacción demasiado elevados para los electrolitos habituales (4.8 y 5.1 V, respectivamente). El $LiMnPO_4$ reacciona a 4.1 V, pero su conductividad iónica no es lo suficientemente elevada y presenta inestabilidad estructural en los procesos de carga y descarga. Para solventar estos problemas se han propuesto diferentes soluciones: la reducción del tamaño de partícula hasta la escala nanométrica, el recubrimiento superficial con un conductor electrónico y la presencia simultánea de diferentes cationes de transición en la estructura [2]. En este sentido, hemos combinado las tres vías para preparar nuevos materiales catódicos basados en el $LiMnPO_4$. Se trata de materiales con diferentes combinaciones catiónicas, nanoparticulados y recubiertos con carbón.

En primer lugar se analizaron las soluciones sólidas $LiMn_{1-x}M_xPO_4$ (M=Fe, Co, Ni, Cu) para determinar que grado de sustitución es viable en cada caso. Para ello, además de los análisis estructurales, a partir de datos de difracción de rayos X, se han realizado medidas de susceptibilidad magnética y espectroscopía EPR, que han demostrado ser mucho más sensibles para la detección de fases secundarias que pueden afectar al rendimiento electroquímico. Una vez determinados los grados de sustitución máximos que podían ser obtenidos de forma totalmente reproducible, se procedió a preparar esas composiciones en forma nanoparticulada dentro de una matriz de carbón. Para ello se empleó la técnica de liofilización, y ácido cítrico como limitador de tamaño de partícula y fuente de carbón. Los nanocomposites obtenidos fueron caracterizados mediante difracción de rayos X, microscopía electrónica, medidas magnéticas y espectroscopía EPR. Finalmente se analizó su comportamiento electroquímico empleando pilas botón de tipo CR2032, con $LiPF_6$ en EC:DEC como electrolito y Li metálico como contraelectrodo. Se observó que la mejor respuesta electroquímica la presentaba el material $LiMn_{0.8}Fe_{0.1}Ni_{0.1}PO_4/C$, con una alta capacidad específica (110 mAh/g), excelente ciclabilidad y buena capacidad de retención a diferentes velocidades (93 % a 1C).

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S9: *Síntesis, Caracterización y Propiedades de Materiales Emergentes*

PEROVSKITAS $SrBiMn_{1-x}Ti_xO_{6-\delta}$ EN FORMA POLIMICROCRISTALINA Y PELÍCULA DELGADA: CARACTERÍSTICAS ESTRUCTURALES Y DIELÉCTRICAS

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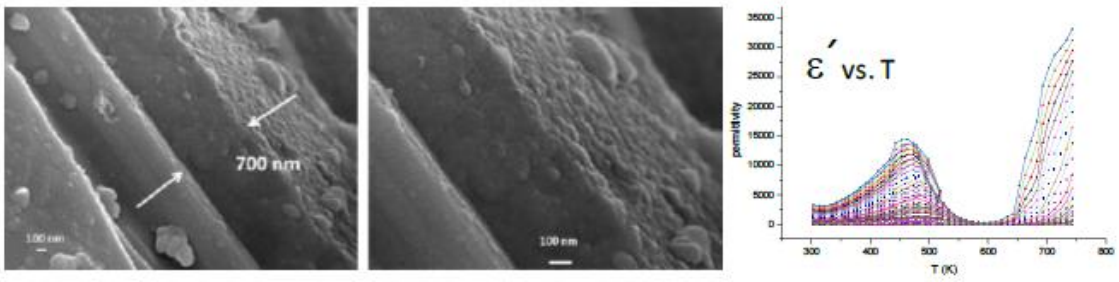
Palabras Clave: *Perovskitas, bismuto, titanio, PLD, dieléctricos*

Las propiedades de los materiales dependen sensiblemente del método de síntesis empleado para su obtención, de modo que pueden modificarse aspectos específicos de su respuesta eléctrica y magnética. Es por ello de gran interés el estudio comparativo de dichos materiales obtenidos a partir de diferentes rutas sintéticas. En particular, la fabricación de películas delgadas permite modular el comportamiento electrónico de las fases mediante la creación de una textura cristalográfica interna o morfología epitaxial.

Este trabajo presenta la caracterización estructural/microstructural y el estudio del comportamiento eléctrico de manganitas de bismuto y titanio: $SrBiMn_{1-x}Ti_xO_{6-\delta}$, que han sido preparadas en forma de polvo polimicrocristalino, mediante la técnica de solidificación de disoluciones liquidas, TSDL; y en forma de películas delgadas, fabricadas mediante depósito por láser pulsado, PLD, de entre 50 y 800 nm de espesor.



La caracterización estructural de las fases polimicrocristalinas, llevada a cabo mediante refinamientos Rietveld de los datos de difracción de rayos X y neutrones, indican transiciones que conllevan cambios de simetría en función de la temperatura y la concentración de Ti.

La respuesta dieléctrica, analizada a partir de medidas de impedancia en función de la temperatura, revelan comportamiento ferroeléctrico relaxor para las fases x= 0.25 and 0.5, mientras que para x = 0.75 se obtiene un comportamiento menos dependiente del tiempo, probablemente asociado a una transición estructural. Las correspondientes temperaturas críticas varían dependiendo del método de obtención empleado. En las películas delgadas, la epitaxialidad se ve incrementada cuando se emplea el sustrato $SrTiO_3$ [111], al favorecerse la presencia de polarización a lo largo de la dirección [111], que implica a los cationes situados en el subretículo A, Sr(II) y Bi(III), presentes en proporción nominal 1:1.

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SUPERCONDUCTIVIDAD EN CUPRATOS M-1212:

Fe EN LA RESERVA DE CARGA

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Palabras Clave: *superconductividad, cupratos, resistividad, magnetismo*

Las fases M-1212, resultantes de la sustitución en el YBCO ($YBa_2Cu_3O_{7-\delta}$; Tc~90 K) de las posiciones cristalográficas Cu(1) por otros metales de transición, son sistemas idóneos para el estudio de las interesantes propiedades de transporte observadas en estos cupratos superconductores de alta temperatura. En particular, se trata de explorar la posible coexistencia de superconductividad y magnetismo [1,2].

A través de la variación tanto de la cantidad y naturaleza del dopante como del contenido en oxígeno, se analizan las relaciones estructura-propiedades en estos sistemas.

En esta comunicación se presenta un estudio de las fases Fe-1212, concretamente del sistema $Fe_xCu_{1-x}YSr_2Cu_2O_y$ (x= 0,25-0,5), focalizado en primer lugar en la evaluación de la concentración óptima de dopante (en este caso hierro) en relación con la temperatura crítica, a través de sus propiedades eléctricas y magnéticas.

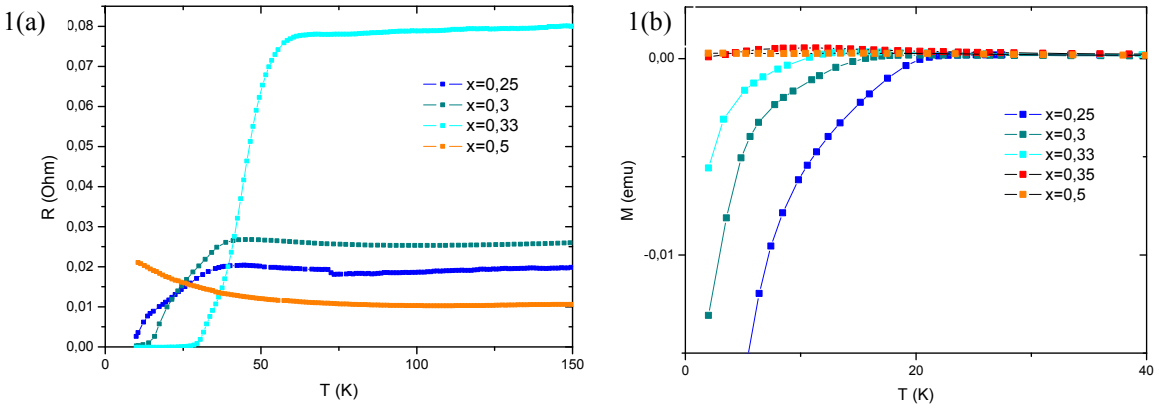

Figura 1.(a) Resistencia y (b) susceptibilidad de las fases $Fe_xCu_{1-x}YSr_2Cu_2O_y$ (x= 0.25, 0.3, 0.33, 0.35 y 0.5) oxidadas en corriente de O_2.

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MODIFICACIÓN DE LAS PROPIEDADES FUNCIONALES EN CERÁMICAS BASADAS EN $Bi_{0,5}Na_{0,5}TiO_3$ - $BaTiO_3$ MEDIANTE DOPAJE

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Palabras Clave: *piezoelectricidad*, *cerámicas libres de plomo, MPB, dopaje*

Los materiales piezoeléctricos que se utilizan actualmente en dispositivos electrónicos están basados en el titanato circonato de plomo (PZT) debido a sus excelentes propiedades piezoeléctricas [1]. Sin embargo, la mayor desventaja que presentan es la elevada toxicidad del plomo. El uso y fabricación de materiales que contienen este elemento han causado serios problemas medioambientales. En consecuencia, durante los últimos años las investigaciones se han centrado en la búsqueda de materiales piezoeléctricos libres de plomo capaces de sustituir al PZT, en concreto, en compuestos que presentan una transición de fase morfotrópica (MPB) similar a la del PZT donde, por lo general, se observa un aumento de la respuesta piezoeléctrica [2]. En este sentido, el sistema formado por $Bi_{0,5}Na_{0,5}TiO_3$ (BNT) y $BaTiO_3$ (BT), es considerado un candidato prometedor. Este sistema presenta una MPB entre las fases romboédrica-tetragonal a temperatura ambiente donde se obtienen unas buenas propiedades piezoeléctricas [3].

Una de las estrategias de mejora de las propiedades eléctricas en cerámicas piezoeléctricas es la modificación de la composición a través de la adición de dopantes en la red cristalina. Siguiendo esta línea se propuso el estudio de la influencia de diferentes elementos dopantes, tanto en la posición A como en la posición B de la perovskita, en cerámicas basadas en el BNT-BT.

Se evaluaron las propiedades funcionales y estructurales de las cerámicas obtenidas con la finalidad de analizar si el dopaje es una forma prometedora de mejora de las propiedades de piezocerámicas basadas en el BNT-BT.

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NUEVOS PIGMENTOS CERÁMICOS BASADOS EN PSEUDOBROOKITA Fe_2TiO_5 E ILMENITA $MgTiO_3$ DOPADAS CON MANGANESO

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Palabras Clave: *Pseudobrookita, Ilmenita, Manganeso, Pigmentos cerámicos, Color*

Los titanatos metálicos con estructuras tipo perovskita [1,2], pseudobrookita [3,4] o ilmenita [5] están siendo investigados como pigmentos o colorantes cerámicos emergentes. En esta investigación se ha analizado el desarrollo de nuevos pigmentos cerámicos basados en el dopado con Mn de la pseudobrookita férrica ($Fe_{2-x}Mn_xTiO_5$) y la ilmenita Mg-Ti ($Mg_{1-x/2}Mn_xTi_{1-x/2}O_3$). Las composiciones estudiadas (x= 0-0.4) fueron preparadas por la ruta cerámica y mediante descomposición de xerogeles tipo citrato (ruta MOD) [2,4]. Los pigmentos obtenidos (1000 y 1200°C/3h) fueron caracterizados por DRX, microscopía electrónica (MEB/EDX), espectroscopia UV-vis-NIR y colorimetría CIE-L*a*b. La disolución sólida del Mn en la pseudobrookita Fe_2TiO_5 fue sólo parcial (hasta x=0.1), dando coloraciones marrones asociadas a las transiciones electrónicas de Mn^{3+} ($3d^4$) y Fe^{3+} ($3d^5$) en entornos octaédricos, más intensas y oscuras al incrementar el dopado con Mn y la temperatura. En el sistema Mn:$MgTiO_3$, el dopado con Mn estabilizó la fase ilmenita a menores temperaturas (1000°C), aunque también acompañada de fase espinela (qandilita Mg_2TiO_4) para cantidades elevadas de Mn (x = 0.2 y 0.4) y a mayores temperaturas (1200°C). Dichas ilmenitas originaron coloraciones marrones asociadas a los iones Mn^{3+}. Como pigmentos, ambos sistemas demostraron ser sólo parcialmente estables en vidriados cerámicos de bicocción, observándose un cambio hacia tonalidades beige en las pseudobrookitas y púrpura en las ilmenitas.

Por su parte, la ruta MOD condujo a resultados similares en la pseudobrookita y a un aumento importante de la reactividad en el sistema Mn-ilmenita (fase única ya a 1000°C), dando lugar a coloraciones bastante similares a las obtenidas por la ruta cerámica, si bien en algunos casos (pseudobrookitas calcinadas a 1200°C) mostraron una mayor estabilidad en el vidriado cerámico.

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ESTUDIO ELECTROQUÍMICO DE $GdBaCo_{2-x}Fe_xO_{5+\delta}$ ($0 < x \leq 1.2$) COMO MATERIAL DE CÁTODO PARA IT-SOFCs

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Palabras Clave: *IT-SFOCs, Perovskitas, TEC, ASR*

El $GdBaCo_2O_{5-x}$ ha mostrado ser un material con interesantes propiedades como cátodo en IT-SOFC [1,2]. Generalmente, las cobaltitas poseen excepcionales valores de conductividad eléctrica y buena conductividad iónica pero la aplicación de estos materiales está limitada por el coeficiente de expansión térmica y la estabilidad química con YSZ. La sustitución de parte del Co por otros metales de transición y la utilización de otros electrolitos como puede ser GDC pueden mejorar de manera importante estos problemas en el empleo en cátodos de pilas de combustible IT-SFOC [3,4].

Presentamos el estudio del efecto de la sustitución de Copor Fe en la estructura cristalina, en el contenido de oxígeno, en los coeficientes de expansión térmicos (TEC), en la conductividad eléctrica y en los valores de resistencia específica de área (ASR) en el sistema $GdBaCo_{2-x}Fe_xO_{5+\delta}$ ($0 < x \leq 1.2$). En el sistema $GdBaCo_{2-x}Fe_xO_{5+\delta}$ se produce un cambio estructural con el incremento en Fe pasando de una simetría ortorrómbica ($0 \leq x \leq 0.4$) a simetría tetragonal ($0.6 \leq x \leq 1.2$). Los coeficientes de expansión térmicos calculados mediante rayos X a diferentes temperaturas y la conductividad eléctrica disminuyen con el contenido en Fe. Hemos empleado la espectroscopia de impedancia compleja en aire y en diferentes presiones parciales de oxígeno para conocer los valores de resistencia específica de área.

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ELECTROCHEMICAL STUDY OF CRYOLITE Li_3TiF_6 AND INTEREST AS CATHODE FOR LITHIUM BATTERIES

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Keywords: *lithium fluorotitanates, electrochemical behavior, lithium batteries*

The search of new cathode materials useful in rechargeable lithium batteries (RLB) has increased in the last decades. In this connection the fluorotitanate Li_3TiF_6 may be of interest because of its adequate topology for lithium intercalation as it exhibits the cryolite structure.
This metal fluoride may be useful as a cathode in RLB due to the high ionicity of the M-F bond that produces a high redox potential of the respective transition metal [1]. In fact, our previous reports on other transition metals such as Vanadium or Iron [2, 3] pointed in that direction. Thus, we have synthesized β-Li_3TiF_6 by the ceramic route (Fig 1.), as previously reported [6] and studied the electrochemical lithium insertion properties in coin cells.
As prepared β-Li_3TiF_6 exhibits a poor electrochemical behavior and capacity was limited to 10 mAh g^{-1} (see Fig.2). However, after processed by ball milling, a decrease of particle size and a better mix of the active fluoride material with carbon, increases the experimental capacity up to 150 mAh g^{-1}, corresponding to the full reduction of Ti(III) to Ti(II).

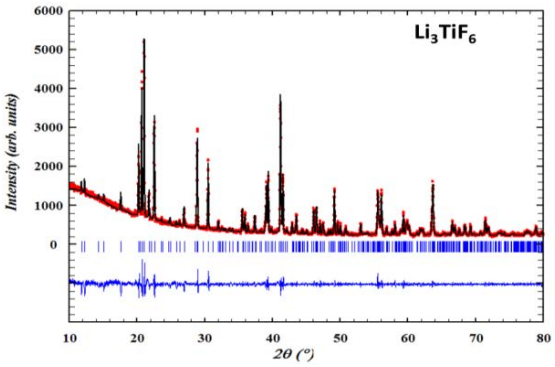

Fig. 1. X-ray diffraction patterns of sample with nominal composition of β-Li_3TiF_6.

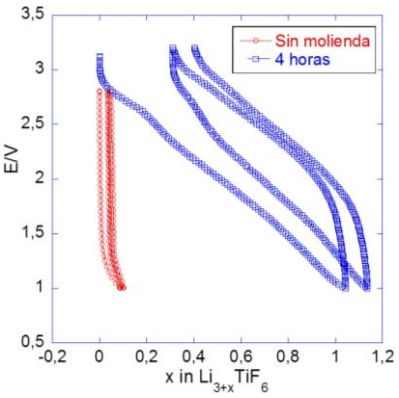

Fig. 2. a) First discharge-charge cycles of a Li cell bearing as positive electrode β-Li_3TiF_6 without milling, b) milled for 4h with carbon.

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SYNTHESIS OF WATER SOLUBLE PEGYLATED MAGNETIC NANOPARTICLES AND THEIR APPLICATION AS LONG CIRCULATING CONTRAST AGENTS BASED ON MAGNETIC RESONANCE IMAGING

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Keywords: magnetic nanoparticles, functionalization, molecular imaging, MRI, contrast agents.

Magnetic Resonance based Molecular Imaging has emerged as a promising technique for early detection and treatment monitoring of a wide variety of diseases, among them, cancer, neurodegenerative disorders, stroke, etc. The limited sensitivity and specificity of conventional MRI are being overcome by the development of novel contrast agents, most of them based on nanotechnology approaches, with improved magnetic and biological properties. In this work, we describe a facile and robust ligand-exchange method to synthesize dual T1 and T2 MRI contrast agents with long circulation times. These MRI contrast agents are based on magnetic nanoparticles (MNPs) covered by a polyethylene glycol (PEG) shell that leads to a great stability of the PEGylated MNPs in aqueous media with high crystallinity and magnetization values, thus keeping the magnetic properties of the magnetic nanoparticles. Moreover, it is reported the effect of different molecular weights PEGylated coating MNPs over the biodistribution in vivo by MRI. Furthermore, the PEGylated MNPs have shown different relaxivities r1 and r2 depending on their size, for instance the 6 nm PEGylated MNP has a r1 value of 13.3 mM-1s-1 and a r2 value of 65 mM-1s-1 with a low ratio r2/r1 of 4.9, resulting in a good dual T1 and T2 contrast agent at clinical magnetic field. On the other hand, the 14 nm PEGylated MNP is an excellent T2 contrast agent at high magnetic field, with a r2 value of 335.6 mM-1s-1. The polymer core shell of the PEGylated MNPs minimizes their cytotoxicity, and permits long blood circulation times (24 h). This combination of cellular compatibility, excellent T2 and r2/r1 values at low fields, together with long circulation times, make these nanomaterials very promising contrast agents for molecular imaging.

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LASER FURNACECOATING SYNTHESIS UNDER EXTREME CONDITIONS

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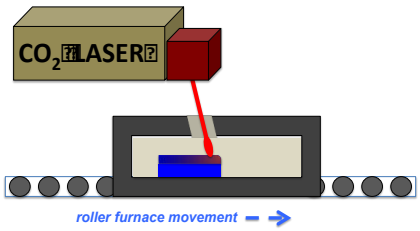
Keywords: *laser furnace, ceramics, superconductors,glazes*

High performance coatings are increasingly demanded for new applications where materials face extreme environments which cause undesired degradation of their mechanical properties, as well as deficient chemical resistance. Expensive and complex coating technologies, such as CVD and PVD, for example, have been developed in the past in order to meet such demands. An alternative route has been developed using SolGel, where expensive precursors are usually required. Moreover, these methods do not offer, in general, the possibility to control microstructure to a desired degree, and are ideal usually for thin coatings, while many foreseen applications require thick, high performance coatings.

The Laser Furnace apparatus presented here combines a continuous, conventional roller furnace with a scanning CO_2 laser. This recently patented system [1] enables melt processing highly refractive materials at low external furnace temperatures, particularly in coating format. Laser emission parameters, together with sample transverse rate and beam scanning sequence determine the final coating microstructure and properties. The method has been used to study structural relationships in eutectic oxides [2] and texture formation in large area metal-oxide superconductors [3], among other phenomena and materials. In addition, the Laser Furnace offers environmental advantages, since it requires lowering the furnace temperature in ceramic sintering and glass treatments. All of these aspects will be discussed in in this work.



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S9: *Síntesis, Caracterización y Propiedades de Materiales Emergentes*

UTILIZATION OF METAL-ORGANIC FRAMEWORKS IN DISPERSIVE MICRO SOLID-PHASE EXTRACTION AND HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY TO DETERMINE PARABENS IN WATERS AND COSMETIC PRODUCTS

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Keywords: *Metal-Organic Frameworks, chromatography, parabens.*

The use of preservatives in cosmetic products, drugs, solar creams, and personal care products (PCPs), is very common, mainly to avoid possible contamination of microorganisms in the product. Parabens (esters of *p*-hydroxybenzoic acid) are among the most frequently used preservatives in PCPs. Recent studies have started to point out possible health risks of parabens, including certain endocrine disrupting activity. Therefore, once a PCP containing parabens is applied onto the human body, harmful effects can take place by direct exposure. Given their intense use by the population and increasing utilization, wastewater treatment plants cannot eliminate them. Certainly, parabens are present in environmental samples at low levels of concentration, but their harmful effect takes place even at those levels. Given such levels, their analytical monitoring is complex, requiring efficient extraction and pre-concentration steps.

Advances in Analytical Chemistry are shifted to the development of novel extraction techniques that minimize (or even eliminate) the organic solvent consumption during the extraction stage. Furthermore, it is advisable the utilization of environmental-friendly materials or at least less toxic than conventional chlorinated organic solvents. Thus, this work pretends the novel use of metal-organic frameworks (MOFs) as promising sorbents.

The purpose is to use MOFs in a microextraction strategy, specifically dispersive micro solid-phase extraction. The overall method tries to fulfill the requirements of green analytical chemistry: elimination of organic solvent consumption in the extraction method, miniaturization of the method (saving reagents and time), and use of novel materials. The analytical application has been optimized and validated in combination with high-performance liquid chromatography and diode array detection (HPLC-DAD), with a group of parabens present in environmental waters as well as in several cosmetic products. Three MOFs has been the subject of study: HKUST-1, MIL-53 and MOF-5, as a screening study of their validity in analytical chemistry [1].

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SÍNTESIS HIDROTERMAL ASISTIDA POR MICROONDAS DE VO_2 CON ESTRUCTURA TIPO PARAMONTROSEITA

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Palabras Clave: *baterías recargables de Li, microondas, óxido de vanadio*

En esta comunicación se presenta la síntesis de uno de los polimorfos del VO_2 con estructura tipo paramontroseita, obtenido mediante síntesis hidrotermal asistida por microondas. Este material resulta interesante como electrodo positivo en baterías recargables de litio debido a la posibilidad de reducir V(IV) a V(III), a su conductividad electrónica y a su estructura con túneles análoga al rutilo (Figura 1), lo que permite insertar Litio durante el proceso de descarga de la batería. Aunque el material ya había sido estudiado previamente[1][2], se trata de la primera vez en que se sintetiza utilizando microondas como fuente de energía lo que permite obtenerlo en pocos minutos y con carácter nanométrico. La caracterización estructural y composicional de este material ha sido llevada a cabo mediante microscopía electrónica de barrido (Figura 2), difracción de rayos X (Figura 3) y espectroscopía infrarroja. El comportamiento como material catódico se ha estudiado en celdas con litio metálico como ánodo. Los resultados obtenidos en este estudio muestran que la inserción está limitada 0.25 Li por fórmula unidad correspondiendo a una capacidad de 80 $mAhg^{-1}$.

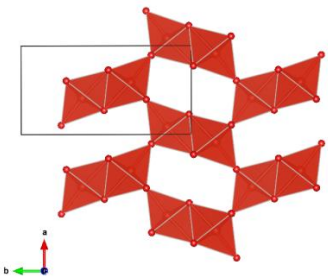

Figura 1: *estructura de la paramontroseita*

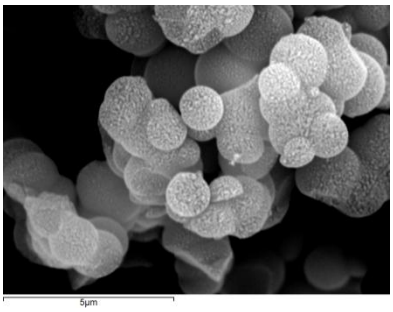

Figura 2: *Imagen de SEM*

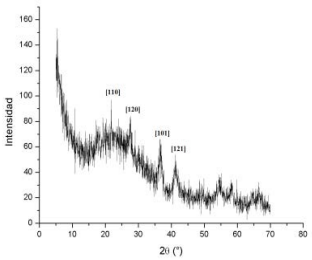

Figura 3: *difractograma de rayos X de VO_2*

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S9: *Síntesis, Caracterización y Propiedades de Materiales Emergentes*

LIGNIN-DERIVED HARD CARBONS AS ANODE MATERIALS FOR SODIUM ION BATTERIES

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Keywords: *sodium ion batteries, anodes, lignin, hard carbons.*

In recent years, sodium ion batteries have been considered a good alternative to lithium technology thanks to the potential lower price related to larger abundancy and wider distribution of raw materials compared to lithium. [1] The development of a negative electrode for sodium ion batteries is a big issue due to the fact that graphite, which is used as a commercial anode for lithium batteries, cannot be implemented in sodium batteries and metallic sodium leads to safety problems. In that sense, hard carbons, which are non graphitizable carbonaceous materials, are promising alternatives for graphite anodes as they insert sodium reversibly between graphene layers. Besides, they show an extra capacity thanks to the insertion of sodium ions into the voids of the disordered hard carbon structure in a process similar to adsorption. [2] Lignin is an aromatic macromolecule and the second most abundant biopolymer on earth after cellulose. It is solubilized by chemical treatment of wood and represents the main component of the black liquor, a byproduct of the paper industry. Although black liquors are commonly incinerated to produce energy, research on the potential uses of lignin has attracted much attention in the last years. [4]

In this work we report the synthesis of hard carbons by pyrolisis of lignin isolated from black liquor. The materials have been characterized by XRD, SAXS, SEM and galvanostatic cycling in order to establish a correlation between their microstructure and electrochemical performance showing that the materials could behave as anodes for sodium ion batteries. At the optimal synthetic conditions, the anodic material shows a promising reversible capacity of 250 mAh/g which is comparable to the performance reported for sugar based hard carbons, [2-3] or commercial hard carbon obtained from petroleum derivatives. [5] This demonstrates that lignin hard carbons can be an alternative to avoid the problems that may arise from the use of a food supply like sugar as carbon precursor.

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¿MEJORAN LAS PROPIEDADES De-NO_X DEL TiO_2 MEDIANTE DOPAJE?

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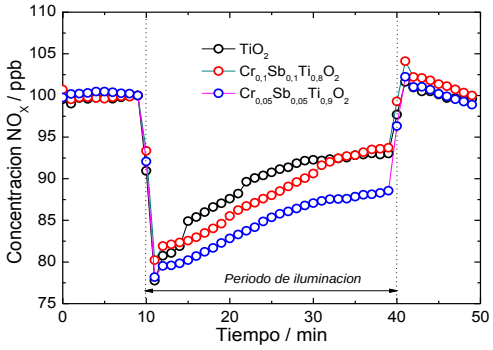
Palabras Clave: *TiO_2, gases NO_X, dopaje químico.*

Son bien conocidas las propiedades fotocatalíticas de la fase anatasa del óxido TiO_2 (band gap = 3,2 eV). Sobre la misma se ha realizado una intensa labor de investigación dado el gran interés de sus aplicaciones: descomposición fotocatalítica de agua y producción de hidrógeno, foto-electroquímica, tratamientos fotoquímicos de aire y agua, etc. Por otra parte, dado el gran efecto tóxico que presentan los gases NO_X, en los últimos años se ha comenzado su uso para la descomposición fotoquímica de estos gases en entornos urbanos (acción De-NO_X), mediante su incorporación en las formulaciones de los materiales de constucción [1]. Esta aplicación es de un gran interés social pues son numerosos los episodios de contaminación NO_X que sufren nuestras ciudades, principalmente Madrid y Barcelona.

La actividad fotoquímica de la anatasa sólo ocurre con la luz UV, 4-5% de la fracción de luz solar que alcanza la superficie de la Tierra, lo que hace que el rendimiento de estos materiales fotocatalíticos en entornos urbanos pueda afectarse seriamente según ciertas condiciones. Por tanto, resulta interesante modificar de forma adecuada la energía de band-gap de la anatasa, de modo que pueda absorber también parte de la luz visible e incrementar así su actividad.

En esta comunicación se presenta por vez primera la anatasa co-dopada en su aplicación como fotocatalizador De-NO_X. Mediante síntesis hidrotermal se prepararon óxidos de fórmula $Cr_xSb_xTi_{1-2x}O_2$ (x = 0,05; 0,1). Los óxidos resultaron ser soluciones sólidas de estructura cristalina única, critalizados en fase anatasa y tamaños de partícula dependiendo del contenido de dopantes de 30 y 50 nm, y siendo productos prácticamente monotamaño. Por efecto del dopaje se origina una capacidad de absorción óptica de la anatasa en el rango Visible de 550 – 800 nm.

El rendimiento de la reacción de oxidación fotoquímica del gas NO disminuyó al incrementar el dopaje. No obstante el proceso De-NO_X no sólo consiste en oxidar el NO a NO_2 (aún más tóxico), sino en retirarlo de atmósfera. Para ello, debe ocurrir una oxidación completa a iones nitrato (o nitrito) que se fijen en la superficie del catalizador (y una posterior lixiviación). En este sentido, el mejor fotocatalizador, desde el punto de vista medioambiental, será el que menos cantidad total de gases NO_X (NO + NO_2) permita que permanezcan en la atmósfera [2].



Como se puede observar en la gráfica, el dopaje permite una acción De-NO_X positiva, siendo las muestras $Cr_{0.05}Sb_{0.05}Ti_{0.9}O_2$ las que mayor cantidad de gases NO_X retiran del entorno.

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INFLUENCIA DEL DOPAJE CON ESTRONCIO SOBRE LAS PROPIEDADES MULTIFERROICAS DE LA PEROVSKITA CUADRUPLE $CaMn_7O_{12}$

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***Palabras Clave**: perovskitas, multiferroicos, polarización inducida magnéticamente*

La búsqueda de nuevos compuestos magnetoeléctricos multiferroicos (es decir, con orden magnético y eléctrico a largo alcance y un fuerte acoplamiento entre estas dos propiedades) despierta gran interés a la vista de las posibles aplicaciones de estos materiales multifuncionales en dispositivos magneto-eléctricos y magneto-ópticos, memorias "multiestado", etc. [1]. No obstante, el número de multiferroicos conocido es pequeño, ya que hay muy pocos compuestos que presenten simultáneamente ambas propiedades y de ellos solo algunos presentan un cierto acoplamiento magnetoeléctrico (ME). Dentro de estos últimos, los llamados multiferroicos tipo II, en los que el orden eléctrico es inducido por el orden magnético, son los que presentan efectos ME más fuertes.

En este trabajo nos centramos en uno de ellos: en la perovskita cuádruple $CaMn_7O_{12}$, que presenta la mayor polarización inducida magnéticamente que se conoce hasta el momento [2], y en la que estudiamos cómo influye el dopaje con estroncio en la posición A de la estructura sobre sus propiedades. El fin último de esta investigación es comprender y controlar los factores que controlan la polarización inducida en este compuesto y relacionados.

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AEROMOFS Y NANOESPUMAS INORGÁNICAS: DOS NUEVAS PROPUESTAS NANOPOROSAS EN UNA

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Palabras Clave: *aeroMOF, aerogel, metalogel, gel, nanoespuma, sólido mesoporoso*

Los geles metal-orgánicos (metalogeles[1]) son polímeros de coordinación reticulados que en el transcurso de la polimerización han ido reteniendo un elevado número de moléculas de disolvente, expandiéndose por ende hasta alcanzar una disposición mecánicamente estable. La evacuación del disolvente en condiciones supercríticas permite consolidar la estructura sobreponiéndose a las tensiones superficiales y dando lugar a una nueva clase de aerogeles (AeroMOFs[2]). Los aeroMOFs, además de estar constituidos por iones metálicos y ligandos orgánicos que confieren al material de multifuncionalidad conjugada con densidades extremadamente bajas (inferiores a 0,1 $g \cdot cm^{-3}$), presentan mayor difusibilidad de los adsorbatos y pueden acoger especies huesped de mayor tamaño respecto a sus competidores directos, los MOFs y las zeolitas, porque sus distribuciones de poro caen en el régimen mesoporoso. Asimismo, tienen la ventaja añadida de que son conformables en cualquier geometría. Dichas características son más que suficientes como para considerarlos potencialmente aptos para su aplicabilidad en campos como la sensórica, la separación de gases, filtración, captura de contaminantes emergentes y la catálisis en fase gaseosa.

En la siguiente ponencia se detallarán las propiedades físico-químicas más relevantes de una familía de aeroMOFs basados en el sistema metal-ditiooxamidato y alternativamente, se describirá una nueva ruta sintética para la obtención de nanoespumas inorgánicas (metálicas y de sulfuros metálicos) a partir de la descomposición térmica controlada de los aeroMOFs en distintas atmósferas. Particularmente, las nanoespumas metálicas[3] son de notable interés porque debido a los fenómenos de confinamiento cuántico que pueden exhibir, las propiedades optoelectrónicas, térmicas y mecánicas varían respecto al estado masivo y la reactividad aumenta proporcionalmente con el área específica.

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ESTUDIO NANOESTRUCTURAL DEL SISTEMA TULIO-AZUFRE

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Palabras Clave: *Sulfuros, Tierras raras, Polimorfismo, Estructuras complejas, Microscopía Electrónica de Transmisión*.

El sistema binario de Tulio-Azufre es singular desde el punto de vista cristaloquímico, presentando fases no sólo con estequiometría variable, sino también abundante polimorfismo. Se conocen 6 polimorfos de la fase Tm_2S_3.Desde el punto de vista estructural, parece que no existen estructuras infinitamente adaptables, sino regiones de dos fases entre las estequiometrías no sencillas descritas en la bibliografía como $Tm_{15}S_{22}$, Tm_5S_7 y Tm_8S_{11}. [1]

En este trabajo se presenta la síntesis y caracterización estructural de sulfuros obtenidos por tratamiento del $Tm(NO_3)_3{\cdot}5H_2O$ con H_2S/Ar, mediante reacción sólido-gas, en un rango de temperaturas entre 773-1273K; con el objetivo de encontrar fases nuevas, por ejemplo: Tm_8S_9 ($TmS_{1.12}$), Tm_3S_4 ($TmS_{1.33}$), $Tm_{11}S_{15}$ ($TmS_{1.36}$).

Las propiedades de estas fases, podrían ser interesantes para su aplicación en dispositivos de conversión y almacenamiento de energía; ya que algunos calcogenuros de metales de transición y tierras raras presentan propiedades termoeléctricas. [2]

La microscopía electrónica de transmisión y técnicas asociadas resultan fundamentales para el estudio de las fases obtenidas en cada tratamiento térmico; habiéndose detectado intercrecimientos en la fase δ-Tm_2S_3 (G.E. $P2_1/m$) (Fig. 1a) y la presencia de Tm_2S_3 tipo corindón (G.E: R-3c) (Fig. 1b) a 1173K. Por otro lado, la transformación de la fase de δ-Tm_2S_3 a 30 kbar de presión y 1373K de temperatura conduce a la aparición del polimorfo ortorrómbico con estructura tipo U_2S_3 (G.E. Pnma) (Fig. 1c).

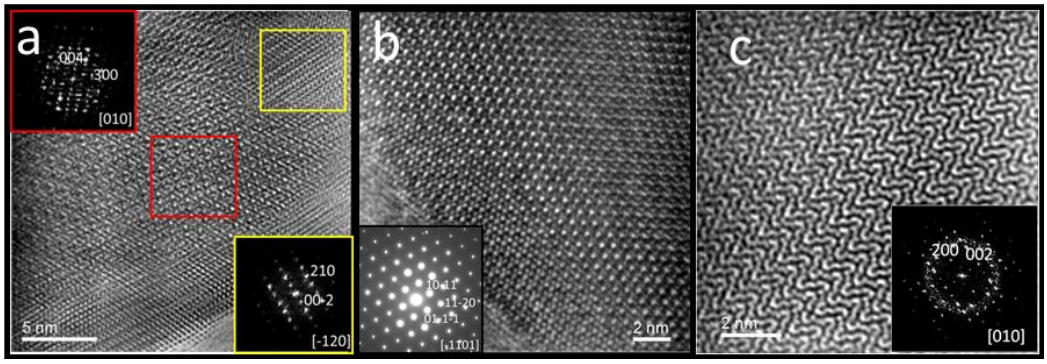

Figura 1: a) HRTEM y FFT del intercrecimiento de la fase δ-Tm_2S_3 en dos orientaciones. b) HRTEM y SAED del Tm_2S_3 tipo corindón c) HRTEM y FFT del Tm_2S_3 tipo U_2S_3.

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FERRITE NANOPARTICLES: EFFECT OF A NON-MAGNETIC MATRIX IN THE MAGNETIC PROPERTIES

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Keywords: *magnetic properties, ferrite nanoparticles.*

Nowadays there are many research groups dedicated to the preparation and the study of magnetic nanoparticles, developing different synthesis methods for controlling the size and shape of the particles to modulate their physicochemical properties. Specifically, ferrite nanoparticles generate great interest due to their potential applications in many fields such as biomedicine, catalysis, or ferrofluids technology [1, 2]. However, the agglomeration due to the interactions between the particles modifies the magnetic behavior and makes difficult the use of these materials in many applications. In order to minimize aggregation various synthetic strategies that include non-magnetic coating with organic or inorganic species or encapsulating them in different matrices have been proposed [3, 4].

The aim of this work is to prepare ferrite nanoparticles with composition MFe_2O_4 where M = Fe, Co, Ni and Zn encased in mesoporous silica matrix and to study their magnetic behavior. Nanoparticles were prepared using matrix as template and salt nitrates as ferrite precursors. The magnetic properties of ferrite nanoparticles inside the channels of the matrix (fig1.) have been studied and the effect of the interparticle interactions has been evaluated. The magnetic behavior of the material after removal of the matrix has been also studied.

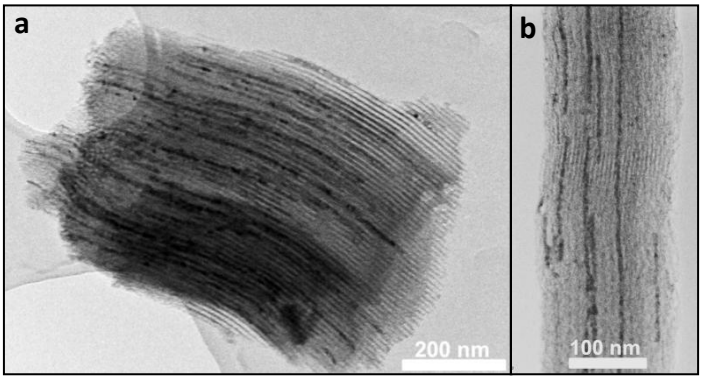

Fig 1. TEM micrographs of $ZnFe_2O_4$ (a) and $NiFe_2O_4$ (b) nanoparticles inside silica matrix.

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S9: *Síntesis, Caracterización y Propiedades de Materiales Emergentes*

MATERIALES PARA SU APLICACIÓN EN CELDAS SOFCs

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Palabras Clave: *componentes SOFC, métodos de síntesis, caracterización de materiales.*

El desarrollo de nuevos materiales, al igual que las técnicas de fabricación de componentes SOFC (celdas de combustible de óxido sólido) avanzados (Figura 1), es clave para conseguir reducir la temperatura de operación, y con ello, el coste, de estos sistemas de generación de energía [1]. Los métodos de combustión, se proponen como una de las vías de síntesis más prometedoras para la preparación de materiales a emplear en esta tecnología [2].

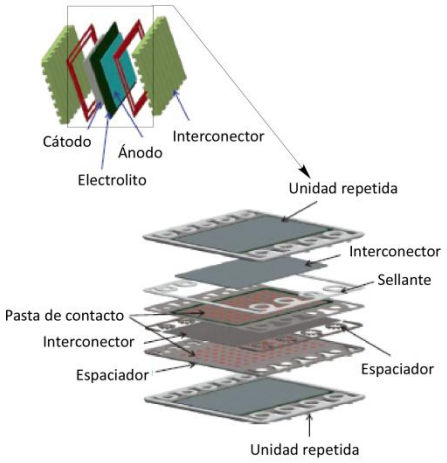

Figura 1. Componentes de una celda SOFC planar.

En este contexto, se han preparado diferentes componentes SOFC mediante el método de combustión con glicina-nitrato. Los materiales obtenidos, se han caracterizado mediante las técnicas de difracción de rayos X (DRX) sobre muestra policristalina, microscopía electrónica de barrido (MEB) y dilatometría (TEC), entre otras.

Agradecimientos: Esta investigación ha sido financiada por el Ministerio de Economía y Competitividad (MAT2013-42092-R) y el Dpto. de Educación, Política Lingüística y Cultura del Gobierno Vasco (IT-630-13). Los autores agradecen a SGIker por el apoyo técnico (UPV/EHU). A. Wain agradece al Ministerio de Ciencia e Innovación por la beca concedida (BES-2014-068433).

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S9: *Síntesis, Caracterización y Propiedades de Materiales Emergentes*

MEJORA DE LA ESTABILIDAD MECÁNICA DEL HKUST-1 CONFINADO EN UN CARBÓN NANOPOROSO

M.E. Casco[1], J. Fernández-Catalá[1], a E.V. Ramos-Fernandez[1], M. Martínez-Escandell[1], F. Rodríguez-Reinoso[1] and J. Silvestre-Albero[1]

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Palabras Clave: *HKUST-1, carbón activado, confinamiento.*

El interés hacia los nuevos materiales adsorbentes llamados *metal organic frameworks* (MOFs) ha ido creciendo en los últimos años de manera exponencial debido a que poseen una porosidad que puede ser diseñada, elevada área superficial y además, poseen centros metálicos expuestos que los hacen atractivos para diversas aplicaciones, por ejemplo, separación de gases, almacenamiento de gases, liberación controlada de fármacos, catálisis, etc. Desafortunadamente, los MOFs presentan el inconveniente de no poder ser compactados sin que su porosidad colapse [1], requisito esencial para cualquier aplicación práctica. El objetivo de este trabajo es la síntesis de nuevos materiales híbridos MOF@carbón activado que permitan mejorar las propiedades mecánicas del MOFs. En este sentido se seleccionó el HKUST-1 que presenta las mejores capacidades de almacenamiento de metano y el carbón activado LMA 726 que presenta una gran resistencia a procesos de conformado [2]. Para obtener los híbridos, se lleva a cabo la síntesis del HKUST-1 en presencia del carbón activado (CA). Se varió el porcentaje de este último para encontrar el óptimo que permita el crecimiento del MOF dentro de la porosidad del mismo y de esta manera conseguir la protección hacia presiones externas. Para el estudio de la porosidad de los híbridos antes y después de compactar, se realizaron las isotermas de adsorción de N2 a 77K. Adicionalmente, se estudió la morfología mediante microscopía electrónica de barrido (SEM) y la cristalinidad mediante difracción de rayos X. Por último se evaluaron las muestras compactadas y sin compactar en la adsorción de metano a 25 ºC y hasta 10 MPa. Los resultados mostraron que el híbrido HKUST-1@AC 50% presenta la mayor estabilidad de la estructura porosa frente a la presión externa, manteniendo significativamente las propiedades de adsorción del HKUST-1 puro.

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S9: *Síntesis, Caracterización y Propiedades de Materiales Emergentes*

ELECTROCHEMICAL SYNTHESIS: A NEW PATHWAY TO ISOLATE GOLD COMPLEXES

Luis Miguel González Barcia,[1] Rosa Pedrido,[1] Ana M. González Noya,[1] M. Inés García-Seijo,[1] Guillermo Zaragoza[2] and Manuel R. Bermejo[1]

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Keywords: *electrochemical synthesis, gold complexes*

Electrochemistry is an important area of chemistry with high applicability both in the laboratory and on the industrial scale. However, a fact sometimes unknown is that electrochemistry can be used for synthesis. Actually, the major use of electrochemical oxidation or reduction lies in organic synthesis. In contrast, the number of experiments involving the preparation of inorganic or organometallic compounds is more limited.

Over the last decades our group and others have been using electrochemical synthesis for the isolation of metal complexes by oxidation of a metal anode in a solution of a ligand bearing weakly acidic groups.[1] A wide variety of main group and transition metals have been successfully employed for obtaining of the corresponding complexes: Mn (II and III), Fe(II), Co(II), Ni(II), Cu(I and II), Ag(I), Zn(II), Cd(II), Pb(II) and Sn(II). However, some transition metals like gold remain unexplored in terms of the electrochemical synthesis of metal complexes.

On the other hand, the coordination chemistry of gold has undergone continuous expansion. Thus, gold compounds have been successfully used for the treatment of rheumatoid arthritis and actually they are being investigated as anticancer and antimicrobial drugs.[2] A second main use for gold compounds lies in the catalysis field in selective oxidation reactions, and more recently in hydrogenation processes.[3] All the aforementioned led us to apply electrochemistry in the search of gold compounds with different structures and new properties.

In this communication we present the first homoleptic neutral gold complex obtained by means of electrochemical synthesis. We have chosen a phosphine-thiosemicarbazone ligand as suitable scaffold for the stabilization of gold ions. The absence of counterions, basis or co-ligands in the cell guarantees the assembly of gold complexes whose architectures differ from those analogues obtained by traditional chemical synthesis. We are convinced that this achievement will make available a wide variety of gold compounds that are being demanded for biomedical or catalytic applications.

We thank Xunta de Galicia for funding (Projects EM2014/018 and 2014-PG097).

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S10. Química en la Frontera con la Biología (QFB) / Chemistry Bordering Biology

Este simposio reunirá a expertos destacados (del ámbito académico y de la industria) que presentarán nueva investigación innovadora en química aplicada a problemas biológicos: reconocimiento molecular, diseño y desarrollo de fármacos, mecanismos moleculares de biomoléculas, y química bioinspirada.

This symposium will bring together leading experts (from Academia and Industry) presenting innovative new research on chemistry applied to biological problems: molecular recognition, drug design and development, molecular mechanisms of biomolecules and bioinspired chemistry.

Organizadores:

Sonsoles Martín Santamaría (CSIC)

e-mail de contacto: smsantamaria@cib.csic.es

Simposio patrocinado por: Laboratorio Farmacéutico Janssen-Cilag, Red de Ciencias y Materiales Moleculares, y Grupos Especializados de Química Biológica, Carbohidratos y RMN

Martes 21 de Julio 2015

08:40 – 09:40	**PL-3**	***Conferencia Plenaria*** (Común a todos los simposios) **Samuel I. Stupp** *"Supramolecular Materials Chemistry"*

Chairman: José Luis Mascareñas **Sesión Patrocinada por Jansen-Cilag**

10:00 – 10:30	**S10-IL-01**	**Karl-Heinz Altmann** *"Synthesis of Macrocyclic Natural Products and their Functional Exploration"*
10:30 – 11:00	**S10-IL-02**	**Andrés Trabanco** *"Challenges in the Discovery of γ-Secretase Modulators for the Treatment of Alzheimer's Disease"*
11:00 – 11:30		Pausa Café

Chairwoman: Sonsoles Martín-Santamaría

11:30 – 12:00	**S10-IL-03**	**José Manuel Andreu** *"Targeting Cell Division of Bacterial Pathogens with Small Molecule Inhibitors of FtsZ Assembly"*
12:00 a 13:00	**S10-OC-01**	**Elena Pazos** *"SERS Detection of Oncogenic Transcription Factors"*
	S10-FC-01	**Sergio A. Alonso de Diego** *"Discovery and Optimization of Potent and Orally Bioavailable 1,4-oxazines as Bace-1 Inhibitors for the Treatment of Alzheimer's Disease"*
	S10-FC-02	**Daniel Lucena-Agell** *"Aplyronine A, a Cytoskeleton Inhibitor with a Novel Mechanism of Action"*
	S10-FC-03	**Elena Valverde** *"Novel soluble Epoxide Hydrolase Inhibitors with Enhanced Lipophilic Ligand Efficiency via Scaffold-Hopping Approaches"*
	S10-FC-04	**Juan M. Priegue** *"Smelling DNA in Lipid Bilayer Membranes"*
	S10-OC-02	**Silvia Cabrera** *"Synthesis and Biological Studies of New Pt(II) and Au(III) Complexes Based on Hydroxyquinoline Derivatives"*
	S10-FC-5	**Gemma M. Rodríguez-Muñiz** *"The (6-4) Photoproduct as Photosensitizer of DNA"*
	S10-FC-06	**Juan Aranda** *"Dynamics and Reactivity of DNA Methyltransferase Enzymes Studied by QM/MM and MD Simulations"*
	S10-FC-07	**Jessica Rodríguez** *"Chemoselective Synthesis of Zinc Finger Conjugates for the Selective Recognition of Specific DNA Sites"*
	S10-FC-08	**Emilio Lence** *"Detailed QM/MM Studies Revealed Enolate Stabilization as the Key Difference between Type II Dehydroquinase from M. Tuberculosis and H. Pylori"*
	S10-FC-09	**G. Jiménez-Osés** *"Active Site Structure and Dynamics in Engineered Enzymes"*
13:00 – 13:30	**S10-IL-04**	**Maria Jesús Blanco** **Patrocinada por la Red de Ciencias Materiales y Moleculares** *"Discovery, Synthesis and Characterization of a Potent and Selective Antagonist of Metabotropic Glutamate 2/3 Receptors"*

Martes 21 de Julio 2015

13:30 – 15:00		Comida
Chairwoman: Concepción González-Bello		
15:00 – 15:30	**S10-IL-05**	**Michal Hocek** *"Enzymatic Sunthesis of Base-modified DNA for Applications in Bioanalysis and Chemical Biology"*
15:30 a 16:00	**S10-OC-03**	**María Tomás-Gamasa** *"Tunable Stable DNA Nanostructures: Artificial Base Pairs Based on Reversible Covalent Bonding"*
	S10-FC-10	**Ara Núñez-Montenegro** *"Synthesis of Rhenium(I) Thiosermicarbazone Complexes and Evaluation of their Binding Affinities towards Estrogen Receptors (α/β)"*
	S10-FC-11	**Lara Villarino Palmaz** *"Supramolecular Assembly of Artificial Metalloenzymes for Enantioselctive Protonation"*
	S10-FC-12	**Noelia González-Ballesteros** *"Antitumor activity in colon cancer of gold nanoparticles obtained from the brown algae Cystoseira baccata (S.G. Gmelin)"*
	S10-FC-13	**Elsa Hernando** *"QSAR Model Performance for Tambjamine Analogs Transmembrane Anion Transport"*
Chairman: Juan Granja		
16:00 – 16:30	**S10-IL-06**	**Neal Devaraj** **Conferencia patrocinada por la Red de Ciencias Materiales y Moleculares** *"Developing Chemoselective Reactions for Applications in Cellular Imaging"*
16:30 – 17:00		Pausa Café
Chairman: Óscar Millet		
17:00 – 17:10		**Entrega de los Premios GEQB Europeo y Nacional Jóvenes Líderes de Grupos de Investigación**
17:10 – 17:40	**S10-IL-07**	**Gonçalo Bernardes (Premio Europeo GE Química Biológica)** *"CHEMISTRY ON PROTEINS FOR BASIC BIOLOGY AND DRUG DEVELOPMENT"*
17:40 a 18:10	**S10-OC-04**	**Manuel Amorín** *"New Peptide Nanotubes with Tunable Cavity"*
	S10-FC-14	**Lucía Pérez-Regidor** *"Looking for New Chemical Scaffolds for the Development of Novel TLR4 Modulators and Probes"*
	S10-FC-15	**Daniel R. Ramos** *"On the Source of Specific Oxidation Properties of Peroxidases"*
	S10-FC-16	**Iria Salvadó** *"DNA-Binding Properties of a Family of Ruthenium(II) Metallopeptides Containing DRRZ Ligands"*
	S10-FC-17	**M. I. Gutiérrez-Jiménez** *"A Chiral Dehydroalanine as Michael Acceptor in the Synthesis od Sulfa-T_N Antigen"*
Chairwoman: Consuelo Jiménez-Molero		
18:10 – 18:40	**S10-IL-08**	**Ramón Hurtado Guerrero (Premio Nacional GE Química Biológica)** *"Uncovering the Mechanisms of Protein O-Glycosilation"*
18:40		***Sesión de Pósteres***

Miércoles 22 de Julio 2015

08:40 – 09:40	**PL-4**	***Conferencia Plenaria*** (Común a todos los simposios) **Luis Liz-Marzán** *"Chemical Growth of Metal Nanoparticles: Why and How?"*

Chairman: Sonsoles Martín-Santamaría

10:00 – 10:30	**S10-IL-09**	**Marcey Waters** *"From Host-Guest Chemistry to the Nucleosome: Studies in Biomolecular Recognition"*
10:30 – 11:00	**S10-IL-10**	**Fernando Cossío** *"Frustrated and Completed (3+2) Cycloadditions: From Offspring Catalysis to Covalently Modified Biocatalysis"*
11:00 – 11:30		Pausa Café

Chairman: Francisco Corzana

11:30 – 12:00	**S10-IL-11**	**Virginie Lhiaubet-Vallet** *"Photosensitized Pyrimidine Dimerization in DNA"*
12:00 a 12:30	**S10-OC-05**	**Alberto Fernández-Tejada** *"Chemical Biology Efforts in the Development of Synthetic QS-21 Variants as New Saponin Vaccine Adjuvants"*
	S10-FC-18	**Pablo Peñalver** *"A Library of New Resveratrol Derivatives: Improved Neuroprotection and Anti-Inflammatory Activities"*
	S10-FC-19	**Ester Jiménez-Moreno** *"Chemical Interrogation of Drug / RNA Complexes: From Chemical Reactivity to Drug Design"*
	S10-FC-20	**Adrián Robles** *"Discovery of New Antimicrobial Agents by Fragment-Based High Troughput Docking"*
	S10-FC-21	**Macarena Sánchez-Navarro** *"Carrying Therapeutic Antibodies Across the Blood-Brain Barrier"*

Chairman: Francisco Corzana **Sesión Patrocinada por los GE de la RSEQ GERMN/HIC/GEQB**

12:30 – 13:00	**S10-IL-12**	**Laura Masgrau** *"Glycosidic-Bond Biosynthesis by Front-Side Nucleophilic Attack. A Shortcut for Effective Sugar Transfer Analyzed by QM/MM Calculation"*
13:00 – 13:30	**S10-IL-13**	**Óscar Millet** *"Protein Folding and Design with 'a Grain of Salt' "*
13:30 – 13:40		**Entrega de Premios a los Mejores Flash y Pósteres de Investigadores Jóvenes**
13:40 – 14:00		**Reunión del Grupo Especializado de *"Química Biológica"***
14:00		Comida

Comunicaciones Invitadas (IL)

S10: *Química en la Frontera con la Biología*

SYNTHESIS OF MACROCYCLIC NATURAL PRODUCTS AND THEIR FUNCTIONAL EXPLORATION

Karl-Heinz Altmann

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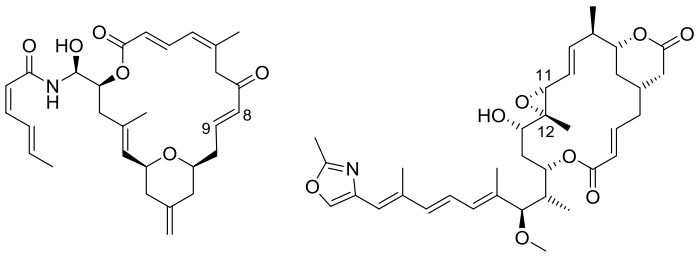
Keywords: *Rhizoxin, total synthesis, tubulin, zampanolide*

Tubulin modulators, i. e. compounds that stabilize cellular microtubules or inhibit tubulin assembly, represent an important group of clinical anticancer agents. Natural products have been the source of a diverse range of tubulin-interacting agents and many of these are macrocyclic structures. This presentation will discuss selected aspects of the synthetic chemistry, SAR, and molecular mechanism of action of the highly potent natural product tubulin modulators (-)-zampanolide (**1**) and rhizoxin F (WF-1360F) (**2**). While **1** is a microtubule-stabilizing agent (MSA), **2** is a tubulin assembly inhibitor; both compounds are potent inhibitors of human cancer cell proliferation *in vitro*.



1 **2**

For zampanoide (**1**) macrocyclic ring-closure was achieved by an intramolecular Horner-Wittig-Emmons reaction between C9 and C10, which proceeded in high yield and with excellent selectivity.[1] The synthesis of **2** was based on ring-closure by ring-closing alkyne metathesis (RCAM) between C11 and C12.[2] Conversion of the triple bond into the desired E double bond involved the selective reduction to the Z double bond followed by radical-induced isomerization. For both compounds high resolution crystal structures of their complexes with tubulin have provided fundamentally new insights into the molecular mechanism of MSA-induced tubulin assembly[3] and the suppression of this process by rhizoxin F (**2**),[4] respectively.

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S10: *Química en la Frontera con la Biología*

CHALLENGES IN THE DISCOVERY OF γ-SECRETASE MODULATORS FOR THE TREATMENT OF ALZHEIMER'S DISEASE

A.A. Trabanco[1], F.P. Bischoff[2], T. Wu[2], F.J.R. Rombouts[2], D. Berthelot[2], D. Oehlrich[2], M. De Cleyn[2], A.I. Velter[2], M. Surkyn[2], S. Van Brandt[2], G. Macdonald[2], H.J.M. Gijsen[2]

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Keywords: *GSM, Alzheimer's disease, amyloid plaques*

γ-secretase modulation has been proposed as a potential disease modifying approach to AD. γ-secretase modulators (GSMs) act by reducing the production of the toxic Aβ42 peptides and biasing the APP processing towards shorter length Aβ peptides. Since the termination of the GSM tarenfurbil in 2008 due to negative phase III trial results, considerable progress has been made towards more potent and better brain penetrable compounds. Most of the potency gain has been achieved by adding lipophilicity, resulting in compounds with low ligand lipophilicity efficiency (LLE). The suboptimal drug-like properties have translated into side effects, such as liver toxicity, for several of these compounds. Here we report on our work on conformationally restricted amino-pyridones, leading to potent but lipophilic GSMs [1,2], and the initial results on the evolution of a simple amide series. Bioisosteric replacement of the amide linker by an imidazole or 1,2,4-triazole heterocycle[3], and conformational restriction into 1,2,4-triazolopiperidines gave potent compounds with reduced molecular weight, aromaticity and lipophilicity as well as reduced liver toxicity.

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S10: *Química en la Frontera con la Biología*

TARGETING BACTERIAL CELL DIVISION WITH SMALL MOLECULE INHIBITORS OF FtsZ ASSEMBLY

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Keywords: *protein self-assembly/interfacial ligands/bacterial cytoskeleton/antibiotics*

FtsZ forms the Z-ring that coordinates the divisomal machinery in most bacteria. FtsZ is a protein homolog of tubulin, assembles into dynamic polar filaments similar to microtubule protofilaments, and hydrolyzes bound GTP at the association interface between consecutive subunits, which triggers disassembly. FtsZ is an attractive target for new antibiotics, needed to fight wide spreading resistant pathogens [1]. Assembly of purified FtsZ can be selectively inhibited with C8 modified nucleotides [2] and with the fluorescent probe *mant*-GTP.

We have replaced FtsZ´s GTP with effective synthetic inhibitors of bacterial cell division [3,4]. We identified a series of small molecules that bind to FtsZ monomers with micromolar affinities, selectively impair FtsZ assembly, the localization of FtsZ-GFP to the division ring in *Bacillus subtilis* (Bs), and display antibacterial activity against Gram-positive pathogens including antibiotic-resistant *Staphylococcus aureus* (Sa).

Large scale molecular dynamics (MD) simulations of Sa-FtsZ filaments [5] identify a coordinated Mg^{2+} ion as the key element in closing the nucleotide site and stabilizing the GTP association interface, whereas with bound GDP the loss of the contacts with loop T7 from the next monomer leads to opened interfaces and curving filaments that are more prone to depolymerization.

In addition to the GTP/GDP chemical signal for assembly/disassembly, the structure of FtsZ subunits switches between a low association affinity conformation in monomers and a high affinity conformation when assembled in filaments. The MD simulations [5] recapitulate the FtsZ assembly switch suggested by structural comparisons, which includes an opening of the cleft between the C-terminal domain and H7 helix, coupled to a tight association interface between consecutive subunits, whereas isolated and minus-end subunits relax into the closed cleft conformation. The effective antibacterial PC190723 binds into the open cleft and allosterically stabilizes FtsZ filaments. We have designed fluorescent PC190723 analogs that bind to Bs- and Sa-FtsZ polymers rather than to monomers, with which we can monitor FtsZ assembly. These small probes permit direct imaging of the Z-ring in living cells and may be also useful to find new antibacterials targeting the FtsZ assembly switch.

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S10: *Química en la Frontera con la Biología*

DISCOVERY, SYNTHESIS, AND CHARACTERIZATION OF A POTENT AND SELECTIVE ANTAGONIST OF METABOTROPIC GLUTAMATE 2/3 RECEPTORS

Maria-Jesus Blanco, Mark D. Chappell, Renhua Li, Stephon C. Smith, Bruce A. Dressman, Eric G. Tromiczak, Allie E. Tripp, Tatiana Vetman, Steven J. Quimby, James Matt, Thomas Britton, Adam M. Fivush, Jeffrey M. Schkeryantz, Albert Khilevich, Carlos Jaramillo, Jeffrey M. Witkin, Xia Li, Carl Overshiner, Xu-Shan Wang, Beverly Heinz, Steven Swanson, John Catlow, Paul Ornstein, and Charles H. Mitch

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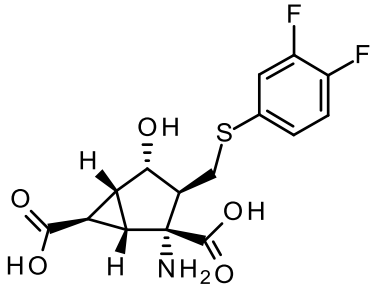
Keywords: *Synthetic chemistry; antagonist; Metabotropic Glutamate; Structure-Activity Relationship (SAR); medicinal chemistry.*

This communication will show the interplay between chemistry and biology in the field of metabotropic glutamate receptors and the identification of novel potent and highly selective mGlu2/3 receptor antagonists.

Glutamate is the major excitatory neurotransmitter in the mammalian central nervous system, activating ionotropic (iGlu) and metabotropic (mGlu) glutamate receptors. Targeting iGlu receptors has been challenging, as these receptors play a direct role in fast synaptic transmission. In recent years, there has been an increased focus of the pharmaceutical industry on targeting mGlu receptors, as these receptors have a modulatory role on neuronal excitability. Metabotropic glutamate 2/3 receptors belong to class C of the G-protein coupled receptors (GPCRs). Negative modulation of the mGlu2/3 receptors has demonstrated an antidepressant, wake-promoting and cognition-enhancing signature in preclinical animal models, thus making these receptors attractive therapeutic targets. This oral presentation will discuss the synthesis and medicinal chemistry optimization of the bicyclo[3.1.0]hexane glutamic acid scaffold to produce selective orthosteric mGlu2/3 antagonists, such as compound 1.



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S10: *Química en la Frontera con la Biología*

ENZYMATIC SYNTHESIS OF BASE-MODIFIED DNA FOR APPLICATIONS IN BIOANALYSIS AND CHEMICAL BIOLOGY

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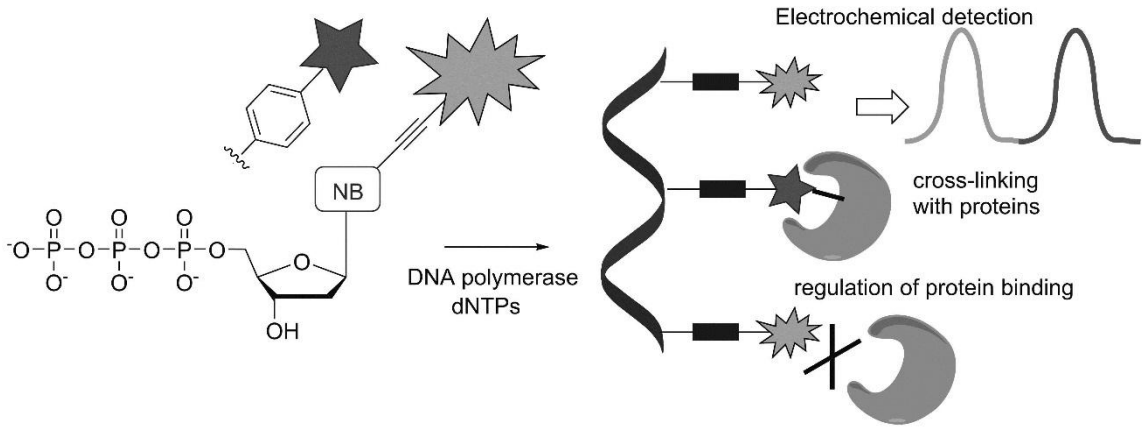
Keywords: *nucleic acids, nucleotides, polymerases*

Base-modified oligonucleotides and DNA can be efficiently synthesized by polymerase incorporation of modified deoxyribonucleoside triphosphates (dNTPs).[1] The talk will summarize the cross-coupling synthesis of diverse modified dNTPs, methods for polymerase incorporations[2] as well as applications in diagnostics,[3] bioconjugation[4] and chemical biology.[5]



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S10: *Química en la Frontera con la Biología*

DEVELOPING CHEMOSELECTIVE REACTIONS FOR APPLICATIONS IN CELLULAR IMAGING

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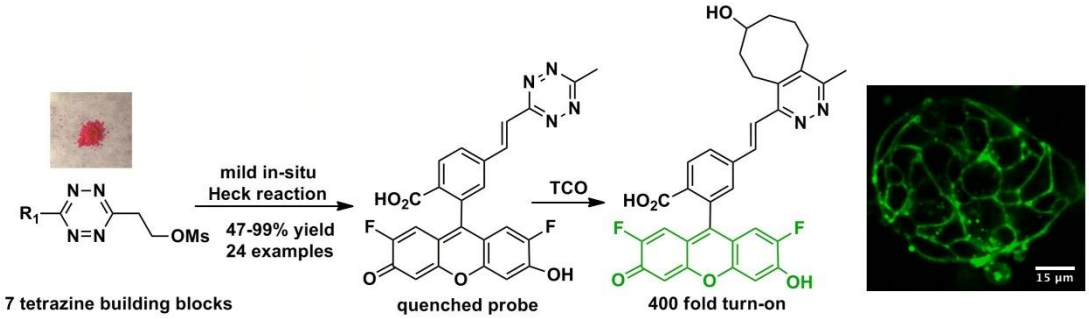
Keywords: *imaging, chemoselectivity, fluorescence, probes*

We are exploring bioorthogonal reactions as tools for addressing problems in biological imaging and bottom up synthetic biology. Recently we have developed and implemented catalytic protocols to synthesize functional 1,2,4,5-tetrazines, either from conveniently obtained precursors or using newly described tetrazine building blocks. These approaches have increased the diversity of accessible tetrazines and have led to the discovery of highly quenched tetrazine fluorophores which can increase >100-fold in fluorescence intensity upon reaction with strained dienophiles such as *trans*-cyclooctene (TCO). We foresee that these probes will become highly useful for cellular imaging applications, by mitigating signals from background probe uptake. Additionally, we have introduced the use of small dienophiles, namely methylcyclopropenes, as stable yet reactive tetrazine ligation partners. These compounds have enabled the use of tetrazine cycloadditions for imaging and labeling applications that require the use of low molecular weight probes. We have implemented cyclopropenes to track the distribution of lipid analogs in live mammalian cells using fluorogenic tetrazine imaging probes. Additionally, we have recently synthesized sugar analogs containing methyl-cyclopropenes, enabling metabolic imaging of glycan synthesis in live cells. Importantly, this technique can be done sequentially with classic “click” chemistry approaches, enabling multicolor imaging of 2 different metabolically incorporated molecules. We are currently implementing the new tetrazines and methyl-cyclopropenes to various cellular imaging applications, such as pretargeted imaging of antibody targeted cancer biomarkers and the fluorescent detection of specific oligonucleotide sequences in live cells.



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S10: *Química en la Frontera con la Biología*

CHEMISTRY ON PROTEINS FOR BASIC BIOLOGY AND DRUG DEVELOPMENT

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Keywords: *Protein Modification; Bioorthogonal Chemistry; Cancer Therapeutics*

Our work centres on reaction engineering for site-selective chemical protein modification and its use to provide insight into biology and for the development of protein therapeutics and vaccines. This lecture will cover recent examples of emerging areas in our group in (i) site-selective modification of proteins via Aza-Michael addition at chemically installed dehydroalanine residues,[1] (ii) a new pH-promoted traceless drug-release strategy[1] and (iii) the use of carbon monoxide (CO) as an immunomodulator signalling molecule for applications in cancer therapeutics.[2,3]

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S10: *Química en la Frontera con la Biología*

UNCOVERING THE MECHANISMS OF PROTEIN O-GLYCOSYLATION

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Keywords: *GalNAc-T2, AFM, SAXS, Metadynamics, Protein X-ray crystallography, Lectin domain, Mucins*

Protein *O*-glycosylation is controlled by polypeptide GalNAc-transferases (GalNAc-Ts) that uniquely feature both a catalytic and lectin domain. The underlying molecular basis of how lectin domains of GalNAc-Ts contribute to glycopeptide specificity and catalysis remains unclear. Herein, we present the first crystal structures of complexes of GalNAc-T2 with glycopeptides that together with metadynamic studies demonstrate a cooperative mechanism by which the lectin domain enables free acceptor sites docking of glycopeptides into the catalytic domain. Atomic force microscopy (AFM) and small angle X-ray scattering (SAXS) experiments show a highly dynamic conformational landscape of GalNAc-T2 and a requirement of compact structures for catalysis. A physical model relates SAXS results to basic free-energy arguments and indicates that the activity profile of GalNAc-T2 is dictated by its conformational heterogeneity, which relies on a flexible linker located between catalytic and lectin domains, unravelling how the action of GalNAc-Ts enables dense decoration of proteins with *O*-glycans.

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S10: *Química en la Frontera con la Biología*

FROM HOST-GUEST CHEMISTRY TO THE NUCLEOSOME: STUDIES IN BIOMOLECULAR RECOGNITION

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Keywords: *molecular recognition, post-translational modifications, histone proteins*

Lysine and arginine methylation are two common post-translational modifications in proteins that trigger complex signaling events that control gene expression. Because dysregulation of Lys and Arg methylation plays a role in many types of cancer, there is a need for new tools for sensing these modifications. To this end, we are utilizing dynamic combinatorial chemistry to identify new synthetic receptors for the different methylation states of Lys and Arg. Through structure-function studies and iterative redesign, we have developed a set of synthetic receptors which differential selectivity for these modified amino acids. Our studies have shown that small changes in the structures of the building blocks can have substantial impact on the selectivity of the receptors, and iterative redesign can significantly improve binding affinity. These receptors are being developed as sensors for histone protein modifications. Results of these studies will be presented.

S10: *Química en la Frontera con la Biología*

FRUSTRATED AND COMPLETED (3+2) CYCLOADDITIONS: FROM OFFSPRING CATALYSIS TO COVALENTLY MODIFIED BIOCATALYSTS

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Keywords: *Cycloadditions, Organocatalysis, DNA-based catalysts, Artificial enzymes*

Despite its relevance in synthetic chemistry [1], frustrated (interrupted) and completed (3+2) cycloadditions do not play any significant role in biochemistry and synthetic biology. We have shown that (3+2) cycloadducts can be used as organocatalysts in aldol (unnatural type I aldolase mimics) and Michael reactions [2]. In this contribution we will show that covalently modified DNA and other biomolecules can be used to catalyze (3+2) cycloadditions (Figure 1A). In addition, we will discuss how emergent organocatalytic properties of unnatural γ–dipeptides lead to the discovery of a novel cyclization reaction (Figure 1B).

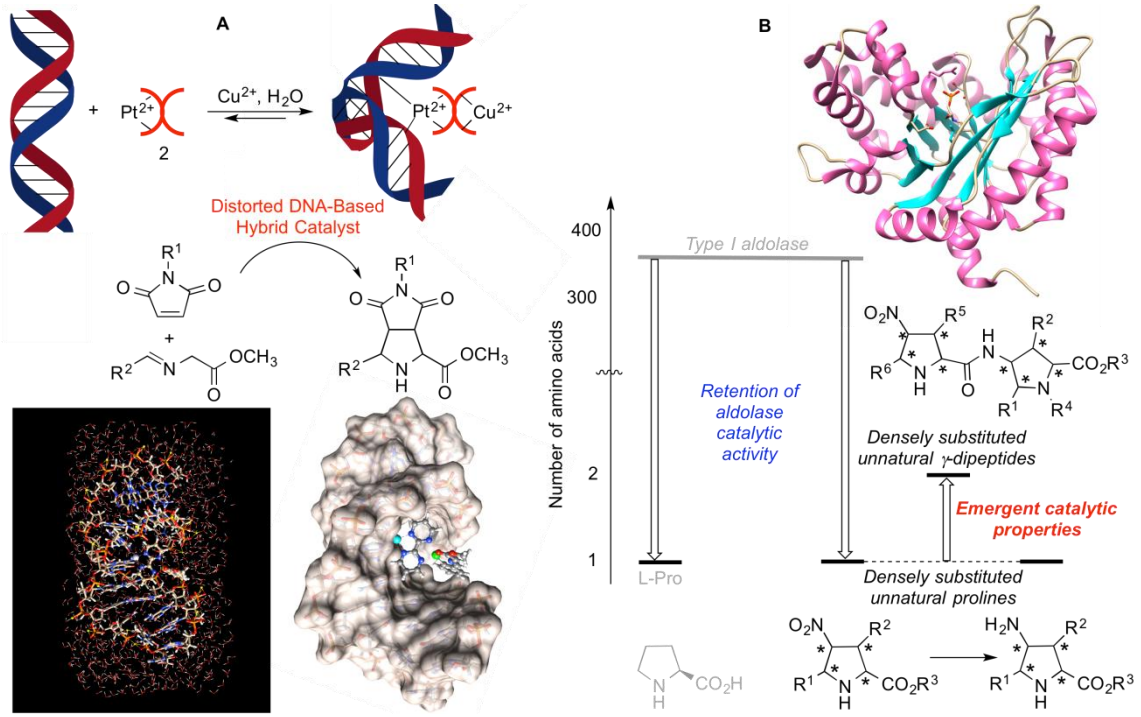

Figure 1

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S10: *Química en la Frontera con la Biología*

PHOTOSENSITIZED PYRIMIDINE DIMERIZATION IN DNA

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Keywords: *cyclobutane thymine dimer, (6-4) photoproduct, thymine photochemistry*

The incidence of skin cancer in humans has increased over the last decades, with melanoma reaching last year the 5th position among the most commonly diagnosed cancers in Europe. In this context, it has been unambiguously established that exposure to solar ultraviolet radiation is involved in the pathogenesis of most types of skin cancer and that DNA is the main target leading to the formation of two major types of damage: the *cis-syn* cyclobutane pyrimidine dimers and the pyrimidine (6-4) pyrimidone adducts.[1] Since their discovery both lesions have been the matter of an extensive work to assess the molecular basis responsible for their induction but also to evaluate their photobiological risk.

Here, we will present our recent outcomes obtained through the combination of analytical, photophysical and biochemical tools. Thymine triplet excited state (^{3}Thy) will be especially considered as it represents an essential species in the processes involved in the photoinduction of the abovementioned DNA damages. On the one hand, the attention will be focused on the formation of thymine (6-4) photoadducts (64TT) that, according to the generally accepted paradigm, are exclusively formed from a si

4 carbonyl group

of one Thy and the C5−C6 double bond of another one, followed by ring opening of the obtained oxetane. Indeed, the Paterno-Büchi reaction is one of the typical processes that involve nπ* triplets; but, the lowest ^{3}Thy is of ππ* nature. Thus, our hypothesis is that part of the assumed singlet Thy photoreactivity should proceed from an upper triplet excited state T_2 with the appropriate nπ* electronic configuration. In this context, the photochemistry of this upper triplet excited state has been explored by a triplet-triplet energy transfer process from a high energetic triplet of benzophenone populated through multiphoton excitation.[2] On the other hand, 64TT exhibit an appealing absorption in the UVA. Study of the photophysical and photobiological properties of their main chromophore, the 1-(β-D-2'-deoxyribosyl)-5-methyl-2-pyrimidone, revealed that it displays the appropriate characteristics of an efficient DNA photosensitizing agent. As a consequence, it appears realistic that the 64TT can act as a Trojan horse promoting DNA lesions in their neighboring.[3] This result is of particular importance in relation with clustered DNA damages, which are hardly repaired and are responsible for critical biological events.

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S10: *Química en la Frontera con la Biología*

GLYCOSIDIC-BOND BIOSYNTHESIS BY "FRONT-SIDE NUCLEOPHILIC ATTACK". A SHORTCUT FOR EFFECTIVE SUGAR TRANSFER ANALYZED BY QM/MM CALCULATIONS.

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Keywords: *sugar transfer, retention of configuration, glycosyltransferases, QM/MM*

Glycans are ubiquitous in all organisms and constitute the most abundant organic molecule on Earth. They play key roles in many biological processes and functions, and have properties very attractive in an array of biomedical and biotechnological applications. Yet, much has to be learnt about how they can be synthesized. Glycosyltransferases (GTs) are the enzymes responsible of their biosynthesis, catalysing the monosaccharide transfer from an activated donor to an acceptor substrate. The chemical mechanism by which they do so, particularly for those GTs that act with retention of the configuration at the anomeric centre, is being the centre of a strong debate. The discussion turns around: First, a double-displacement mechanism with formation of a glycosyl-enzyme covalent complex (Fig1A). Second, a controversial front-side attack in which the acceptor nucleophile attacks by the same side where the leaving group via an oxocarbenium transition state (Fig 1B) or ion-pair intermediate (Fig 1C).

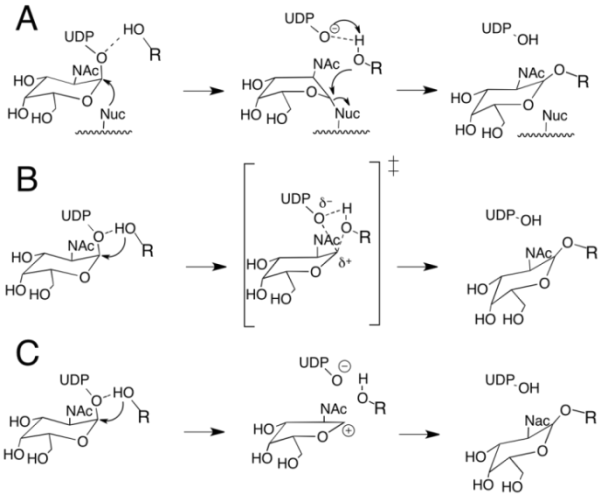

Fig 1. Proposed mechanisms for retaining glycosyltransferases. (A) Double-displacement with formation of a glycosyl-enzyme intermediate, and front-side attack via oxocarbenium (B) transition state or (C) ion pair intermediate.

In this talk, a compiling summary of the computational results obtained in the group [1] in the last years for several retaining GTs will be presented and discussed in the light of the latest experimental data. Molecular insights will be given that show why the debated front-side attack is not only possible but also very efficient for glycosidic-bond biosynthesis. The possible appearance of a double-displacement mechanism only in some GTs will also be analyzed.

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S10: *Química en la Frontera con la Biología*

PROTEIN FOLDING AND DESIGN WITH *A GRAIN OF SALT*

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Palabras Clave: *estabilidad de proteínas*, *plegamiento, organismos extremófilos, RMN*

Halophilic organisms are extreme forms of life that thrive in highly saline environments. The adaptation mechanism is universal and simple: molar quantities of cosolutes, mainly KCl, are accumulated in their cytoplasms. To cope with these extreme conditions, proteins from halophilic organisms enrich their surface in acidic and short polar side chains, whereas lysines and bulky hydrophobic residues are deselected. We have emulated the evolutionary process of haloadaptation with natural and designed halophilic proteins and, using solution state NMR, studied the different mechanisms contributing to haloadptation at a per-residue level. We have identified and quantified free energy contributions that synergistically modify the folding energy landscape for halophilic proteins: selective ion exclusion and electrostatic repulsion between charged residues destabilise the denatured state ensemble, while progressive and cumulative weak ion-protein interactions stabilise the folded conformations. Our work, thus, provides a deeper understanding of the interplay between high salt concentrations and the biased amino acid composition found in haloadapted proteins.

Comunicaciones Orales (OC)

S10: *Química en la Frontera con la Biología*

SERS DETECTION OF ONCOGENIC TRANSCRIPTION FACTORS

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Keywords: *Transcription factors, oncoproteins, peptide, nanoparticles, SERS.*

Transcription factors (TFs) are proteins that bind to specific regulatory regions of the genes and control the initiation of their transcription. It is known that many anomalous cell processes, such as uncontrolled cellular proliferation, are intimately related to the aberrant expression of some of these TFs [1], and therefore their straightforward and reliable detection would have important diagnostic and therapeutic value.

In recent years, surface-enhanced Raman scattering (SERS) spectroscopy has emerged as one of the most powerful analytical techniques for the fast and sensitive detection of specific targets [2]. We have developed a SERS-based sensor for the detection of oncoproteins exploiting their known heterodimerization properties. Thus, we have designed chemically modified peptide receptors that incorporate a thiophenol group, which anchors the protein onto the metal substrate, and works as an effective SERS probe for sensing the structural rearrangements associated with the heterodimerization of the target protein [3].

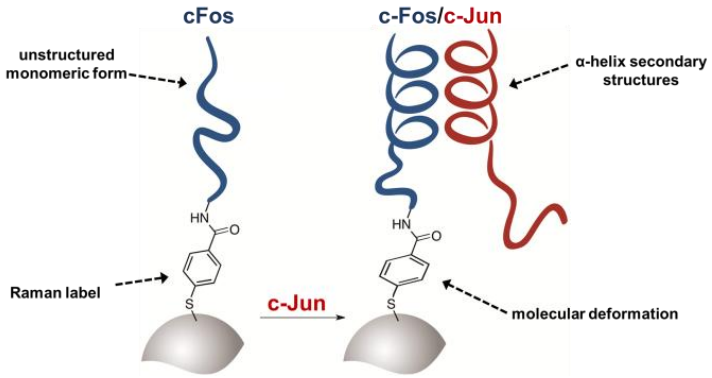

Figure: Outline of the c-Fos/c-Jun dimerization on the metal surface and the resulting deformation of the Raman label structure.

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S10: *Química en la Frontera con la Biología*

SYNTHESIS AND BIOLOGICAL STUDIES OF NEW Pt(II) AND Au(III) COMPLEXES BASED ON HYDROXYQUINOLINE DERIVATIVES

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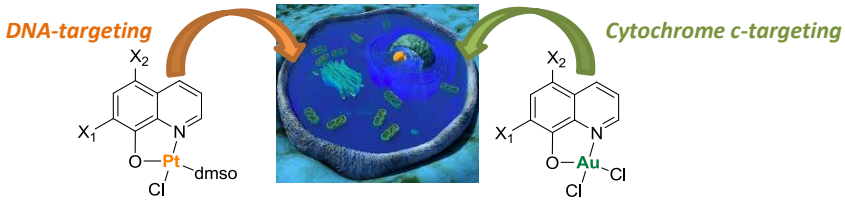
Keywords: *metallo-drugs, anticancer compounds·*

The therapeutic application of metallic complexes in cancer treatment is one of the main areas of bioinorganic chemistry, where cisplatin represents the principal drug in widespread clinical use. Traditionally, research was conducted with the aim of circumventing cisplatin's limitations developing new generations of platinum compounds, in which our group has a long experience[1]. In addition, in the last years, the attention has been turn into the search of anticancer complexes with other metals such us Au(III) complexes[2].

Herein, we will describe the synthesis, characterization and cytotoxic activity of two novel families of promising antitumor Pt(II)[3a] and Au(III)[3b] complexes based on hydroxyquinoline derivatives. Although these Pt(II) and Au(III) complexes are isoelectronic and isostructural, they were found to manifest deeply different biological profiles and mechanisms of action. A comparative study of the properties of both families of complexes will be also carried out.



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S10: *Química en la Frontera con la Biología*

TUNABLE STABLE DNA NANOSTRUCTURES: ARTIFICIAL BASE PAIRS BASED ON REVERSIBLE COVALENT BONDING

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Incorporation of unnatural base pairs into DNA has emerged as an important goal of chemical and synthetic biology. In recent years research has focused largely on three different strategies: hydrogen bonding patterns[1], hydrophobic packing interactions[2] and metal coordination forces.[3]

This communication reports on the implementation of the reversible imine bond formation as a new design for DNA base pairing. The application of this methodology provides an enzymatically processable cross-link that affords DNA structures with high but also reversible stability. In this sense, the here reported cross-link represents a "post-it" type glue for DNA duplexes and, consequently, also for nanostructures in low salt conditions. The new structure is a heterobase pair To^{I}-S^{II} composed out of an aromatic amine with the amino group embedded in a *trans*- stilbene substructure and an ortho-hydroxyl benzaldehyde base (Fig. 1). During assembly, a reversible interstrand cross-link between the nucleobases is formed *via* an imine bond over time that can, however, be reopened by heating. Nanostructures containing up to five To^{I}-S^{II} base pairs do not melt any more showing that they resist even harsh denaturing conditions. Moreover, enzymatic incorporation of our new cross-link into oligonucleotides by DNA polymerases is possible. The crystal structure reveals that To:S^{II} mimics the shape of the canonical base pairs.[4]

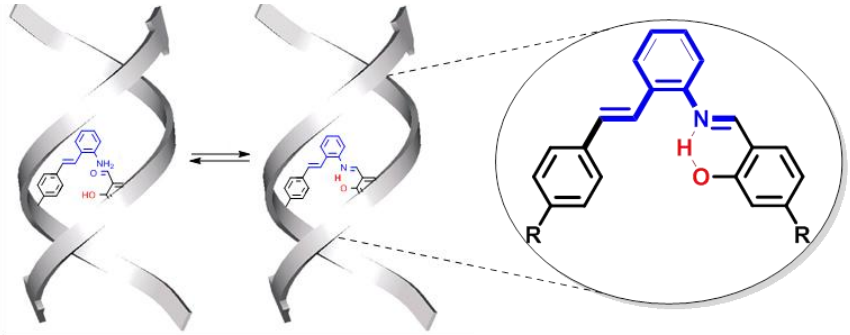

Fig. 1 Structure of the new cross-link T_o-S^{II} based on a reversible covalent bond formation inside the double helix

Apart from its own interest within DNA chemistry, hopefully this research might be helpful for designing new DNA-based nanostructures.

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S10: *Química en la Frontera con la Biología*

NEW PEPTIDE NANOTUBES WITH TUNABLE CAVITY

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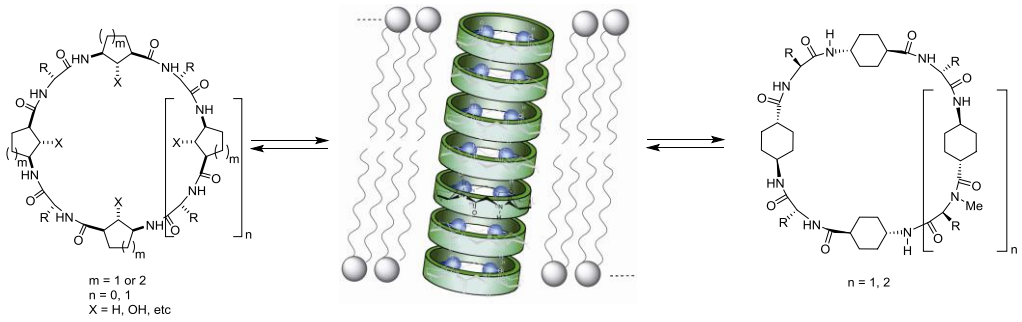
Keywords: *gamma-Amino Acids, delta-Amino Acids, Cyclic peptides, Peptide Nanotubes, Supramolecular Chemistry.*

The nanoscale materials arouse a great interest due to their structural and biomedical applications.[1] One of the most promising structures are the nanotubes, in particularly, those obtainable by a process of self-assembly, such as the peptide nanotubes.[2] Our group works with this kind of structures made from cyclic peptides constituted by alpha-, gamma- and delta-amino acids. In our designs the alpha-amino acids side chains functionalize the external surface of the nanotube thus they are responsible of the interaction with the medium. Furthermore, the gamma-amino acids are used to modulate the internal cavity of the nanotube, because one of its carbons is oriented towards the inner channel.[3] Recently, we have started to work with delta-amino acid because two of the carbons are inward oriented that bring further opportunities for nanotube cavity functionalization. These building blocks make feasible the design and construction of nanotubes with a tunable cavity for the development of efficient and selective transmembrane channels.[4]



This work was supported by the Spanish Ministry of Economy and Competitivity (MEC) and the ERDF [CTQ2013-43264-R], by the Xunta de Galicia (GPC2013-039 and EM2014/011). N. R.-V. and H. L. O. also thank the MEC for their FPU fellowships.

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S10: *Química en la Frontera con la Biología*

CHEMICAL BIOLOGY EFFORTS IN THE DEVELOPMENT OF SYNTHETIC QS-21 VARIANTS AS NEW SAPONIN VACCINE ADJUVANTS

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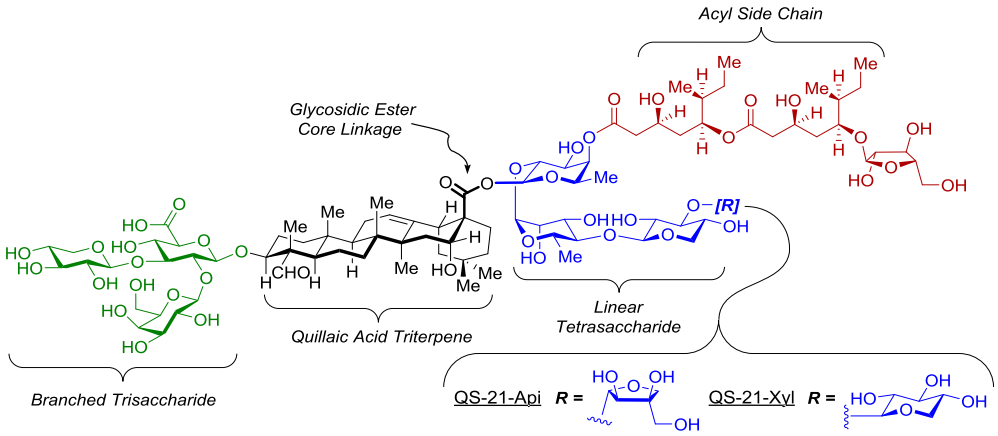
Keywords: *carbohydrates*, *synthetic saponins, QS-21, vaccine adjuvants*

Despite the promise of the saponin natural product QS-21 in numerous vaccine clinical trials to potentiate the immune response against the co-administered antigen, there are several limitations for its widespread use as a vaccine adjuvant, including scarcity, toxicity, chemical instability, and an enigmatic mechanism of action.

To address these challenges, we previously designed and synthesized a range of QS-21 variants with extensive modifications in the four structural domains that yielded critical information of the substructures required for adjuvant activity, and provided novel saponin probes with increased potency and reduced toxicity that were used to gain early insights into the mechanism of action.[1] Herein, we present additional saponin molecules based on QS-21 with further specific variations in their structure that have been accessed through a newly designed, versatile synthetic strategy.



A. F.-T. thanks postdoctoral funding from the Ministry of Education of Spain & Fulbright Program as well as the European Commission through a Marie Curie International Outgoing Fellowship.

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S10: *Química en la Frontera con la Biología*

DISCOVERY AND OPTIMIZATION OF POTENT AND ORALLY BIOAVAILABLE 1,4-OXAZINES AS BACE-1 INHIBITORS FOR THE TREATMENT OF ALZHEIMER'S DISEASE

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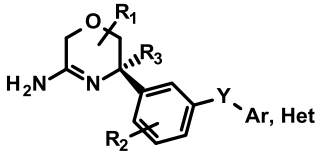
Keywords: *BACE inhibitors, 1,4-oxazines,morpholine, amidine, Alzheimer´s disease*

Alzheimer's disease (AD) is a progressive neurodegenerative disorder and the most common form of dementia in aged population.[1] The cause of AD is unclear but Tau fibrils and amyloid beta (Aβ) deposits are characteristic neuropathological hallmarks and may be associated with disease pathogenesis.[2] These insoluble deposits are predominantly aggregates of Aβ peptides of 39–43 amino acids formed via the sequential cleavage of β-amyloid precursor protein (APP) by aspartyl proteases, β- and γ-secretase.[3] The inhibition of β-secretase 1 (BACE-1) may therefore represent a potential disease modifying treatment for AD.[4]

Herein we present the discovery, synthesis and optimization of potent 1,4-oxazine amidine-like BACE-1 inhibitors (**I**) which show good *in vitro* inhibition in enzymatic and cellular BACE-1 assays. We describe a lead optimization process focused on reducing the amidine pK_a whilst interactions in the BACE-1 active site are improved. Our strategy based on introducing substitutions in the oxazine ring permitted the modulation of properties such as permeability and P-glycoprotein efflux. This led to compounds orally bioavailable and centrally active which showed robust lowering of Aβ levels *in vivo* in mouse and dog. The amyloid lowering potential of these molecules makes them valuable leads for the treatment of amyloidosis in Alzheimer's disease.



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S10: *Química en la Frontera con la Biología*

APLYRONINE A, A CYTOSKELETON INHIBITOR WITH A NOVEL MECHANISM OF ACTION

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Keywords: *Aplyronine, cytoeskeleton, actin, tubulin*

The search and characterization of novel compounds which inhibit cell migration and division is a crucial feature in the fight against cancer. These compounds usually target two of the major components of the cell cytoskeleton, actin and tubulin, affecting its polymerization/depolymerization dynamics [1]. Currently, most of the chemotherapeutic drugs in use alter the microtubule dynamics by promoting or inhibiting microtubule polymerization. However, although several different compounds with a similar effect upon actin are known, none of them have demonstrated its usefulness as antitumor agent. Recently, studies on Aplyronine A (ApA), a novel compound with a marine origin, have demonstrated that it acts as an actin polymerization inhibitor [2]. Moreover, this new chemical agent presents a novel mechanism of action, affecting microtubule dynamics through the formation of a ternary complex between ApA, actin and tubulin, being the first compound ever found that is able to interact with both cytoskeleton components [3].

In the present work we have examined the effects of a synthetic ApA upon microtubule and microfilament dynamics. Our first results based on the characterization of ApA cytotoxicity in different cell lines have demonstrated that we are in front of a potent cytotoxic agent. In addition, using *in vitro* actin polymerization assays we have observed that synthetic ApA is a strong inhibitor of actin polymerization in the same manner as the natural ApA. On the other hand, we have proved using HPLC analyses that this synthetic ApA is able to interact with actin and tubulin at the same time.

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S10: *Química en la Frontera con la Biología*

NOVEL SOLUBLE EPOXIDE HYDROLASE INHIBITORS WITH ENHANCED LIPOPHILIC LIGAND EFFICIENCY *VIA* SCAFFOLD-HOPPING APPROACHES

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Keywords: *sEH inhibitors, scaffold-hopping, lipophilic ligand efficiency, ER stress*

Soluble epoxide hydrolase (sEH) is a promising pharmacological target whose inhibition is of significant interest for the treatment of multiple conditions, such as hypertension, metabolic syndrome and inflammatory and painful states.[1] Since its discovery, there has been a significant and rapid development of sEH inhibitors featuring mainly a urea or amide group, and a vast number enclose an adamantane moiety.[2] The high lipophilicity of the inhibitors, furnished chiefly by the adamantane unit, results in an increased likelihood of binding to multiple targets as well as metabolic clearance and poor water solubility. Hence, it seems evident that the adamantane ring does not possess the optimal properties as a scaffold for sEH inhibitors. A decrease in the overall lipophilicity will lead to more soluble and metabolically stable compounds which will therefore be more "drug-like".[3] In this sense, there is an urgent need for the development of new scaffolds that provide compounds with more optimal physicochemical properties to avoid attrition in later stages of the drug discovery process.

Herein we report the use of a scaffold-hopping approach for the development of polycyclic structures as adamantane surrogates of known sEH inhibitors (Figure 1). The new compounds are potent against human sEH and show lower lipophilicity than the adamantane-based standard, as it is reflected in the lipophilic ligand efficiency (LipE). We have identified a few promising scaffolds that improve notably the LipE as well as the water solubility compared to the adamantyl compound while retaining nanomolar inhibitory activity against sEH. The selected inhibitors have been tested in *in vitro* studies for the investigation of their effects on endoplasmic reticulum stress signaling in liver tissue by sEH inhibition.

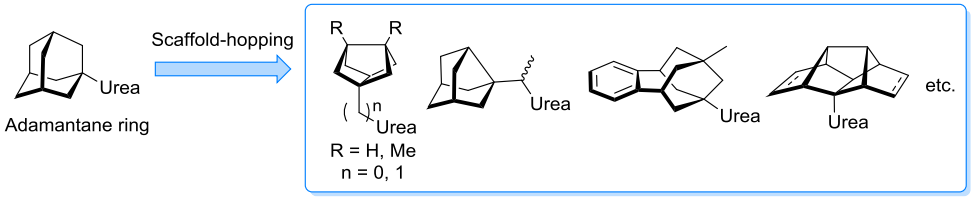

Figure 1. Scaffold-hopping for new sEH inhibitors.

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S10: *Química en la Frontera con la Biología*

SMELLING DNA IN LIPID BILAYER MEMBRANES

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Keywords: *pattern generation, pattern recognition, amphiphiles, vesicles, DNA, transport, sensor.*

Pattern generation and recognition constitutes a powerful process and an extended universal methodology in nature, arts and science. The olfactory sensory system allows the detection of thousands of different odorants with only hundreds of olfactory receptors. However, this system is incompatible with a 1:1 recognition.[1] The assisted transport (by small cationic amphiphiles) of anionic polymers (DNA, RNA...) across artificial membranes has been recently applied for the generation of fluorogenic-transport patterns that allowed the differentiation of similar hydrophobic analytes.[2] In the current abstract we report on the potential of pattern-generation in lipid bilayer membranes for the differentiation of anionic biopolymers with biological relevance (i.e. RNA, DNA). The differences in the transport of different DNA molecules across lipid bilayers allowed the differentiation of a broad collection of DNA examples including the challenging of recognition single nucleobase mutations.[3]

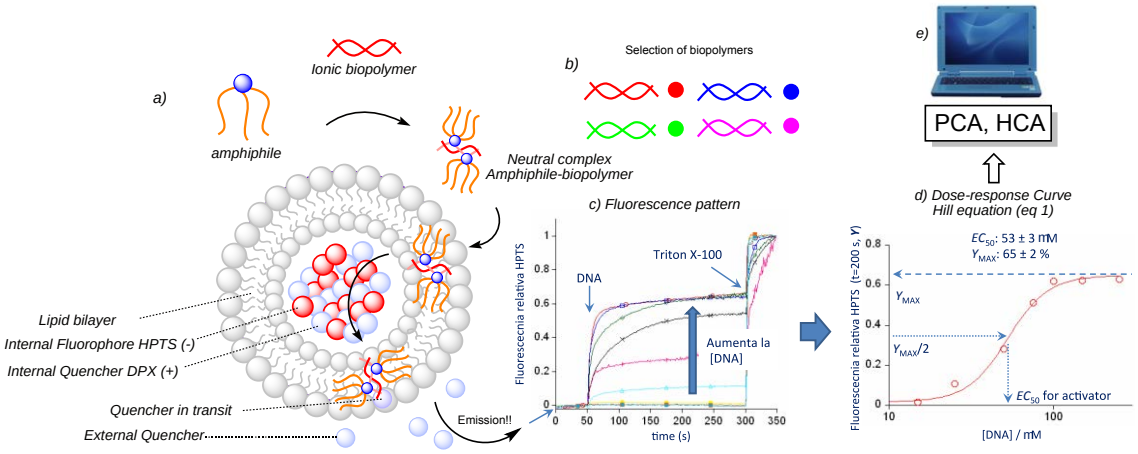

Figure 1. Pattern generation for new "smelling" sensing methods.

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S10: *Química en la Frontera con la Biología*

THE (6-4) PHOTOPRODUCT AS PHOTOSENSITIZER OF DNA

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Key Words: *DNA damage, (6-4) photoproducts, pyrimidones.*

Ultraviolet (UV) light is able to modify the chemical composition of natural DNA inducing changes in the structure of the nucleobases.[1] Cyclobutane pyrimidine dimers (CPDs) and the so called (6-4) photoproducts (6-4PPs) are relevant DNA lesions caused by UV light exposure.[2] The UV absorption of pyrimidines bases displays a band centered at 260 nm, which disappears in the CPDs. Conversely, 6-4PPs exhibit a new UV band appearing at 320 nm associated with the presence of a 5-methyl-2-pyrimidone chromophore. With this background, it appears feasible that photogeneration of the pyrimidone chromophore within the double helix could actually constitute the insertion of a potential endogenous sensitizer absorbing in the UVA-UVB range.

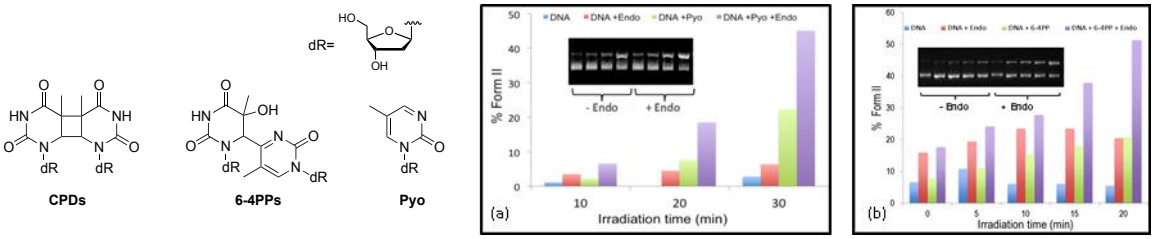

Figure: CPDs, 6-4PPs and 1-(β-D-2'-deoxyribosyl)-5-methyl-2-pyrimidone (Pyo), left. Right: Electrophoresis experiments of Pyo(a) and 6-4PP(b)

In a first approach we selected Pyo as model of 6-4PPs to investigate its behaviour as photosensitizer. Electrophoresis combined with steady state and laser flash photolysis demonstrates that Pyo can be responsible for CPDs formation and ROS-mediated oxidative damage.[3] Our next step was to synthesized the real 6-4PP damage. After performing the electrophoresis and photochemical studies and comparing the results with those obtained with the Pyo, we were able to conclude that Pyo is the main chromophore of the 6-4PPs. As a consequence, the 6-4PPs can result in even more mutations than estimated, acting as Trojan horses and extending the active fraction of light towards the UV range.

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S10: *Química en la Frontera con la Biología*

DYNAMICS AND REACTIVITY OF DNA METHYLTRANSFERASE ENZYMES STUDIED BY QM/MM AND MD SIMULATIONS

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Keywords: *DNA-MTases, Epigenetics, Computational Chemistry, QM/MM, MD*

Our work is focused on the study of the family of DNA-Methyltransferases (DNA-MTases) enzymes. The DNA-MTases catalyze the methyl transfer to a target nucleic base of the DNA. The methyl transfer takes place from the cofactor, S-adenosyl-L-methionine (SAM), to an adenine or a cytosine base which are part of a specific sequence of nucleic bases which are recognized by the enzyme.[1]. The family that constitutes the DNA-MTases can, in turn, be divided in two subfamilies: the N-MTases and the C-MTases. The N-MTases methylate the N6 position of an adenine or the N4 position of a cytosine and they are only found in prokaryotes. The C-MTases methylate the C5 position of a cytosine base and they are found in both eukaryotes and prokaryotes.

We have examined and characterized the reaction mechanisms in the N4,[2,3] N6 [4] and C5 [5] DNA-MTase enzymes making use of methodologies which simulate *in silico* enzymatic environments in a realistic way. We have employed classical molecular dynamics (MM) simulations for the purpose of building appropriate models of the Michaelis complexes of the enzymes studied. In these simulations the interactions stablished between the protein, the cofactor and the DNA were analyzed. We have also carried out QM/MM molecular dynamics simulations for the purpose of determining the free energy profiles associated to the studied reactions. For this, different methodologies implemented in our research group were used as the string method and the construction of path coordinates which permit to explore complex reaction mechanisms.[6]

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S10: *Química en la Frontera con la Biología*

CHEMOSELECTIVE SYNTHESIS OF ZINC FINGER CONJUGATES FOR THE SELECTIVE RECOGNITION OF SPECIFIC DNA SITES

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The covalent modification of proteins is a powerful strategy to modulate their macromolecular function. Many bioconjugation strategies have relied on the reactivity window provided by the nucleophilic sulfur atom in cysteine side chains.[1] However, a major problem of this strategy arises when the peptide or protein of interest has more than one cysteine residue, because of the competitive formation of polyalkylated products. Herein we report the chemoselective modification of a cysteine residue incorporated into a zinc finger peptide featuring two additional cysteines as part of a classical Cys_2His_2 motif. The success of the approach relies on a temporary protection of these two cysteines by trapping them into the ββα secondary structure that is formed after the coordination of Zn (II) (Fig. 1, left). The strategy allows a straightforward synthesis of zinc finger derivatives from peptides containing only natural amino acids. As an application of the method we have synthesized several conjugates capable of recognizing specific DNA sequences with very good affinities (Fig. 1, right).[2]

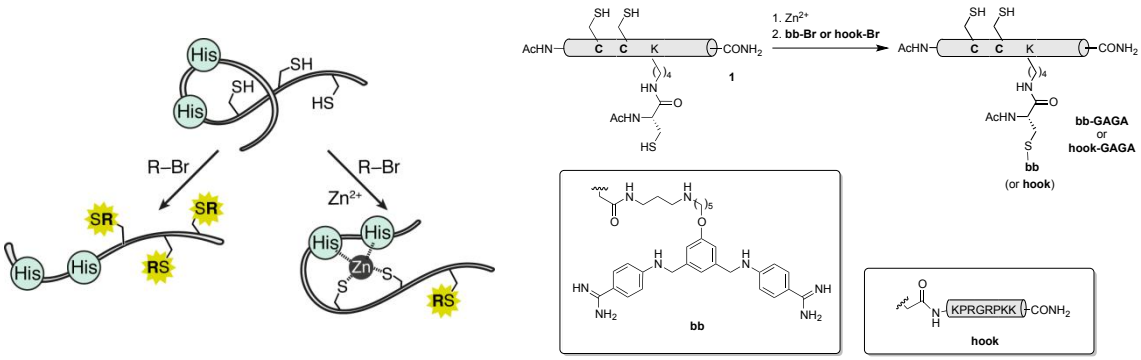

Fig. 1 Left: Schematic illustration of the "natural" cysteine protection approach. Right: Synthesis of the peptide conjugates **bb-GAGA** and **hook-GAGA**.

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S10: *Química en la Frontera con la Biología*

DETAILED QM/MM STUDIES REVEALED ENOLATE STABILIZATION AS THE KEY DIFFERENCE BETWEEN TYPE II DEHYDROQUINASE FROM *M. TUBERCULOSIS* AND *H. PYLORI*

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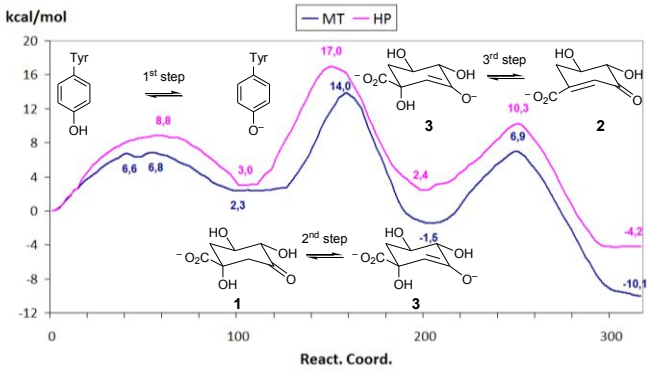
Keywords: *QM/MM calculations, enzymatic mechanism, computational chemistry*

Type II dehydroquinase (DHQ2) is an essential enzyme for the survival of relevant pathogenic bacteria, such as *Helicobacter pylori* (HpDHQ2) and *Mycobacterium tuberculosis* (MtDHQ2). DHQ2 is not present in humans, what makes it an attractive target for the development of new antibacterial agents. It has been shown previously that the reaction catalyzed by DHQ2 consists in a three step mechanism involving an enolate intermediate **3**, whose formation is the partially rate limiting step of the reaction (2nd step).[1,2] In this work, we explore the difference between the reaction mechanisms in both enzymes using detailed QM/MM MD simulations. Corrections of the free energy profiles (semi-empirical SCC-DFTB/MM level) with single-point MP2/MM energy calculations, led to results that are fully consistent with experimental data. These calculations were used to identify and quantify the importance of key residues in catalysis and identify the key difference between both enzymes. MtDHQ2 is capable of a more efficient stabilization of the enolate **3**. The essential arginine, which is located in the substrate-covering loop that closes over the active site, is the major contributor to the enolate stabilization, while the presence of a water molecule in HpDHQ2 needed for the 1st step destabilizes both the transition state of the 2nd step and the enolate **3**.



Acknowledgments: Bristol's ACRC (bluecrystal) and Santiago's CESGA (SVG) for providing the computational resources. E. L. also thanks Xunta de Galicia for a post-doctoral fellowship.

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ACTIVE SITE STRUCTURE AND DYNAMICS IN ENGINEERED ENZYMES

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Keywords: *Enzyme design, Molecular Dynamics, Protein Motions, Biocatalysis*

Understanding and utilizing the enormous catalytic power of enzymes is a grand challenge for chemical biology. Our group has collaborated with biologists to design new enzymes with functions different from those evolved by Nature. In spite of these successes, our understanding is not sufficient to rationally tune the global architecture of the protein that ultimately determines catalysis in order to achieve efficiencies rivaling those of the natural enzymes. Instead, experimental directed evolution is often used to achieve several orders of magnitude of acceleration beyond that achieved by the designed protein.

We have used molecular dynamics (MD) simulations to reveal how mutations alter the structure and organization of enzyme active sites, studying the fluctuations between active and inactive conformations normally concealed to crystallography. We first describe the importance of dynamics in evaluating a series of computationally designed and experimentally evolved enzymes for the Kemp elimination, a popular subject in the enzyme design field. In the second example, we show how microsecond MD has been used to uncover the role of remote mutations in the active site dynamics and catalysis of a transesterase, LovD, a useful commercial catalyst for the production of the drug simvastatin. X-ray analysis of inactive and active mutants did not reveal differences in the active sites, but relatively long time scale MD in solution showed that the active site of the wild-type enzyme preorganizes only upon binding of the acyl carrier protein (ACP) partner. In the absence of bound ACP, a noncatalytic arrangement of the catalytic triad is dominant. Unnatural truncated substrates are inactive because of the lack of protein−protein interactions provided by the ACP. Directed evolution is able to gradually restore the catalytic organization of the active site by motion of the protein backbone that alters the active site geometry.

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S10: *Química en la Frontera con la Biología*

SYNTHESIS OF RHENIUM(I) THIOSEMICARBAZONE COMPLEXES AND EVALUATION OF THEIR BINDING AFFINITIES TOWARDS ESTROGEN RECEPTORS (α/β)

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Keywords: *Rhenium complexes; Thiosemicarbazone ligands; Estrogen receptor*

The estrogen receptors (ERα and ERβ) are members of the steroid/thyroid hormone nuclear receptor superfamily and they bind estrogens with high affinity [1]. They play an important role in the growth of hormone-dependent breast cancer. The discovery of the relationship between a high concentration of ERα and the sensitivity of the breast cancer to antiestrogenic molecules led to the possibility of designing drugs to predict the response to antihormonal therapy. We initially hypothesized that the rational design of thiosemicarbazone (TSC) ligands would lead to molecules with specific affinity for the estrogen receptor, bearing in mind that the NH (thioamide) group can emulate one of the OH groups present in all molecules that have high affinity for this receptor.

A series of rhenium(I) thiosemicarbazone derivatives were prepared and the values for the displacement of [^{3}H]-17β-estradiol from the estrogen receptor subtypes (ERα and ERβ) were determined by a competitive standard radiometric assay. In general, the values of Ki for both ER subtypes suggest an appreciable selectivity towards ERα. These results are comparable to those obtained with other rhenium/technetium derivatives [2] but, because most of them are based on conjugation of the metal fragment to estradiol, our synthetic approach is significantly more straightforward.

We have demonstrated that the coordinative behavior of the TSCs enables the possibility of modulating properties, such as affinity for ER, by modification of the coordinative environment of rhenium, which reaffirms the usefulness of this type of ligands in the design of new targeted radiopharmaceuticals.

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SUPRAMOLECULAR ASSEMBLY OF ARTIFICIAL METALLOENZYMES FOR ENANTIOSELECTIVE PROTONATION

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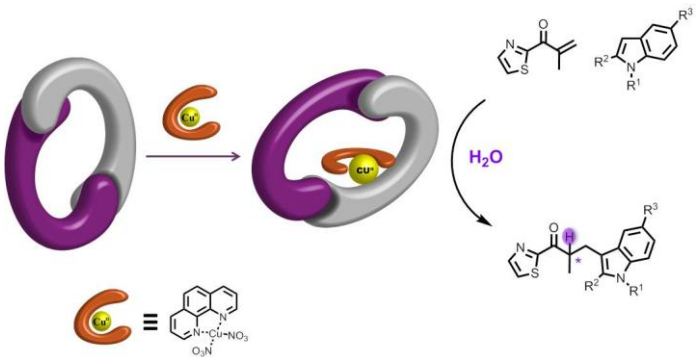
Keywords: *Artificial Metalloenzymes, Supramolecular Chemistry, Enantioselective Catalysis*

Artificial metalloenzymes are hybrid catalysts in which a catalytically active transition metal complex is incorporated into a host biomacromolecule, typically a protein or DNA. The aim is combine the best of both worlds, that is, broad catalytic scope, a hallmark of homogeneous catalysis, and high activity and selectivity under mild conditions, which typically characterizes enzymatic catalysis.[1]

The key parameter in artificial metalloenzymes design is the second coordination sphere provided by the biomolecular scaffold. The Roelfes group developed a novel concept for the creation of artificial metalloenzymes, which involves the creation of an active site in the dimer interface of the transcription factor "Lactococcal multidrug resistance Regulator" (LmrR). A copper(II)-phenantroline complex was anchored in the hydrophobic pocket of the protein using a cysteine conjugation strategy. This new metalloenzyme was successfully employed in the catalytic asymmetric Diels-Alder reaction, with up to 97% ee, [2] and in the conjugate addition of water with up to 84% ee. [3]

Supramolecular assembly of the transition metal complex is very attractive, since the hybrid catalyst is prepared by self-assembly. Thus, there is no need for chemical modification and subsequent purification steps, which greatly facilitates the discovery, optimization and application of novel artificial metalloenzymes. Herein, we present the supramolecular assembly of a novel artificial metalloenzyme based on LmrR and its application in a highly challenging reaction: the tandem Friedel Crafts/Enantioselective protonation in water (Scheme 1). [4]



Scheme 1

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S10: *Química en la Frontera con la Biología*

ANTITUMOR ACTIVITY IN COLON CANCER OF GOLD NANOPARTICLES OBTAINED FROM THE BROWN ALGAE *CYSTOSEIRA BACCATA* (S.G. GMELIN)

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Keywords: *AuNP, Cystoseira baccata, Antitumor, Caco-2, Colorectal Cancer.*

In the context of our research project which is focused on the green synthesis of new nanomaterials with biomedical application, an aqueous extract of *Cystoseira baccata* was used to synthesize gold nanoparticles by reduction of $HAuCl_4$ at room temperature. *C. baccata* is a common brown algae widely distributed along the subtidal rocky shores of the NE Atlantic Ocean, from the UK to northern Spain. The formation of spherical AuNPs with mean diameter of 8.4 ± 2.2 nm has been demonstrated by UV-Vis spectroscopy, TEM, HRTEM and STEM (Fig 1). Moreover, EELS and EDS confirmed the elemental composition of the extract and nanoparticles. The extract appears to act as a protective agent that keeps the particles separated avoiding aggregation and coalescence.

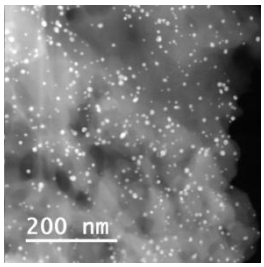

Fig. 1: STEM image where many gold nanoparticles are embedded in the extract matrix

Cytotoxicity of Au@CB reflected as (% of cell viability) was assessed in the human colon carcinoma cell line (Caco-2) by the Vybrant MTT cell proliferation assay. After data analysis a significant antiproliferative effect was observed at doses 400, 200, 100 and 50 μM compare with the untreated control. Resulting in the following metabolic activity percentages: 38.72 ± 1.56%, 39.98 ± 1.815 %, 46.67 ± 4.42%, 49.85 ± 6.98% and 96.23 ± 2.96%. The calculated IC_{50} for Au@CB was 26.73 μM. In order to study more in depth the effect of Au@CB in our cultures, an apoptosis assay was performed by employing Flow Cytometry. Our results reflect that Au@CB has a dosage dependent apoptotic activity and is cytotoxic *in vitro*, therefore new studies will be conducted to clarify the compound antitumoral properties.

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QSAR MODEL PERFORMANCE FOR TAMBJAMINE ANALOGS TRANSMEMBRANE ANION TRANSPORT

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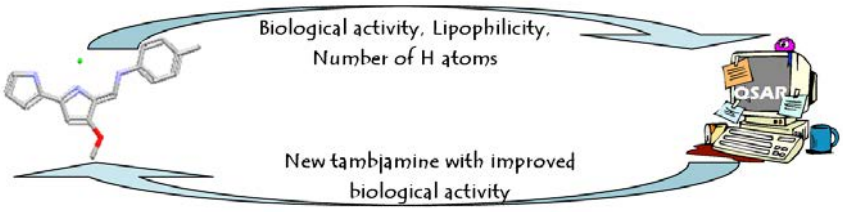
Keywords: *transmembrane anion transport, tambjamines, QSAR*

Cell membranes are frontiers between the internal and external environment of the cell. Although neutral small molecules diffuse readily across them, they are essentially non permeable to polar species or charged particles, consequently ions cannot diffuse passively through the lipid bilayers. The development of new transport systems for anionic species is an attractive and growing research field.**[1]** Tambjamines are natural products with anion transport properties. They are characterized by a 4-methoxy-2,2´-bipyrrole unit with an enamine substituent.**[2]** Recently, we have demonstrated that the ionophoric activity of tambjamines plays an important role in their citotoxicity.**[3]** Their easy synthetic access gives advantage to obtain insights into anion transporter design. An extended series of tambjamine synthetic alkaloids bearing aromatic enamine substituents were synthesized and fully characterized. Employing QSAR methods it has been tried to elucidate the parameters that govern the ainophoric activity of these compounds.**[4]** Moreover, we aim to clarify how these drug-like molecules work and which features characterize a potent transporter.



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S10: *Química en la Frontera con la Biología*

LOOKING FOR NEW CHEMICAL SCAFFOLDS FOR THE DEVELOPMENT OF NOVEL TLR4 MODULATORS AND PROBES

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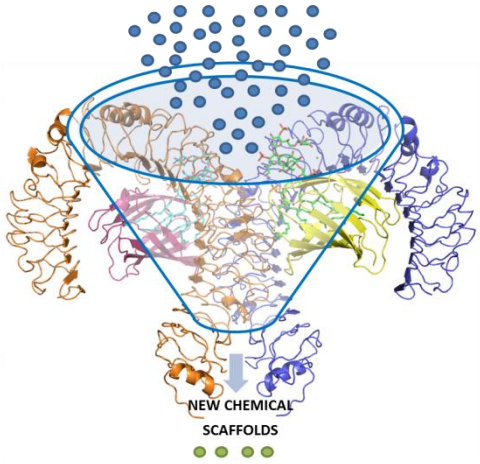
TLR4 is a member of the Toll-like receptors (TLRs) family located in the plasma membrane, where binds to lipopolysaccharides, a membrane constituent of Gram-negative bacteria, and together with MD-2 protein, forms a heterodimeric complex which leads to the activation of the innate immune system response. TLR4 activation has been associated with certain autoimmune diseases, noninfectious inflammatory disorders, and neuropathic pain, suggesting a wide range of possible clinical settings for application of TLR4 antagonists. However, agonists of TLR4 can also be useful as adjuvants in vaccine development and in cancer immunotherapy [1].



We have undertaken computational studies in order to characterize at atomic level, the molecular recognition processes involving reported TLR4/MD-2 modulators [2]. Virtual screening strategies from commercial and in-house libraries, followed by biological assays, have allowed us to identify new chemical scaffolds for the development of novel TLR4 modulators.

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S10: *Química en la Frontera con la Biología*

ON THE SOURCE OF SPECIFIC OXIDATION PROPERTIES OF PEROXIDASES

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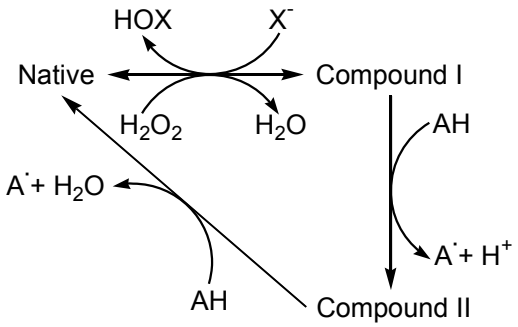
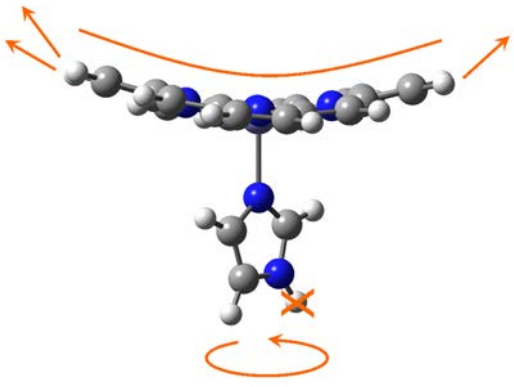
Keywords: *peroxidases, redox potential, electronic density calculations*

Peroxidases form a family of enzymes that typically catalyze oxidation reactions using hydrogen peroxide as substrate, but they can also promote halogenation reactions.



While some plant peroxidases mediate iodination, mammalian peroxidases (peroxidase-cyclooxygenase superfamily) present higher redox potentials and may be able to also catalyze bromination, or even chlorination in the case of myeloperoxidase. This enzyme plays a relevant role in the human immune system and is closely associated to several chronic, degenerative, and fatal diseases. The study of the origin of this particularly high oxidation potential could lead to the ability to modulate the potential or to inhibit the activity of this important enzyme.



Peroxidases share the same active site with a similar environment, their specific redox profiles may arise from subtle changes in their structures. Contrary to plant peroxidases, animal peroxidases present a curved heme that is covalently linked to peptide; besides, the rotation angle of proximal imidazole is different, and a recent paper has proposed that this group is unprotonated, at least in myelo-peroxidase. We analyze these variations by means of electronic density calculations, employing a minimal molecular model common to all enzymes (Fe-centered porphine and proximal imidazole) at the PCM//UB3LYP/6-31G* computational level.

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DNA-BINDING PROPERTIES OF A FAMILY OF RUTHENIUM (II) METALLOPEPTIDES CONTAINING *DPPZ* LIGANDS

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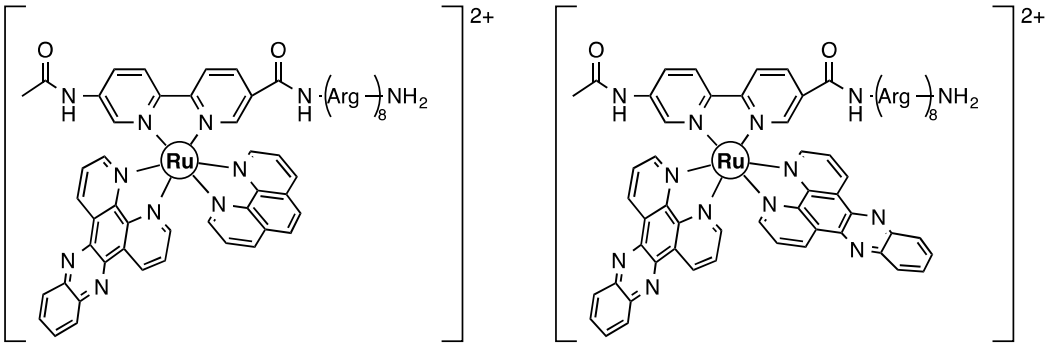
Keywords: *ruthenium, metallopeptides, DNA-binding agents*

The past few years have witnessed an increased interest on the application of coordination compounds as DNA-targeted probes, reactive agents and therapeutics. An example is the well-known monomeric "light-switch" $[Ru(phen)_2dppz]^{2+}$ (*phen* = 1,10-phenanthroline; *dppz* = dipyrido[3,2-a:2,3-c]phenazine), which intercalates into DNA thanks to its *dppz* moiety. The intercalation of the dppz results in a 1000-fold enhancement of the luminescence emission.[1] Cell-penetrating peptides (CPPs) are cationic peptides—typically with high content of arginine residues in their sequence—that display excellent cell translocation properties.[2] Herein we report the synthesis of two CPP-tagged ruthenium(II) metallopeptides containing one or two dppz ligands in the Ru(II) coordination sphere through a modified solid-phase peptide synthesis approach developed in our group.[3] We have studied the binding properties of these new systems with G-quadruplex and duplex DNA using a variety of techniques including CD, UV-Vis and fluorescence spectroscopies, melting experiments and AFM microscopy.



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S10: *Química en la Frontera con la Biología*

A CHIRAL DEHYDROALANINE AS *S*-MICHAEL ACCEPTOR IN THE SYNTESIS OF SULFA-T_N ANTIGEN

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Keywords: *Michael addition · stereoselectivity · glycosylamino acid · Tn antigen*

The most common types of glycosylation involve a covalent linkage between a sugar and an amino acid sidechain (*N*- or *O*-linked), whereas *S*-linked glycopeptides are very rare. However, from the discovery of three bacterial glycopeptides[1] containing carbohydrate moieties covalently linked to the sulfur atom of cysteine residue, the development of *S*-glycosylation methods has re-emerged as an important topic in carbohydrate chemistry. In this field, we reported the synthesis of new chiral dehydroamino acid derivatives, which presented high yields and stereoselectivities in sulfa-Michael additions with cysteine derivatives[2] and protected thiocarbohydrates.[3] As an extension of this work, we report here a new chiral bicyclic acrylate derivative (**1**). This new compound was reacted with tri-*O*-acetyl-2-acetamido-2-deoxy-1-thio-α-D-galactose, affording the corresponding sulfa-Michael adduct (**2**) as the only diastereoisomer. This adduct (**2**) was easily hydrolyzed to obtain the corresponding *S*-glycosylamino acid, which can be regarded as a mimic of Tn antigen (sulfa-Tn antigen). Thus, an alternative route to this important compound has been developed. Moreover, we also obtained the corresponding diastereomer of sulfa-Tn antigen by performing the Michael reaction with the enantiomer of compound **1** (Figure **1**).

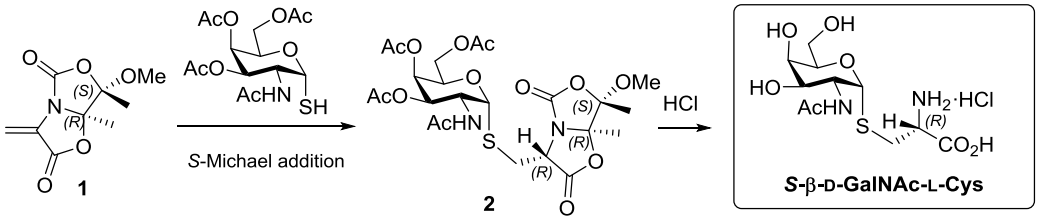

Figure 1. Synthetic route to sulfa-Tn antigen from chiral dehydroalanine **1**.

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S10: *Química en la Frontera con la Biología*

A LIBRARY OF NEW RESVERATROL DERIVATIVES: IMPROVED NEUROPROTECTION AND ANTI-INFLAMMATORY ACTIVITIES

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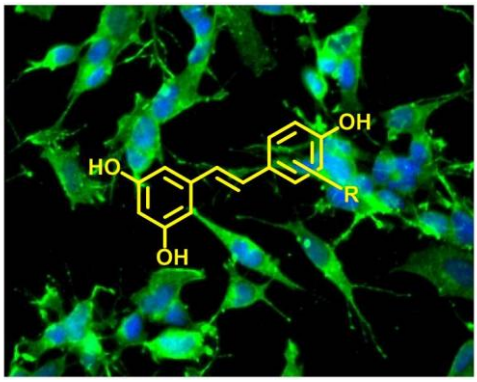
Keywords: *polyphenol, resveratrol, neuroprotection, inflammation*

Neurodegenerative diseases are becoming the plague of the XXI century. Alzheimer's disease (AD), Pakinson's disease (PD) and Huntington's disease (HD) are the more prevalent ones. Among the different strategies being investigated for potential treatments, oxidative stress and inflammation are known to be key factors to most of these diseases.[1] Several phenolic antioxidants have been reported for their potential neuroprotective properties.[2] Resveratrol (RES) has been one of the most promising candidates which has shown to reduce plaque pathology in a transgenic model of AD,[3] to decrease neuroinflammation *in vivo*[4] and has advanced to Phase II clinical trials for AD treatment.

Here we present the synthesis of a library of alkylated and silylated RES derivatives. Seven of these compounds showed considerably better viability than RES in a H_2O_2 induced oxidative stress model in a SH-SY5Y neuroblastoma cell line. These derivatives also diminished several inflammatory parameters (TNF-α, NO and IL-6) to a higher extent than RES in a LPS induced inflammation model in RAW macrophages.



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S10: *Química en la Frontera con la Biología*

CHEMICAL INTERROGATION OF DRUG/RNA COMPLEXES: FROM CHEMICAL REACTIVITY TO DRUG DESIGN [1]

Ester Jiménez-Moreno[1], Irene Gómez-Pinto[2], Francisco Corzana[3], Andrés G. Santana[1], Julia Revuelta[1], Agatha Bastida[1], Jesus Jiménez-Barbero[4], Carlos González[2], Juan Luis Asensio[1]

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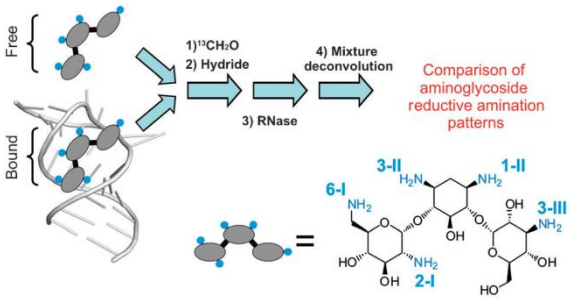
Keywords: *aminoglycoside/RNA complexes; combinatorial chemistry; drug design*

Medicinal chemistry efforts oriented to the optimization of bioactive compounds have traditionally relied on the synthesis and evaluation of a large number of structurally related chemical derivatives. This procedure, in most cases expensive and time consuming, represents a major challenge for complex molecular architectures containing numerous equivalent reactive positions. Unfortunately, such feature is common among natural ligands as carbohydrates or polyamine RNA binders as aminoglycosides (a family of antibiotic RNA-binding oligosaccharides).



Inspired by the principles of dynamic combinatorial chemistry [2], we hypothesized that the chemical reactivity exhibited by the aminoglycosides in complexes with their target RNAs could provide valuable guidelines for accessing to a reduced number of binders. As a proof of principle, we have analyzed kanamycin-B methylation (a chemical modification of general importance for the molecular recognition of nucleic acids) in the context of three different RNA fragments, whose structures in complex with aminoglycosides have already been described. The proposed methodology is based on the detailed comparison of the drug *N*-methylation patterns obtained from reductive amination reactions performed with the free and RNA-bound drug and our results shown that this methodology can provide relevant information, from the molecular recognition and medicinal chemistry perspective. Finally, this novel protocol may be exploited and adapted to a variety of examples within the molecular recognition and drug design fields.

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S10: *Química en la Frontera con la Biología*

DISCOVERY OF NEW ANTIMICROBIAL AGENTS BY FRAGMENT-BASED HIGH-THROUGHPUT DOCKING

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Keywords: *Fragment screening, drug-like inhibitors, stomach cancer, dehydroquinase*

Fragment screening is a wide accepted technique to identify relatively simple hit-compounds that possess a high binding affinity per heavy atom, and thus are ideal compounds for optimization into clinical candidates with good drug-like properties [1]. This technique has emerged as an important alternative to high-throughput screening because it has the advantage that incorporates the structural information of the target to preselect the molecules that are most likely to show binding and inhibitory activity. The available experimental knowledge of known inhibitors is incorporated by using pharmacophore constraints to preselect compounds for docking and therefore reducing computation times. Computer-aided fragment-based approaches are being increasingly proven as a successful means of generating novel hits for drug discovery programs [2]. Here we present the application of the anchor-based library tailoring screening approach to the discovery of new inhibitors of *Helicobacter pylori* type II dehydroquinase, an essential enzyme in this pathogen. This bacterium is a major cause of gastric and duodenal ulcers and it has been classified as class I carcinogen. Life-long infection with *H. pylori* increases the risk for mucosa-associated lymphoid tissue lymphoma and gastric adenocarcinoma. Recent studies have revealed that eradication rates are at the lowest levels seen in the past decade and are likely to fall further as antimicrobial resistance becomes more prevalent worldwide. Therefore, the development of new agents that are able to overcome existing resistance mechanisms or that have novel mechanisms of action is much needed. In this communication, the synthesis of the identified potential inhibitors, the biological activity of these compounds and the optimization of the most active compound obtained in this study will be provided.

Financial support from the Spanish Ministry of Economy and Competitiveness (SAF2013-42899-R), Xunta de Galicia (GRC2013-041) and the European Regional Development Fund (ERDF) is gratefully acknowledged. AR thanks the Spanish Ministry of Economy and Competitiveness for his FPI fellowship.

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CARRYING THERAPEUTIC ANTIBODIES ACROSS THE BLOOD-BRAIN BARRIER

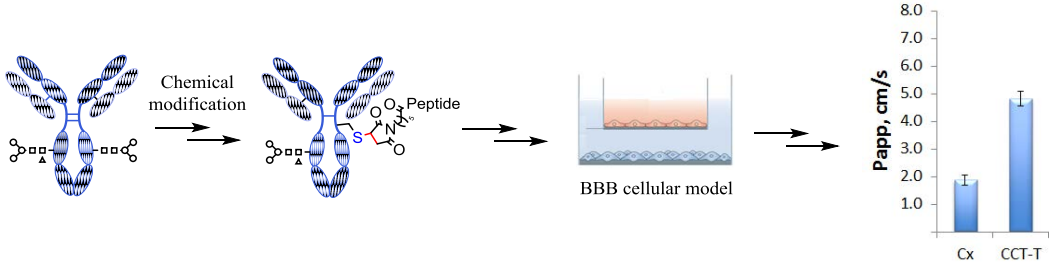
Macarena Sánchez-Navarro,[1] Benjamí Oller-Salvia,[1] Meritxell Teixidó,[1] Ernest Giralt [1,2]

Keywords: *Blood-brain barrier, peptide, antibody, BBB-shuttles.*

The ageing of the population in the first world increases the incidence of pathologies related to the central nervous system (CNS) ranging from inflammatory or cerebrovascular to neurodegenerative diseases.[1] The Blood Brain Barrier (BBB) protects the brain parenchyma from the intrusion of undesired molecules. However, it is also the first obstacle to overcome in the targeted delivery of pharmacological agents. Large molecules, such as monoclonal antibodies (mAb), intended for therapeutic treatment of the CNS are never commercialized because of their inability to enter the brain.[2]

We present an approach to increase antibody passage through the BBB that envisages the use of peptides that actively cross the BBB (BBBshuttles).[3] We hypothesize that mAb-BBBshuttles conjugates will penetrate the brain, enhancing the effect of the therapeutic mAb. Two main parameters, namely the location and the number of the peptide shuttles, need to be controlled in order to achieve maximal permeability with the lowest perturbation of binding affinity and pharmacokinetics.

Several conjugation strategies are explored to link selected BBBshuttles to two therapeutic antibodies (Avastin® and Erbitux®). Each of these methods allows the attachment of a controlled number of peptides to different parts of the mAb. The effect on the binding affinity of all these conjugates and the transport of these conjugates in a human BBB cell based model is also studied.



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R. J. Brea

S10: *Química en la Frontera con la Biología*

COMPUESTOS POTENCIALMENTE ANTINEOPLÁSICOS DE RUTENIO(ii) HETEROLÉPTICOS CON LIGANDOS BIPIRIDINA Y DIFOSFINA

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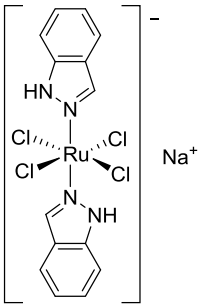
Palabras Clave: *Antineoplásicos. Compuestos de Coordinación. Difosfinas.*

Desde los años 90, paralelo a la investigación orientada a la preparación de potenciales metalofármacos basados en el Pt, se comenzó la exploración de compuestos de Ru como antineoplásicos (Figura 1) [1], algunos de los cuales se encuentran ya en la segunda fase de ensayos clínicos, mostrando una elevada capacidad de inhibir el desenvolvimiento y crecimiento de la metástasis. En el caso particular de los derivados de Ru(II) que contienen en su estructura ligandos piridilo, se ha encontrado que presentan unas propiedades fotoluminiscentes características, lo cual, unido la capacidad de estos ligandos para intercalarse en el ADN, ha suscitado un interés creciente en el estudio de los mismos para evaluar su actividad biológica [2].



(N)KP1339

FIGURA 1

Sobre la base de estos antecedentes, se han preparado nuevos compuestos derivados de Ru(II) con un perfil estructural del tipo Ru-polipiridilo (Figura 2), en los que se han incorporado, en disposición relativa cis, ligandos bidentados con átomos donadores de fósforo con una cadena de unión entre los dos átomos de fósforo de distinta naturaleza. Los compuestos han sido estudiados por espectroscopia de RMN y de IR, espectroscopia de masas, difracción de RX de monocristal y análisis in vitro frente a diversas líneas celulares de cáncer.

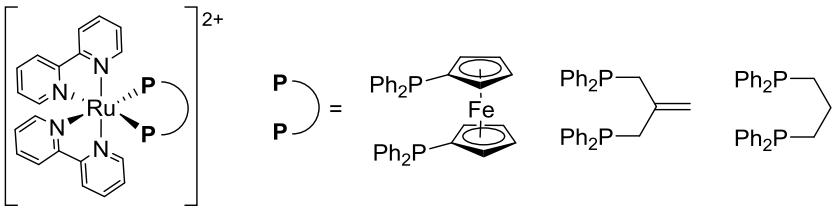


FIGURA 2

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DISEÑO DE NUEVOS METALOCICLOS DE RUTENIO DERIVADOS DE LIGANDOS BIDENTADOS CON ÁTOMOS DONADORES DEL GRUPO 15 CON POTENCIAL APLICACIÓN BIOLÓGICA

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Palabras Clave: *Compuestos de Coordinación. Rutenio(II). Metalofármacos.*

En los últimos años, la síntesis de compuestos de Ru(II) que presentan en su estructura ligandos derivados de bipiridina ha experimentado un creciente interés, puesto que los estudios in vitro de la actividad biológica de estos derivados constatan el descubrimento de aplicaciones quimioterapéuticas para estos derivados de rutenio, que actúan de modo diferente al cis-platino y la mayor parte de los compuestos contra el cáncer conocidos en general. Así, algunos de estos complejos con ligandos quelatantes, tanto mono- como dinucleares (FIGURA 1) mostraron una actividad biológica marcada [1].

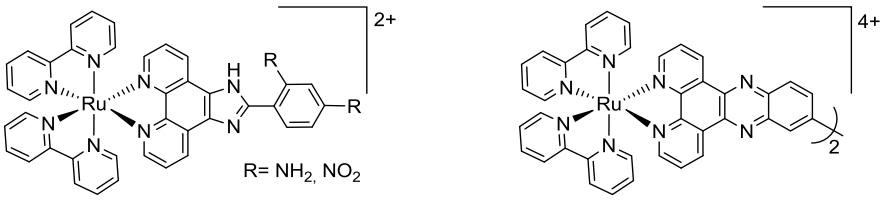

FIGURA 1

La presencia de ligandos que formen anillos quelato en el entorno del metal confiere una gran estabilidad al compuesto, que de este modo puede interaccionar de forma más controlada con dianas biológicas específicas, en función de factores como la propia naturaleza, electrónica y estérica, de los ligandos polidentados, la carga del complejo y/o su carácter lipofílico. Teniendo en cuenta estas consideraciones, se han preparado complejos de Ru(II) derivados de bipiridina con distintos ligandos quelatantes que presentan átomos dadores del grupo 15, de fórmula general $[Ru(bipy)_2(A\text{-}B)]X_2$ (A, B = N, P, As), homo- y heterobidentados, con el objetivo de realizar un estudio comparativo de sus propiedades estructurales y de su actividad citotóxica.

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S10: *Química en la Frontera con la Biología*

NOVEL COMPOUNDS OF HYBRID STRUCTURE PYRIDAZINONE/COUMARIN AS INHIBITORS OF PLATELET AGGREGATION

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Keywords: *pyridazinone, coumarin, platelet aggregation, Perkin's reaction*

Pyridazinone and coumarin are useful scaffolds for drug discovery and both have contributed significantly to the development of agents acting on the cardiovascular system, such as platelet aggregation inhibitors. Thus, on the one hand, substitution at C6 of pyridazinone core with aryl or heteroaryl groups, as well as with several functionalized alkenyl or alkyl groups, has provided compounds with relevant platelet antiaggregatory activity, which in some cases increases with the N2 substitution [1]. On the other hand, antiaggregatory properties were also described for some 3-arylcoumarins [2].

For this reason, we are studying the potential as inhibitors of platelet aggregation of hybrid compounds pyridazinone/coumarin. The proposed compounds (Figure 1) can also be regarded as new 6-heteroarylpyridazin-3(2H)one analogues substituted or not in N2, in which the heteroaryl groups are differently substituted coumarins.

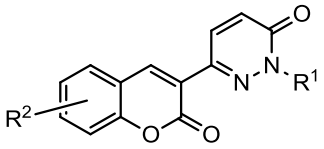

Figure 1. General structure of the hybrid compounds pyridazinone/coumarin

The novel compounds were synthesized following a multi-step strategy based on Perkin's reaction of the appropiate ethyl oxopyridazinylacetate with the corresponding *o*-hydroxybenzaldehyde. The ethyl oxopyridazinylacetates, key intermediate for this approach, were obtained in four steps starting from maleic anhydride, which via a sequence of Diels-Alder, Wittig and retro Diels-Alder reactions gave the ethyl (5-oxofuran-2-ylidene)acetate, which by reaction with several hydrazines provides the desired ethyl acetates.

The synthesized compounds are being studied *in vitro* against different platelet aggregation inducers. The preliminary results of this study reveal the target compounds as promising antiplatelet agents and suggest that, when N2 lacks of substituent, the antiaggregatory effect can be efficiently modulated by an appropriate substitution on the coumarin core.

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DEVELOPMENT OF NEW ANTIBIOTICS TARGETING SHIKIMATE KINASE: STRUCTURE-BASED DESIGN OF INHIBITORS

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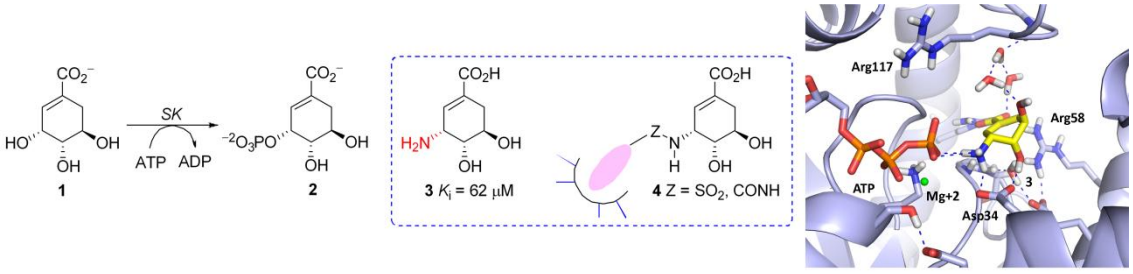
Keywords: *inhibitors, structure-based design, shikimate kinase*

In the past few years a great deal of effort has been focused on the discovery of new inhibitors of the enzymes involved in the biosynthesis of aromatic amino acids in which chorismic acid is synthesized. These enzymes are recognized as attractive targets for the development of new antibacterial agents because they are essential in important pathogenic bacteria, such as *Mycobacterium tuberculosis* and *Helicobacter pylori*, but do not have any counterpart in human cells [1]. Our group is very much interested in the development of efficient inhibitors of one of those enzymes, in particular, Shikimate kinase (SK) that catalyzes the stereospecific phosphorylation of the C3 hydroxyl group of shikimic acid (**1**) by transferring the γ-phosphate group of ATP to the hydroxyl group to provide shikimate 3-phosphate (**2**) and ADP.

We have shown recently that (3*R*)-3-aminoshikimic acids (**3**), which is a mimetic of the natural substrate, is a reversible competitive inhibitor of the *M. tuberculosis* enzyme with a K_i value of 62 μM [2]. Docking and MD simulation studies showed that this compound would interact with the γ-phosphate of ATP through a strong electrostatic interaction and it would cause a dramatic reduction in the flexibility of the LID and the shikimic acid binding domains. Based on these initial results and on the reaction mechanism, we are studying the possible improvement of the inhibition potency of **3** by replacement of the C3 amino group by diverse sulfonamide and carbamate moieties. Our recent results on this project will be presented [3].



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CROMÓFOROS CATIÓNICOS INTERCALANTES DE ADN: DESARROLLO DE UNA FAMILIA BASADA EN EL NÚCLEO PIRIDOIMIDAZOPIRIDAZINIO

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Palabras Clave: *Fluorescencia, Intercalación de ADN, Cromóforos catiónicos heteroaromáticos*

La visualización de componentes celulares o procesos en el interior de la célula es una tarea esencial en la química bioanalítica. En este sentido, la detección fluorimétrica de biomacromoléculas se ha mostrado como una técnica clave en este área de investigación. Como consecuencia, se han desarrollado muchas sondas fluorescentes que permiten la detección selectiva de células o componentes celulares. [1] En especial, la utilización de sondas fluorescentes cuya intensidad de fluorescencia aumente tras la asociación con una biomacromolecula (*light-up probes*) es de gran utilidad como marcadores en genómica y proteómica. [2]

Los cationes heteroaromáticos con un nitrógeno cabeza de puente son una familia representativa de intercalantes de ADN con buenas propiedades de fluorescencia. [3] Sin embargo, la mayoría de ellos presentan disminución en su intensidad de fluorescencia tras la formación de un complejo con ADN. [4,5]

En este trabajo, se presenta la síntesis y los estudios de fluorescencia, interacción con ADN y tinción celular de una quimioteca de compuestos catiónicos heteroaromáticos con nitrógeno cabeza de puente basados en un núcleo piridoimidazopiridazinio. Estos derivados presentan sustituyentes con libertad conformacional, por lo que poseen una baja intensidad de fluorescencia intrínseca.

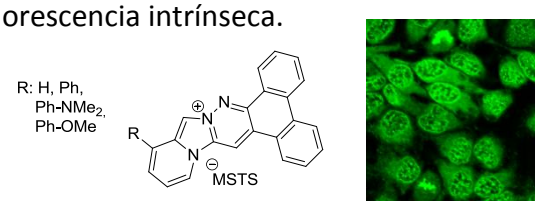

Fig. 1. Familia de Cromóforos estudiados. Tinción celular de células HeLa

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STRUCTURAL AND DYNAMICAL PROFILE OF NEUROMEDIN C AT DIFFERENT TFE/WATER RATIOS AND UNDER ITS MICELLE BOUND STATE

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Keywords: *NMR, folding, micelle interaction, peptide dynamics*

Neuromedin C (NMC) is an endogenous 10-residue peptide that regulates various physiological processes in the central nervous system and the gastrointestinal tract through its interaction with the bombesin receptor subtype-2 (BB_2R) [1]. Hence, BB_2R antagonists have pharmacological potential to treat disorders that appear as a result of NMC dysfunction or misregulation [2,3]. However, the efficient design of such antagonists requires a detailed understanding of the structural features of NMC, which hitherto are unknown.

Hence, we have used NMR spectroscopy to determine the conformational ensembles of NMC in aqueous solution, at five different TFE/water percentages to decode its folding pathway upon lipid/receptor interaction, and under its SDS micelle bound state that likely resembles the receptor-triggered conformation. We have observed that NMC displays a disordered but well-defined backbone architecture, which undergoes a progressive coil-to-α-helix transition in the presence of increasing TFE concentrations, first at the C-terminus and then at the N-terminus. NMC also adopts a C-terminal α-helical conformation when it binds to SDS micelles. The formation of this complex is directed by thermodynamically favored hydrophobic interactions that occurs concomitant with the unfavorable deprotonation of His^8 and its further insertion into the micelle.

Moreover, we have observed that NMC in the presence of 60% TFE displays a structure similar to that adopted when it is embedded into the SDS micelles. Therefore this constitutes an unique example to discriminate the folding and the binding effects on the residue level dynamics. NMR relaxation data have demonstrated that the acquisition of the micelle bound α-helical conformation constrains the NMC flexibility more than the confinement itself.

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S10: *Química en la Frontera con la Biología*

INHIBICIÓN DEL PROCESO DE FIBRILACIÓN DE LA LISOZIMA POR COMPUESTOS DERIVADOS DE LA 3-HIDROXI PIRIDINA

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Palabras Clave: *Fibrilación de proteínas, Lisozima (HEWL), Inhibición.*

La amiloidosis engloba a un grupo de enfermedades degenerativas que se caracterizan por la deposición de agregados fibrilares insolubles de naturaleza proteica. A este grupo pertenecen las enfermedades de Parkinson, Alzheimer y Huntington [1]. Actualmente, los esfuerzos para combatir las enfermedades amiloideas se centran en el diseño de compuestos que inhiban el proceso de fibrilación. Estudios recientes indican que compuestos estructuralmente parecidos a los polifenoles, como los hidroxiindoles pueden actuar como inhibidores de estos procesos [2]. En este trabajo, se ha analizado el proceso de fibrilación de la lisozima de clara de huevo (HEWL), una proteína globular que forma agregados fibrilares en medio ácido. Se ha estudiado el proceso de fibrilación en ausencia y en presencia de vitámeros B6 (ya que se ha comprobado que estos compuestos previenen la disfunción sináptica en la enfermedad de Alzheimer [3]) y de cinco compuestos derivados de la 3-hidroxipiridina (5-cloro-3-hidroxipiridina, 2-cloro-3-hidroxipiridina, 3-hidroxi-2-metil-piridina, 3-hidroxi-6-metil-piridina y 3-hidroxi-2,6-dimetil-piridina). De los compuestos estudiados, la 3-hidroxi-2-metil-piridina, la 3-hidroxi-6-metil-piridina y la 3-hidroxi-2,6-dimetil-piridina inhiben completamente la fibrilación de la lisozima en medio ácido. Mediante la utilización de diversas técnicas biofísicas (espectroscopia de fluorescencia, calorimetría diferencial de barrido, dicroísmo circular y RMN) hemos comprobado que los derivados metilados de la 3-hidroxipiridina inhiben la transición conformacional alfa-beta en la lisozima que precede a la formación de fibras, aumentando la estabilidad de la proteína. Por otra parte, los estudios de ^{15}N-HSQC han permitido identificar las zonas de interacción entre estos compuestos y la proteína monomérica.

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SYNTHESIS AND STRUCTURAL STUDIES ON TRIFLUOROMETHYLPYRAZOLES DERIVED FROM HEMICURCUMINOIDS

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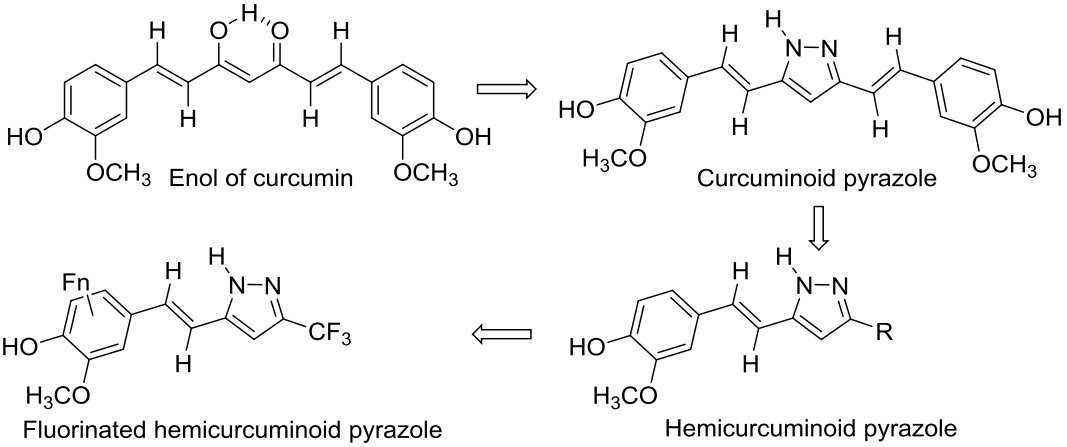
Keywords: *β-diketones, pyrazoles, fluorination effect, NMR, B3LYP/6-311++G(d,p)*

The interest in curcumin has prompted many studies on the tautomerism of this β-diketone as well as on the synthesis and structural research of hemicurcuminoids, compounds resulting from the substitution of one styryl branch of curcumin (2-methoxy-4-vinylphenol) by a simpler group [1,2]. The discovery that the six-membered pseudoaromatic ring of the enol of curcumin [(1*E*,4*Z*,6*E*)-5-hydroxy-1,7-bis(4-hydroxy-3-methoxyphenyl)hepta-1,4,6-triene-3-one] can be replaced by the five-membered ring of the heteroaromatic 1*H*-pyrazole maintaining but also modifying the biological properties of curcumin, has generated several works from our group [3,4].

The combination of both approaches results in hemicurcuminoid pyrazoles and we present here our studies on the case where R = CF_3. There is ample information in the literature that a trifluoromethyl group is an interesting pharmacophore even in pyrazole derivatives including the well-known anti-inflammatory Celecoxib.



(Work financed by the Ministerio de Economía y Competitividad of Spain, CTQ2014-56833-R)

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INTRINSIC PROTON AFFINITY OF NEUROTRANSMITTERS

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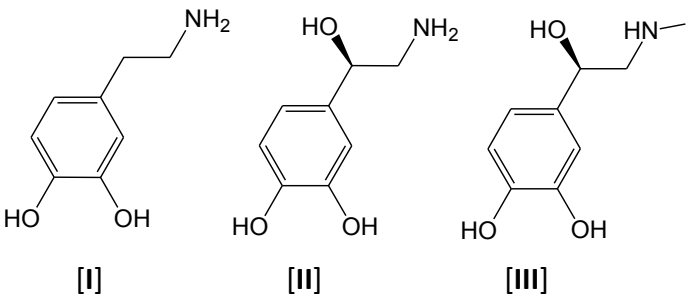
Key words: *Neurotransmitters, proton affinity, ESI-mass spectrometry, EKM, DFT*

In this work we present experimental and theoretical study of protonation of catecholamine neurotransmitters (**NT**s). The gas phase protonation enthalpy (or proton affinity, *PA*) of dopamine [**I**], noradrenaline [**II**] and adrenaline [**III**] have been experimentally determined by the Extended Kinetic Method (EKM) [1,2] using ESI-triple-quadrupole mass spectrometry (ESI-TQ/MS). The experimental results were supported and rationalized by Density Functional Theory (DFT) calculations.

NT, a crucial specie that activates adrenergic receptors, takes basically the monocationic form in aqueous solution [3], being the amino groups the preferred sites of protonation [4]. With respect to its binding to a receptor, the protonated form is the most important as, according to a general view, this protonation state is preserved in the activated receptor-ligand complex.

Relevant and consistent set of structural and thermochemical data have been determined for the **NT**s and their resulting protonated forms (**NT**H^+). From the experimental results the following *PA* values for [**I**], [**II**] and [**III**] have been derived (in kcal/mol): 225.5 ± 2.0, 225.1 ± 2.0 and 232.3 ± 2.0, respectively.



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MOLECULAR RECOGNITION STUDIES OF TOLL-LIKE RECEPTOR 4 MODULATORS

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Keywords: *Toll-like receptor 4, lipopolysaccharides, Bradyrhizobium, docking, molecular dynamics.*

Toll-Like receptors (TLRs) designates a group of proteins which play a major role in the immune system by recognizing membrane microbial components[1]. TLR4 is specialized in the recognition of Gram-native bacteria lipopolysaccharides (LPS). For instance, it has been proposed [2] that a LPS from *Bradyrhizobiu*m, named BTAi (Figure A), interacts with TLR4-MD2 complex (Figure B), its binding mode remains unknown.
In an attempt to explain the bioactivity of recently discovered TLR4 modulators at an atomic level, we have undertaken molecular recognition studies using computational tools in order to propose different binding modes and possible interactions accounting for the putative TLR4 antagonist mechanism. In the case of *Bradyrhizobiu*m LPS, the unusual combination of hopanoid and LPS molecule makes the problem unprecedented thus increasing its complexity.

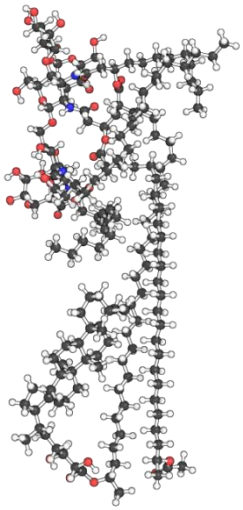

Figure A

Figure B

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S10: *Química en la frontera con la Biología*

MODELIZACIÓN DEL *CLO* FOTOSINTÉTICO CON COMPLEJOS Mn_4 DE DIFERENTE TOPOLOGÍA: CARACTERIZACIÓN Y ACTIVIDAD FOTOLÍTICA

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Palabras Clave: *fotólisis, manganeso, fotosíntesis, bioinorgánica,*

El complejo liberador de oxígeno (CLO), un cluster $CaMn_4O_5$, es el enzima nativo que cataliza de forma eficiente la descomposición fotolítica del agua en la fotosíntesis. El modelado del CLO con complejos inorgánicos artificiales es una poderosa herramienta para testar diferentes aspectos e hipótesis científicas sobre la naturaleza y el comportamiento del cluster CLO [1], pero esta investigación también representa una vía para desarrollar un catalizador estable y activo para la oxidación de la molécula de agua.

En esta comunicación se presenta la obtención de dos complejos tetrámeros Mn_4, modelos sintéticos del CLO, con diferente topología: estructura tipo adamantano y estructura tipo dímero de dímeros (Figura 1). En el presente trabajo también se discute la caracterización y propiedades foto-físicas de estos compuestos así como sus estructuras cristalinas. La capacidad de estos complejos para oxidar la molécula de agua se ha estudiado a través de experimentos de fotólisis, en los cuales la evolución del dioxígeno liberado se ha medido en medio acuoso en presencia de un aceptor de hidrógeno (*p*-benzoquinona) cuya reducción se ha seguido por espectroscopía UV-Vis [2].

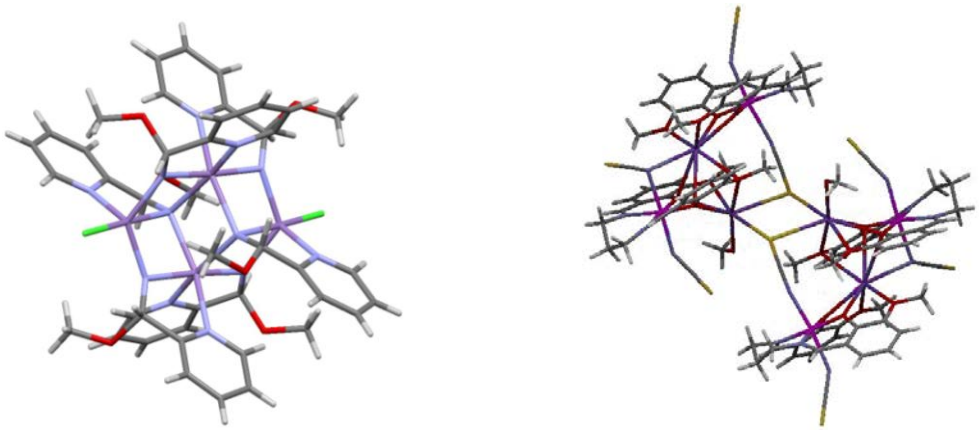

Figura 1. Estructura cristalina de los modelos Mn_4 del CLO con estructura tipo adamantano (izquierda) y estructura tipo dímero de dímeros (derecha)

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S10: *Química en la frontera con la Biología*

ANTIMICROBIAL AGENTS BASED ON PEPTIDE NANOTUBES

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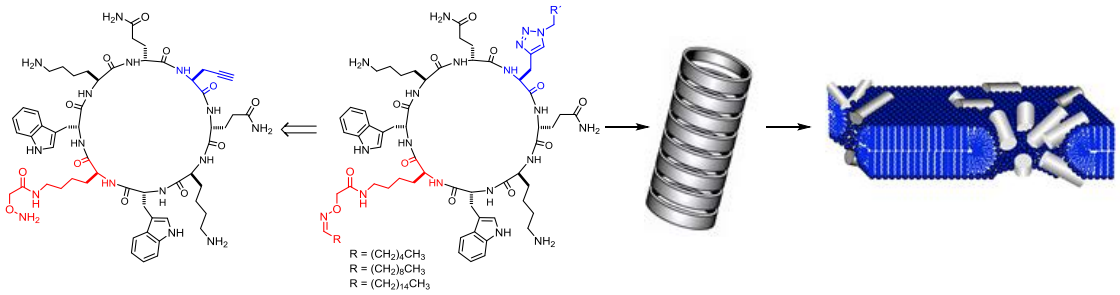
Keywords: *Peptide Nanotubes, Self-assembly, Antimicrobial.*

Despite numerous antimicrobial agents discovered in the twentieth century that seemed to have solved the infectious diseases problems, the emergence of microorganisms resistance to most of them has revealed the necessity of developing a new generation of antimicrobial agents.[1] In nature there are numerous antimicrobial agents that target bacterial membrane such as the antimicrobial peptides (AMP).[2] Therefore, we are designing peptide nanotubes composed by α-cyclic peptides that adopt a flat conformation in which the nanotube formation is induced by the lipid membranes through a self-assembly process.[3] The resulting nanotubes would have cationic and amphipathic character in which the hydrophobic area would interact with lipid membranes, while the hydrophilic residues would contact with the membrane surface components.[4] In this way, the nanotubes would permeate the membrane, destroying the electrochemical gradient required for cell survival. In this communication, we will present new α-cyclic peptide designs based on a modular synthetic strategy, in which different hydrophobic and hydrophilic moieties will be incorporated at the end of the cyclic peptide synthesis using orthogonal reactions like click chemistry or oxime formation.



This work was supported by the Spanish Ministry of Economy and Competitivity (MEC) and the ERDF [CTQ2010-15725, and CTQ2013-43264-R], by the Xunta de Galicia (GPC2013-039 and EM2014/011).

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S10: *Química en la Frontera con la Biología*

HOW DIFFERENT SUGAR PRESENTATION IN G-QUADRUPLEX LIGANDS AFFECT BINDING AFFINITY AND SELECTIVITY TO G-QUADRUPLEX DNA

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Keywords: *DNA, G-quadruplex, ligands, carbohydrates, molecular recognition*

Several G-quadruplex (G4) ligands modified with carbohydrates have been reported previously. Some of them contain neutral carbohydrates attached to aromatic rings[1] and others contain charged aminoglycosides.[2] We have prepared a new family of G4 ligands based on simple aromatics modified with different sugar presentations. We will show how the sugar presentation affects binding affinity and selectivity to DNA G-quadruplex.

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SINTESIS Y EVALUACIÓN BIOLÓGICA DE *(E)*-METOXIESTIRILPIRIDINAS Y PIRIMIDINAS COMO POTENCIALES AGENTES ANTICÁNCER

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Palabras Clave: *resveratrol, angiogénesis, VEGF, telomerasa, hTERT, c-Myc*

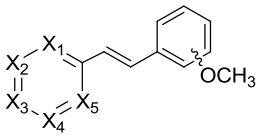
El resveratrol (*trans*-3,5,4'-trihidroxiestilbeno) es un producto natural con múltiples actividades, entre las que destacan su alto poder antioxidante y su alta eficiencia como agente quimiopreventivo, además de poseer diversas aplicaciones terapéuticas como inhibidor de la angiogénesis y de la telomerasa.[1]

La angiogénesis es el proceso de formación de nuevos capilares a partir de vasos sanguíneos preexistentes. En adultos este proceso se encuentra desactivado, activándose solo en casos necesarios como la cicatrización de heridas o el ciclo reproductivo femenino. Sin embargo, en enfermedades como el cáncer, el proceso angiogénico se encuentra activado, permitiendo el aporte de oxígeno y nutrientes al tumor, lo que facilita su rápido crecimiento y desarrollo.[2] La familia de proteínas VEGF desempeña un papel fundamental en la activación de la angiogénesis, siendo por tanto el VEGF una buena y específica diana terapéutica contra el proceso angiogénico tumoral.[3]

Los telómeros son estructuras nucleoproteicas no codificantes situadas en las extremidades de los cromosomas cuya longitud predice la capacidad replicativa de las células. La enzima telomerasa es la encargada del alargamiento telomérico.[4] En células somáticas esta enzima se encuentra desactiva, sin embargo, en gran diversidad de cánceres se activa impidiendo el acortamiento telomérico, dotando de *inmortalidad* a las células tumorales. El componente proteico de la telomerasa, denominado hTERT, está regulado por factores transcripcionales como c-Myc. Tanto hTERT como c-Myc se presentan como interesantes dianas biológicas en procesos tumorales donde está especialmente activada la telomerasa.[5]

En esta comunicación se presentará la síntesis de (*E*)-metoxiestirilpiridinas y pirimidinas relacionadas con el resveratrol y su acción citotóxica sobre las líneas celulares tumorales HT-29 y MCF-7, así como su capacidad inhibitoria de la secreción de la proteína VEGF y su capacidad inhibitoria de la expresión de los genes VEGF, hTERT y c-Myc.

X_2=X_3=X_4=X_5=CH; X_1=N;
X_1=X_3=X_4=X_5=CH; X_2=N;
X_1=X_2=X_4=X_5=CH; X_3=N;
X_2=X_3=X_4=CH; X_1=X_5=N;
X_1=X_3=X_5=CH; X_2=X_4=N;



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S10: *Química en la Frontera con la Biología*

TOWARDS EFFICIENT METAL CATALYZED REACTIONS IN AQUEOUS AND BIOCOMPATIBLE MEDIA

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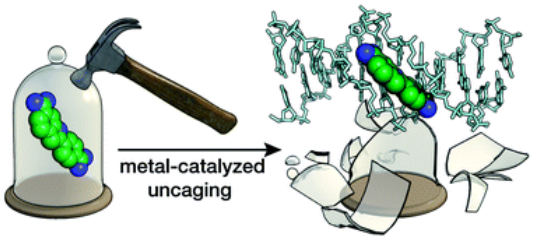
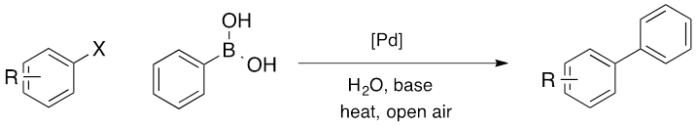
Keywords: *Palladium, bioorthogonal, uncaging, Suzuki-Miyaura.*

Examples of bioorthogonal catalysis in living systems promoted by artificial organometallic compounds are extremely scarce. However, recent ground breaking results suggest that ruthenium or palladium catalysts can catalyse designed reactions in living environments. [1],[2]



Scheme 1. Catalytic chemical uncaging of DNA binders [2]

We have now developed a serial of biocompatible palladium heterogeneous catalysts that can promote bioothogonal transformations, including a Suzuki-Miyaura coupling, in aqueous and biological medium. [3, 4]. Among the different catalysts, we have explored palladium mesoporous capsules that have been purposely constructed to avoid cellular toxicity.



Scheme 2. Model Cross-Couplings with [Pd] Catalyst

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S10: *Química en la frontera con la Biología*

STRUCTURE AND BIOPHYSICAL CHARACTERIZATION OF α MATING PHEROMONE FROM THE FUNGUS *Fusarium oxysporum*

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Keywords: *NMR, 3D structure, α-pheromone, F. oxysporum*

Sexual development in ascomycetous fungi is initiated by the perception of diffusible peptide pheromones via G protein-coupled plasma membrane receptors (GPCRs). Binding of pheromone to the cognate GPCR elicits a range of cellular responses including transcriptional reprogramming, cell cycle arrest, shmoo formation and chemotropic growth. High-resolution NMR studies of the *S. cerevisiae* α-pheromone tridecapeptide (WHWLQLKPGQPMY) in solution identified a transient type II beta-turn spanning residues 7-10, which are required for activation of the cognate receptor. Here we have characterized the α-pheromone of *Fusarium oxysporum*, a fungal pathogen of plants and humans. The chemically synthesized decapeptide WCTWRGQPCW was shown to elicit a chemotropic response in *F. oxysporum* germ tubes which is dependent on the cognate GPCR Ste2. Substitution of the conserved G6 and Q7 residues by alanines abolished the biological activity of the peptide. In order to understand the structural bases of its biological properties the wild type (wt) peptide and a scrambled sequence (WRWPCCWGQT) were analysed by biophysical methods including NMR spectroscopy. By HPLC, the two peptides behave as single molecular species, with no disulphide bridges. Far-UV CD was consistent with the presence of a β-turn in the wt pheromone. 1H and 13C NMR spectra were recorded and assigned in H2O and H2O/TFE (70/30 v/v) mixtures. 13C chemical shifts confirm the oxidised state of the Cys residues in both peptides. In agreement with the CD data, the α-pheromone adopts a β-turn in H2O involving the central 4WRGQ7 sequence. By contrast, NMR data of the scrambled peptide do not provide evidence for a regular secondary structure in H2O solution. In the presence of TFE, both peptides showed stabilised secondary structure. On the basis of the chemical shifts and assigned NOEs the 3D structures were calculated. The structure of the α-pheromone is a β-hairpin, containing the central 4WRGQ7 β-turn, stabilised by strong W4-W10 π/π interactions. In TFE, the scrambled sequence mainly adopts a β-turn conformation spanning the central 4PCCW7 residues. Collectively, these data indicate that the hairpin adopted by the wt pheromone could be relevant for its biological activity and for the establishment of interactions with the cognate receptor or other biological partners.

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NOVEL 3-HETEROARYLCOUMARINS BASED ON PYRIDAZINE SCAFFOLD AS SELECTIVE MAO-B INHIBITORS

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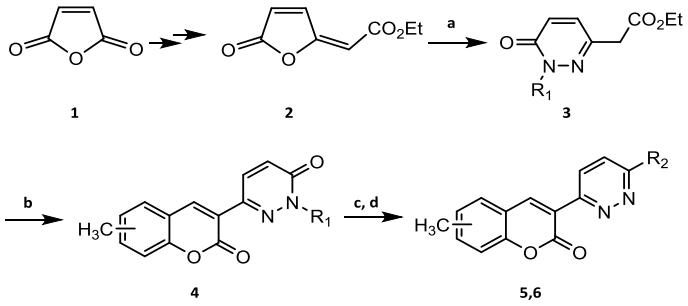
Keywords: *coumarin, pyridazine, monoamine oxidase B, Perkin's reaction*

The discovery of antiparkinsonian and neuroprotective effects derived from inhibition of monoamine oxidase B (MAO-B) has promoted the search of selective MAO-B inhibitors (MAOI-B). The research in this field has resulted in a significant number of compounds based on a great variety of cores, among them it is noteworthy the coumarin scaffold [1]. Differently substituted coumarins have been studied as potential selective MAOI-B. We have reported that aryl substitution at position 3 causes strong and selective MAO-B inhibition, this MAO-B selectivity remains when the phenyl group was replaced by some heteroaryl cores, like thiophene or indole [2].

In continuation of our research program on novel MAOI-B of coumarin structure, we describe herein new series of methyl coumarins substituted at C3 with a functionalized pyridazine ring. Thus, the novel 3-heteroaryl analogues (compounds **4**-**6**) combine in their structure two privileged scaffolds for drug design, coumarin and pyridazine, and were proposed with the aim to analyze the effect of bioisosteric substitution benzene/pyridazine on MAO-B affinity and selectivity.



Scheme 1: **a) R_1NHNH_2, Et_3N, EtOH; b) *o*-hydroxybenzaldehyde, piperidine, isopropanol; c) $POCl_3$; d) $NaOCH_3$, MeOH**

The compounds **4-6** were synthesized following the multi-step strategy shown in Scheme 1 and based on Perkin's reaction of pyridazinone intermediates **3** with the appropriate *o*-hydroxybenzaldehyde. The key intermediates **3** were obtained in four steps starting from maleic anhydride, which via a sequence of Diels-Alder, Wittig and retro Diels-Alder reactions gave the ethyl (5-oxofuran-2-ylidene)acetate **2**, suitable synthon for pyridazinones **3**. Finally, standard procedures were applied to replace the carbonyl of the pyridazinone ring by the desired functionality. The results of this study will be reported.

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S10: *Química en la Frontera con la Biología*

A VERSATILE SYNTHESIS OF β^2-AMINO ACIDS BY RING-OPENINIG REACTION OF SULFAMIDATES

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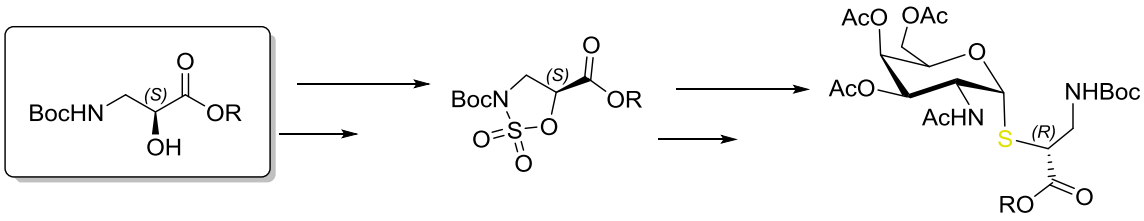
Keywords: *sulfamidate*, *β^2-amino acid, Tnantigen,*

Among diverse alterations, the incorporation of β-amino acids in peptides is a valuable method to modulate their conformational preferences.[1]The modification of β-amino acids by different functional groups is a synthetically remarkable target in chemical biology field and it requires versatile methodologies. Moreover, glyco-β-peptides are important not only for structural studies on the glycosylation's effect on the backbone structure, but also for analysis on how the artificial backbone of β-peptide affects the molecular recognition of the natural carbohydrates attached.[2]In this field, *S*-glycopeptides,[3] mimics of *O*-glycopeptides with special properties, have recently emerged as new post-translational modifications.

Our research group has focused attention in the ring-opening reaction of quaternary sulfamidate to gain diverse *S*-glycopeptides.[4]However, in this work, the synthetic strategy involves the ring-opening reaction by nucleophilic attack of the new chiral five-membered cyclic sulfamidate derived from isoserine. We show the synthesis of this new chiral building block and we demonstrate its versatility to synthesize severalβ^2-amino acids. Moreover, we extend this methodology to gain a new Tn antigen analogue by ring-opening reaction with $(OAc)_4$GalNAc-α-SH as a nucleophile.



R = Me, Bn, ^{t}Bu

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S10: *Química en la Frontera con la Biología*

UNNATURAL MUC1 DERIVATIVES BASED ON ALLO-THREONINE AS A SUITABLE TOOL TO GET FURTHER INSIGHTS INTO THE MOLECULAR RECOGNITION OF MUC1 DERIVATIVES BY ANTIBODIES

I. A. Bermejo, N. Martínez-Sáez, V. J. Somovilla, J. L. Asensio, J. Jiménez-Barbero, G. J. L. Bernardes, R. Hurtado-Guerrero, J. H. Busto, A. Avenoza, F. Corzana, J. M. Peregrina

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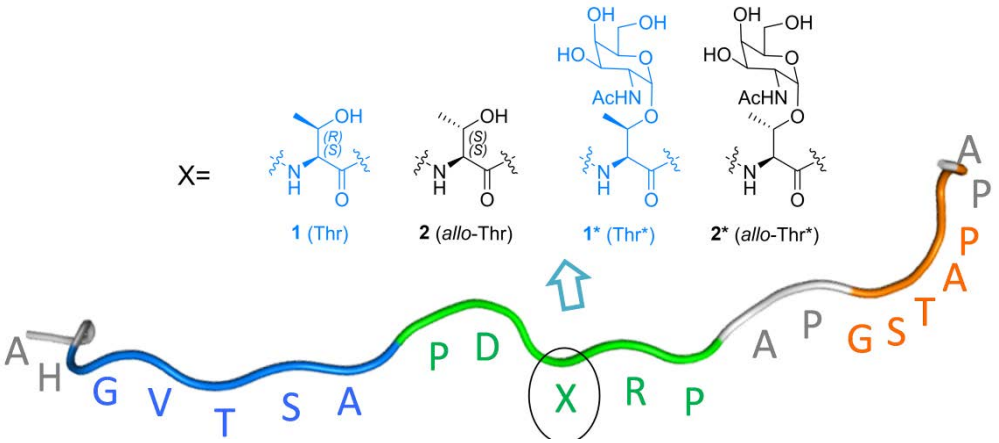
Keywords: *glycopeptide, antibodies, molecular recognition, Molecular Dynamics*

MUC1 mucin is an *O*-glycoprotein that is being widely studied as a potential cancer vaccine.[1] The development of novel MUC1 derivatives with high affinity binding to anti-MUC1 antibodies could be helpful in detecting tumors in early stages. In this regard, the unnatural MUC1-related peptide containing L-*allo*-threonine and the glycopeptide with GalNAc were synthesized and compared with the corresponding threonine derivatives. Their binding affinities were studied by SPR and ELISA tests, using SM3 and VU-3C6 as representative anti-MUC1 antibodies. The results showed marked differences between the glycosylated moieties, whilst the naked peptides remain similar.

To understand the different antigen-antibody interactions, we performed Molecular Dynamics simulations on the MUC1 derivatives in the free state and in complex with SM3 antibody, using the X-ray crystal structure of the epitope APDT(GalNAc)RP bound to SM3 antibody as starting geometries.[2] These calculations showed how the conformation of the glycosylated epitope relies on the configuration of the carbon-β.

This study provides valuable insights into mechanisms and specificities of mucins in recognition events.



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S10: *Química en la Frontera con la Biología*

ASSESSING MOLECULAR RECOGNITION BY NMR FROM THE LIGAND'S PERSPECTIVE. LESSONS FROM THE INTERACTION OF ^{77}Se AND ^{19}F-CONTAINING GLYCOMIMETICS TO GALECTINS

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Keywords: *Molecular recognition, ligand-based NMR, ^{77}Se, ^{19}F.*

NMR spectroscopy and molecular modelling methods are key techniques to unravel ligand-protein interactions. In the molecular recognition field, NMR methods are extremely useful for monitoring interactions, and may provide robust answers, depending on the employed technique. [1] Ligand-based NMR methods are usually employed for screening purposes. Additional benefits of this protocol rely on the possibility of using NMR-active nuclei other than ^{1}H, especially those who are absent in protein receptors. [2] This nucleus can be employed as direct probe for detecting the interaction or as "spy" nucleus to deduce the binding of other molecules in completion-type experiments.

We herein show that a combined approach using multinuclear NMR methods provides a full description of the binding process for detecting the binding of similar molecules to different receptors. In particular, human galectin-1 and human galectin-3 have been employed as protein models. We compare the results obtained by the recently proposed ^{77}Se-based method [3] to the most commonly employed ^{19}F- and ^{1}H-based protocols, using lactose and galactose analogues alternatively or simultaneously labelled with the two ^{77}Se and ^{19}F nuclear probes.

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S10: *Química en la Frontera con la Biología*

COMPLEJOS DE Cu(II) CON 7-AMINO-1,2,4-TRIAZOLO[1,5-a]PIRIMIDINA CON POTENCIAL ACTIVIDAD ANTIPARASITARIA

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Palabras Clave: *complejos metálicos, triazolopirimidina, análisis térmico, difracción de rayos X, leishmaniasis*

Siguiendo nuestra línea de investigación dirigida hacia la síntesis y caracterización de complejos metálicos con potencial actividad antiparasitaria, se han aislado y caracterizado estructuralmente dos complejos de Cu(II) que contienen como ligando a la 7-amino-1,2,4-triazolo[1,5-a]pirimidina (7-atp) [1]. Estos complejos se han caracterizado utilizando técnicas espectroscópicas y análisis térmico (TG y DSC)

Ambos complejos se han aislado en fase monocristal, por lo que su estructura ha podido ser resuelta mediante difracción de rayos X. Dichos complejos son isoestructurales y presentan coordinación octaédrica. En los dos casos los ligandos 7-atp se unen al Cu(II) en forma monodentada a través del átomo de nitrógeno en posición 3, ocupando posiciones apicales, mientras que las moléculas de agua y los aniones cloruro o nitrato ocupan posiciones axiales.

Los dos complejos presentan un comportamiento térmico muy parecido, deshidratándose en su totalidad a temperaturas inferiores a 150°C. Los compuestos anhidros son estables en un intervalo de temperatura de unos 100°C y se descomponen térmicamente para dar CuO como producto final de la pirolisis. En la actualidad se está ensayando la actividad antiparasitaria de estos complejos frente a *leishmania brazilensis.*

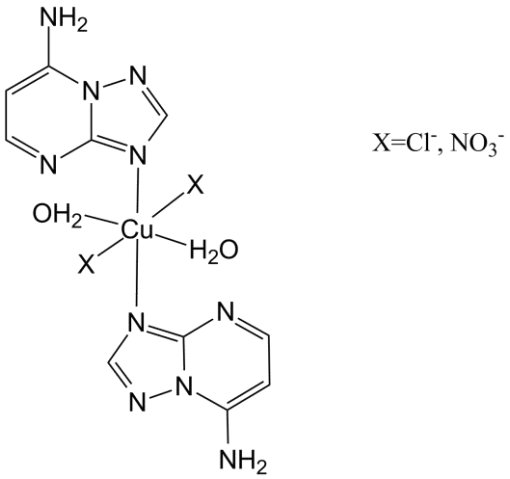

Figura 1. Estructura de $Cu[(7\text{-atp})_2(X)_2(H_2O)_2]$

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S10: *Química en la Frontera con la Biología*

TOWARDS THE DEVELOPMENT OF LIGHT-SWITCHABLE MINOR GROOVE DNA BINDERS

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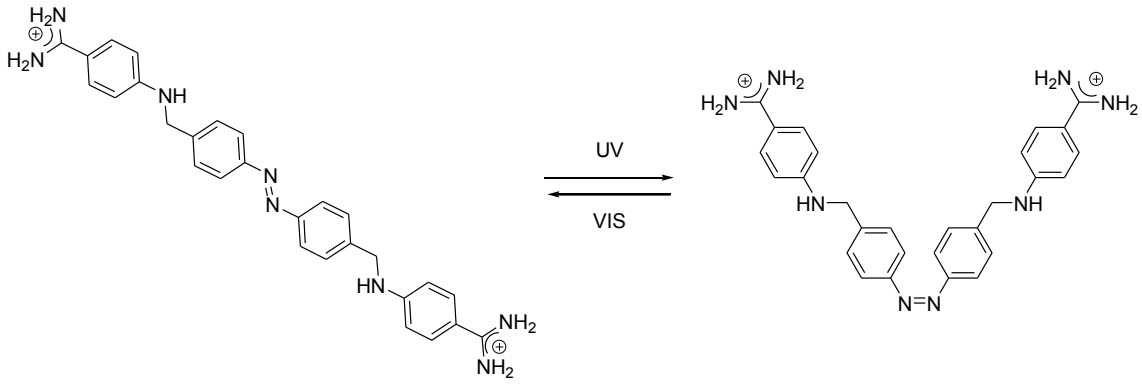
Keywords: *DNA, azobenzenes, light, switch*

Discovering methods to control selectively and efficiently the interaction between different molecules with nucleic acids is one of the biggest challenges at the boundary between chemistry and biology. [1]

This project aims are the design and synthesis of switchable systems capable of interacting specifically with the minor groove of AT-rich sequences of DNA [2] in a reversible and externally controllable manner. Toward this end we intend to incorporate in the systems molecular elements that undergo a significant structural change when irradiated with light of different wavelengths. [3] We describe herein the synthesis and preliminary photophysical and DNA binding properties of a series of azobenzene-bisbenzamidine derivatives that have been purposely designed to exhibit different DNA binding properties depending on whether they are in a *cis* or in a *trans* form.



trans (E) **cis (Z)**

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S10: *Química en la Frontera con la Biología*

SYNTHESIS OF α/β-PEPTIDES BY NUCLEOPHILIC OPENING OF CYCLIC SULFAMIDATES INCORPORATED INTO α-PEPTIDES

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Keywords: *α/β-peptide · nucleophiclic substitution · sulfamidate · CH/π interactions*

It is well-known that the incorporation of β-amino acids into peptides provides a high degree of stability.[1] In this context, the combination of proteinogenic α-amino acid residues and β-amino acids opens the door to a larger pool of accessible structures with potential applications. A lot of studies exists in this field, but there are few analysed cases on $\beta^{2,2}$-amino acids incorporated in peptide chains.[2] Our research group has developed an efficient strategy to the synthesis of $\beta^{2,2}$-amino acids through the ring opening of cyclic sulfamidates.[3]

In this work, we present the synthesis of several mixed peptides by the incorporation of $\beta^{2,2}$-amino acids in different peptides through ring opening of cyclic sulfamidates with thiocarbohydrates and pyridine derivatives as nucleophiles. Conformational studies of selected compounds were obtained by combination of NMR experiments and molecular dynamics calculations. Remarkably, some CH/π interactions contribute to stabilize the backbone conformation (Figure 1).

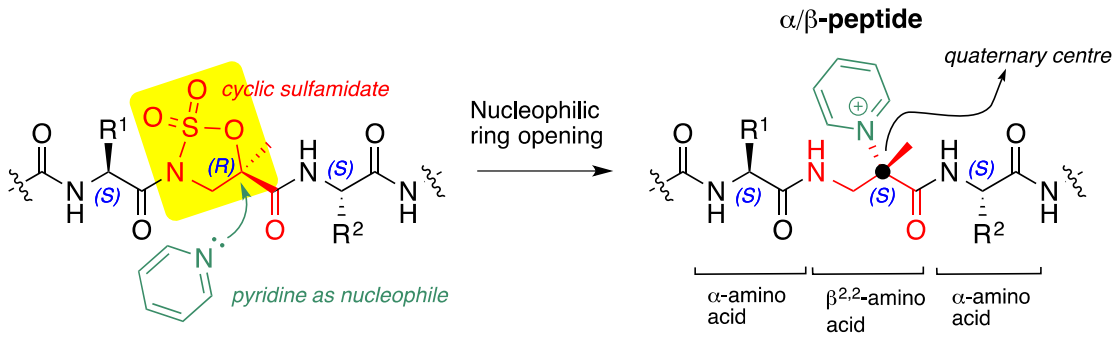

Figure 1. Synthesis of α/β-peptides.

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S10: *Química en la Frontera con la Biología*

BICYCLIC C-GLYCOSIDES AS SELECTIVE □-GLUCOSIDASE INHIBITORS: A NEW PHARMACOLOGICAL CHAPERONE FOR GAUCHER DISEASE

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Keywords: *glycosidase inhibitor, Gaucher disease, C-glycoside, chaperone*

The synthesis of new specific glycosidase inhibitors is attracting a deal of interest for the development of new drugs, since glycosidases have an important role in several biological processes.[1] In this work and following a methodology recently reported by our research group,[2] we carried out the synthesis of a battery of conformationally locked *C*-glycosides having a bicyclic D-galactose—3,3-disubstituted pyrrolidone skeleton (APP, Figure **1**).

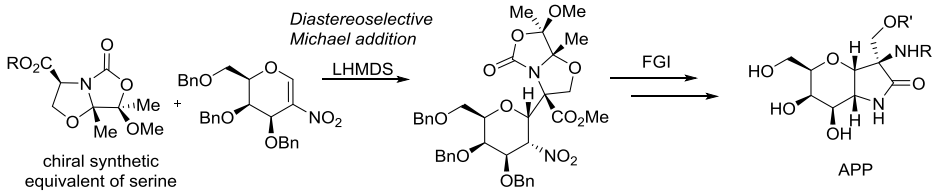

Figure 1. Synthetic scheme of conformationally locked *C*-glycosides based on the bicyclic APP scaffold.

This disubstitution pattern offers the opportunity to exploit a general approach that allowed us the incorporation of non-glycone moieties (e. g. alkyl substituents) with the aim of elaborating selective glycosidase inhibitors. Some of them showed a highly specific inhibition of bovine β-glucosidase and human β-glucocerebrosidase (GCase), two enzymes known to recognize *gluco* and *galacto* configurational patterns, at μM level. In addition and significantly, these APP derivatives were further assayed as pharmacological chaperones in Gaucher disease fibroblasts. Activity enhancements in N370S and F213I GCase mutants analogous to those achieved with the reference compound ambroxol were attained for one of the candidates.

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S10: *Química en la Frontera con la Biología*

OPEN-TO-CLOSED TRANSITION IN APO GLUCOSE/GALACTOSE-BINDING PROTEIN ELUCIDATED BY PARAMAGNETIC NMR AND MD SIMULATION

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Keywords: *GGBP, paramagnetic NMR, MD*

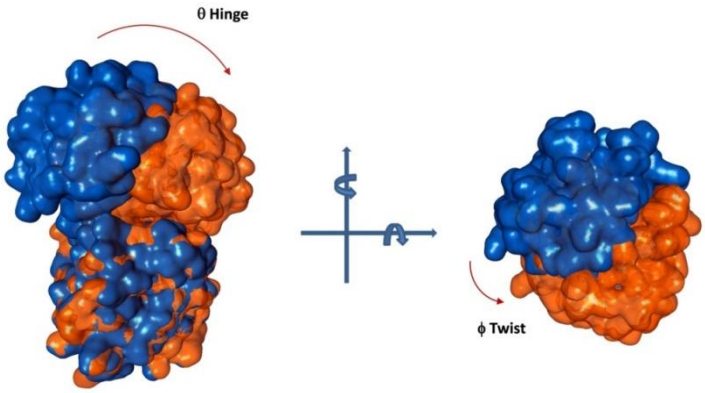
Large-scale domain rearrangements in proteins are intricately correlated to function but are still rarely complemented by a detailed analysis of the dynamic process.

Crystal structures of the apo and holo states for glucose galactose binding protein provide structural information for domain rearrangement upon ligand binding; however the key structural determinants for such concerted dynamics have been so far elusive.

Even more the nature and amplitude for the collective dynamics have to be elucidated in order to prove the existence of significant open-closed equilibrium in solution for apo form and the nature of binding mechanisms.

In the present work, we want to add a new piece of knowledge about the periplasmic binding protein family. Here we use anisotropic NMR parameters induced by self-alignment of paramagnetic metal ions to achieve the complete description of the ensemble of conformations adopted by the glucose galactose binding protein in solution while the rate of interconversion between the determined structures was elucidated by long molecular dynamic simulation on two states of GGBP, the closed-liganded (CL) and open-unliganded (OU).

We show that although pseudo contact shift and residual dipolar coupling enhanced by paramagnetic tag are consistent with a rapidly exchange between open and closed like species, the presence of the ligand is the necessary driving force for unbalance the equilibrium to the real closed form.



S10: *Química en la Frontera con la Biología*

MODULATING WEAK INTERACTIONS FOR MOLECULAR RECOGNITION: A DYNAMIC COMBINATORIAL CHEMISTRY ANALYSIS FOR ASSESSING THE CONTRIBUTION OFELECTROSTATICS TO THE STABILITY OF CH/? BONDS IN WATER [1]

Laura Montalvillo-Jiménez[1], Ester Jiménez-Moreno[1], Ana M. Gómez[1], Agatha Bastida[1], Francisco Corzana[2], Gonzalo Jiménez-Oses[2], Jesús Jiménez-Barbero[3], and Juan Luis Asensio[1]

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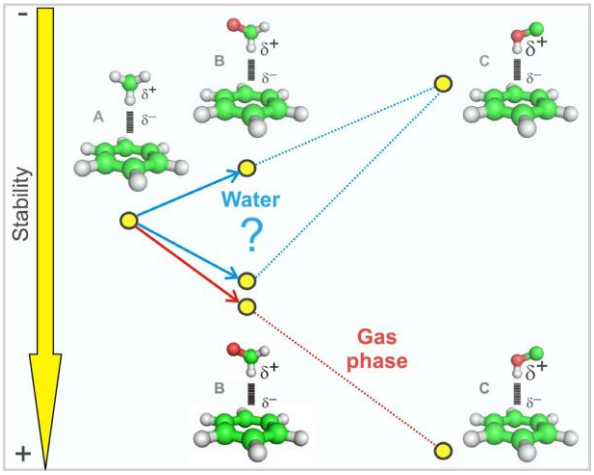
Keywords: *CH–π interactions; drug design; dynamic combinatorial chemistry; molecular recognition*

Nowadays it has become clear that CH/π interactions play a key role in a variety of molecular recognition processes including conformation stabilization, crystal packing, formation of gas phase clusters, or chiral discrimination. Nevertheless, there are still aspects of these interactions that remain poorly understood.



Thus, electrostatic and charge-transfer contributions to CH/π complexes can be modulated by the attachment of electron-withdrawing substituents to the carbon atom leading to a stabilization of the complex in gas phase. Intriguingly, the outcome of this simple chemical modification in water is more difficult to predict. In fact, exposed R-OH/π contacts are usually highly destabilized in water due to the competence provided by the stronger and ubiquitous ROH/H_2O conventional hydrogen bonds. Following a similar reasoning, the polarization of a particular CH could also enhance its own polar interactions with the solvent, thus leading to a minor stabilization, a null effect, or even a significant destabilization of the CH/π bonds. However, to the best of our knowledge, no unambiguous experimental evidences have been presented so far to support the stabilizing role of CH polarization in water. These questions have evident implications in the molecular recognition and drug design fields.

Our work provides an unambiguous and quantitative answer to this question employing a simple strategy based on dynamic combinatorial chemistry that is of general relevance for different fields of chemistry and biology.

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S10: *Química en la Frontera con la Biología*

MOLECULAR RECOGNITION OF A α-*S*-GalNAc-GLYCOPEPTIDE BY AN ANTI-MUC1 MUCIN ANTIBODY IN SOLID STATE

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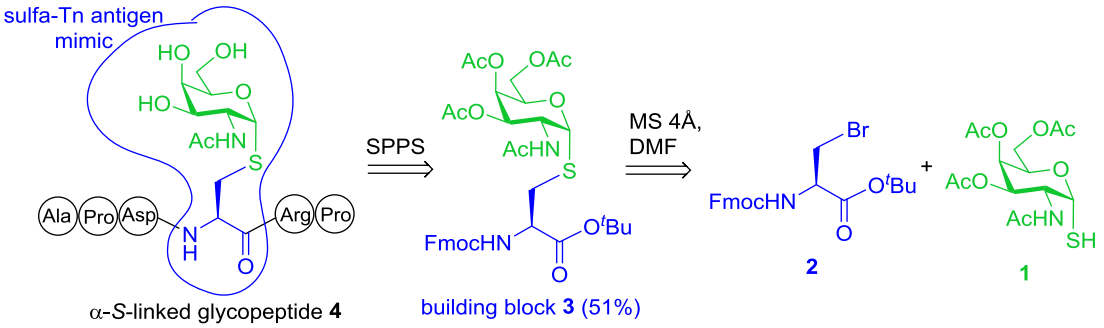
Keywords: *Tn antigen, S-glycopeptide, antibody, molecular recognition, X-ray structure*

In naturally occurring glycopeptides, the carbohydrate moiety and the peptide backbone are most commonly joined by an *O*-glycosidic linkage. However, these natural products present, in general, a low chemical stability. Because of this, recent research has focused on the development of synthetic methods to obtain S-inked glycopeptides. These methods have been applied, in general, to the synthesis of □-*S*-glycosyl amino acids and □-*S*-glycopeptides. However, these synthetic methods fail to access to □-*S*-GalNAc-glycopeptides since the strong basic conditions are not compatible with Fmoc-protected building blocks. Only three methodologies have been developed.[1-3] Because of this, in this report, we have used a new mild methodology based on the anomeric thiol group *S*-alkylation (GalNAc-α-SH, **1**) with a Fmoc-protected □-bromoalanine (**2**) that simply requires activated molecular sieves (4 Å) as a base to selectively promote *S*-alkylation. Once obtained compound **3**, as a further step, the synthesis of the α-*S*-glycopeptide Ala-Pro-Asp-Cys(α-*S*-GalNAc)-Arg-Pro (**4**) was achieved by using the SPPS protocol, starting from this building block **3**. This peptidic sequence was selected because Ala-Pro-Asp-Thr(α-*O*-GalNAc)-Arg-Pro corresponds to the most immunogenic epitope of the glycoprotein named MUC1 mucin. In this case, the Tn antigen (α-*O*-GalNAc-Thr) has been replaced by the mimic sulfa-Tn antigen (α-*S*-GalNAc-Cys). Additionally, to show that this *S*-glycopeptide **4** behaves as a mimic of natural one, we achieved a X-ray structure of the complex of glycopeptide **4** with the SM3 antibody, which is an anti MUC1 monoclonal antibody that recognises the natural epitope with high affinity. As a result, the backbone conformation of **4** matched the conformation of natural peptide.



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S10: *Química en la frontera con la Biología*

PYRIDAZIN-3(2H)ONE DERIVATIVES AS SELECTIVE INHIBITORS OF MAO-B

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Keywords: *pyridazinone, dithiocarbamate, MAO-B inhibitors, one-pot reaction*

Monoamine oxidase B inhibitors (MAOI-B) are currently used for symptomatic treatment of Parkinson's disease. In addition, these drugs may have potential for the treatment of Alzheimer´s disease and other neurodegenerative disorders [1], and therefore have attracted much attention of medicinal chemists. Different oxygen and nitrogen containing heterocycles, such as coumarin or indole, are used as scaffold for discovering novel MAOI-B [1,2], including a great variety of poly-substituted cyclic hydrazines, like pyrazoline or pyridazine [3].

In continuation of our research program on synthesis and biological study of novel MAOI-B [2], we describe herein the first examples of pyridazinone-based selective MAOI-B (Figure 1). The novel pyridazin-3(2H)-one analogues are substituted at C4, C5 or C6 with several dithiocarbamate moieties, a recognized pharmacophoric group for neuroprotection [4], linked to the cyclic hydrazine through an alkyl chain of varying magnitude.

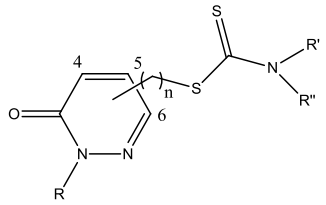

Figure 1. General structure of the novel MAO-BI

The target compounds were synthesized following a multi-step strategy, based on alkylfurans oxidation by singlet oxygen, in which the appropriate 4(5 or 6)-hydroxyalkylpyridazin-3(2H)-ones are the key intermediates [5]. The hydroxyalkyl pyridazinones were converted into the corresponding bromoalkyl derivatives, by reaction with CBr_4 and PPh_3, that finally by a one-pot reaction, with different secondary amines and CS_2 in the presence of K_3PO_4, provided the new pyridazinone analogues in good yield.

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S10: *Química en la Frontera con la Biología*

DETERMINACIÓN DE CONSTANTES DE AFINIDAD DE SISTEMAS AUTOASOCIATIVOS LIGADOS A UNIÓN DE DROGAS MEDIANTE ULTRACENTRIFUGACIÓN ANALÍTICA

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Palabras Clave: *tubulina, HPLC, AUC, ligando, cáncer.*

La determinación de las constantes de equlibrio de un sistema de unión de un ligando que induce autoasociación de su proteína diana es un problema complejo debido al acoplamiento de las constantes de autoasociación de la proteína y las de unión del ligando. Sin embargo estos sistemas son de gran importancia en la quimoterapia al ser una de sus dianas más relevantes la tubulina, un sistema autoasociante cuya regulación es esencial en el proceso de división celular, siendo por tanto los compuestos que afectan a este proceso potenciales antitumorales. En el caso de la tubulina, la autoasociación de los dímeros en presencia de un ligando está regulada tanto por la unión del compuesto que afecta a la constante de autoasociación, como por la constante de autoasociación isodésmica que afecta a la unión del ligando.

El sistema modelo empleado ha sido la interacción del ligando CSCCD062112, un ligando interfacial de la tubulina que aumenta su autoasociación. Con el fin de caracterizar de forma más precisa la unión, se ha desarrollado un método indirecto que permite diferenciar entre ambos procesos y cuantificar así la contribución de cada uno al proceso global de autoasociación. Para ello se determinan mediante ultracentrifugación analítica (AUC) los coeficientes de sedimentación promedio de la proteína y utilizando el programa Sweq desarrollado en nuestro laboratorio, se calculan constantes de asociación aparentes en función de la concentración de la proteína[1]. De forma paralela, se determina la concentración de ligando libre mediante cromatografía líquida de alta eficacia (HPLC). La representación de las constantes aparentes calculadas frente a la concentraciones de ligando libre obtenidas, permite la caracterización de las constantes reales de afinidad[2], y por tanto, permite distinguir la contribución que tienen ambos procesos.

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S10: *Química en la Frontera con la Biología*

DESIGN AND MULTICOMPONENT SYNTHESIS OF 2-PYRROLIN-5-ONES AS POTENTIAL HIV INTEGRASE INHIBITORS

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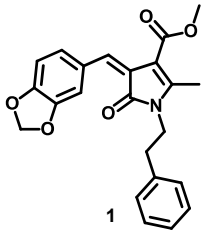
Palabras Clave: *Multicomponent reactions, focused microwave, integrase inhibition*

A 2-pyrrolin-5-one derivative (**1**) has been recently identified as a potential HIV integrase inhibitor by virtual screening methods. [1] However, the detailed study of compound **1** was thwarted by the lack of suitable synthetic methodology. In fact, in spite of its simplicity, the 2-pyrrolin-5-one framework has received very little attention and has never been previously synthesized using a one-pot protocol.



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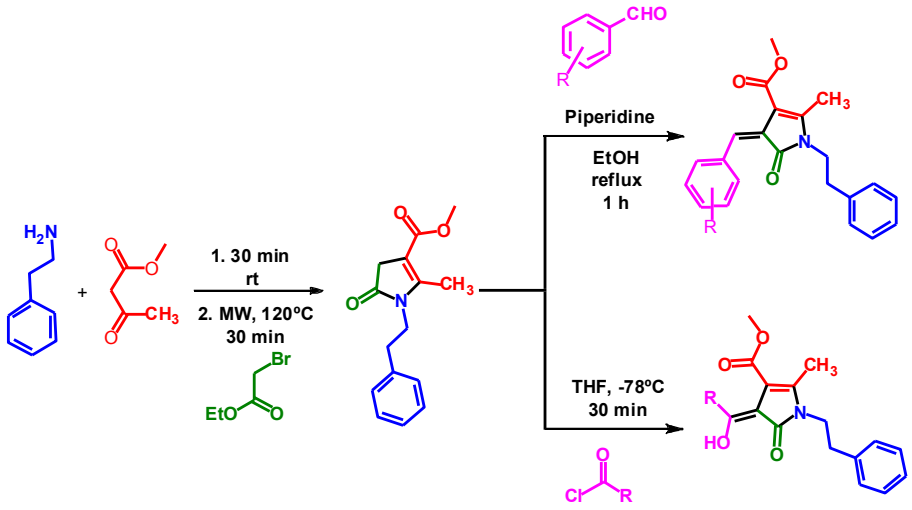
We now report a multicomponent access to this system based on a modification of the classical Hantzsh pyrrole synthesis [2]. Primary amines, β-dicarbonyl compounds and α-haloesters were reacted in the presence of indium trichloride as a Lewis acid catalyst and DIPEA as a Brönsted acid trap, under focused microwave irradiation. This reaction has been applied to the preparation of compound **1** and a library of 4-arylmethylen-2-pyrrolidin-5-ones and 4-hydroxymethylen-2-pyrrolidin-5-ones that show promising results in integrase docking studies



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S10: *Química en la frontera con la Biología*

MONITORING GLYCAN-PROTEIN INTERACTIONS BY NMR. A SIMPLE TAG THAT MIMICS NATURAL CH/pi INTERACTIONS

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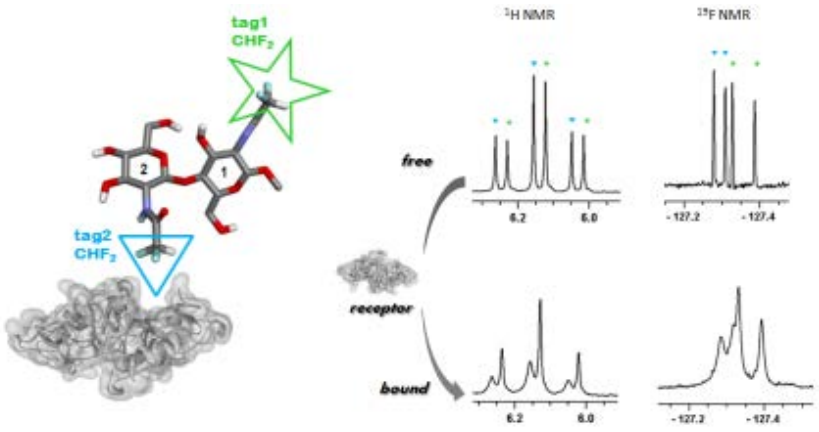
Keywords: *molecular recognition, glycan, NMR, lectins, chemical tag*

Detection of molecular recognition processes requires robust, specific and easily implementable sensing methods, especially for screening applications. Here we propose the difluoroacetamide moiety as a tag for detecting by NMR those glycan-protein interactions that involve N-acetylated sugars. In particular, we have employed it as a specific sensor to monitor interactions between GlcNAc-containing glycans and a model lectin (wheat germ agglutinin). This tag contains geminal ^{1}H and ^{19}F atoms that allow both ^{1}H- and ^{19}F-observed NMR methods for easy and robust detection of molecular recognition over a wide range of binding affinities.



S10: *Química en la frontera con la Biología*

CONFORMATIONAL FEATURES AND MOLECULAR RECOGNITION OF COMPLEX-TYPE BIANTENNARY N-GLYCANS BY PROTEIN RECEPTORS

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Keywords: *complex N-glycans, lectins, molecular recognition, NMR Spectroscopy*, MD Simulations

The recognition of saccharides presented as part of natural scaffolds (glycoprotein, sphingolipids) by protein receptors (lectins) can be considered as a key factor in some biological processes.[1] Then, understanding the sugar-lectin interactions at high resolution level becomes required.[2] In this context, natural complex-type N-glycans are sophisticated saccharidic structures attached to proteins that affect their physical and biological functions. Their structures may be altered in diseases, and thus, in certain cases they have been proposed as biomarkers. In particular, the presence of core α1,6-fucose in complex N-glycans has been related to human cancer.[3] Their detection can be carried out through their binding to specific lectins. *Pisum sativum* lectin (PSA) and *Lens culinaris* lectin (LCA) have been shown to specifically recognise core fucosylation [4].

However, large glycan structures can present more than one binding motif, and their sequence and shape can determine the interaction mode with lectins.[5] Herein, by combining MD simulations and NMR spectroscopy we have analyzed the conformation features of a core-fucosylated biantennary octasaccharide N-glycan and its interaction mode with PSA and LCA lectins (Figure 1).

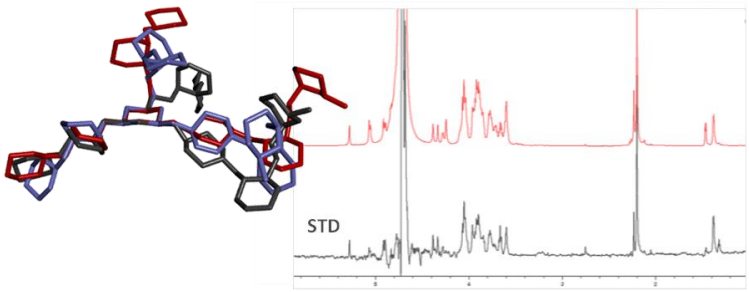

Figure 1

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S10: *Química en la frontera con la Biología*

STRUCTURE-BASED DESIGN OF POTENT SMALL-MOLECULE BINDERS TO THE ECF TRANSPORTER FOR THIAMINE IN PATHOGENIC BACTERIA

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Keywords: *ECF transporter, membrane proteins, molecular recognition, structure-based design, X-ray diffraction*

Energy-coupling factor (ECF) transporters are a class of ATP-binding cassette (ABC) transporters that mediate the uptake of vitamins in prokaryotes. They consist of an energizing module and a substrate-binding protein (S-component). Different S-components can interact with the same energizing module.[1,2] ThiT is the thiamine-specific S-component.[3] Based on the co-crystal structure of ThiT-thiamine (**1**), we have designed and synthesized thiamine analogues to identify which residues are key for substrate binding and to elucidate the mechanism of transport.

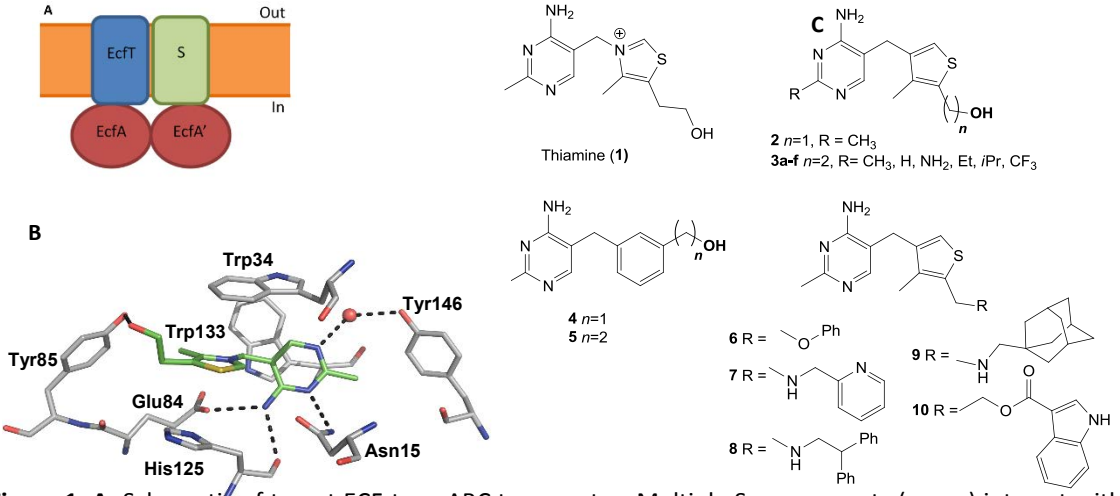

Figure 1. A: Schematic of target ECF-type ABC transporter. Multiple S-components (green) interact with the same energizing module (red and blue). **B:** Binding of thiamine in the substrate-binding pocket of ThiT. **C:** Structure of thiamine (**1**) and the designed and synthesized ligands (**2–10**).

Ligand-binding assays have been performed and they showed that the new compounds bind with high affinity to ThiT (K_d = 4–660 nM). Co-crystallization studies of compounds **2**, **3a**, **4** and **5** with ThiT confirmed the predicted binding mode and provide insight into the molecular recognition of thiamine by ThiT. The newly synthesized molecules may be potent inhibitors of the transporter and would validate it as a target for the development of antibiotics with a novel mode of action.[4]

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S10: *Química en la frontera con la Biología*

POLYGLUTAMATE - BASED COMBINATION THERAPY IN THE TREATMENT OF ADVANCED BREAST CANCER

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Palabras Clave: *drug delivery, combination therapy, polyglutamate, breast cancer*

Polymer Therapeutics comprise a variety of rationally designed nanoscale systems in which a water-soluble polymer carrier is provided with bioactive species. A branch of Polymer Therapeutics are Polymer-Drug conjugates, in which one or more drugs as well as different targeting moieties are chemically bound to the polymer backbone via a biodegradable spacer. Conjugation of two different drugs covalently to the same polymer vehicle through protease cleavable or pH sensitive linkers allow to control the release kinetics profile [1,2]. We combined chemotherapeutic agent with endocrine agent in the proper synergistic ratio by binding to the same polymer carrier, bringing significant advantage versus single treatments. We have previously reported the first polymer drug conjugate of this type: the non-biodegradable HPMA copolymer bearing the combination of the aromatase inhibitor Aminoglutethimide (AGM) with the anthracycline Doxorubicin (Dox)[3,4]. In vivo proof of concept of this conjugate, has already been achieved in an orthotopic 4T1 murine metastatic breast cancer model and its mechanism of action has been studied [5]. Then we moved to a biodegradable and multivalent poly(L-glutamic acid) (PGA) that allows to increase the conjugate molecular weight, enhancing the loading possibilities, reducing the immunogenicity and increasing the tumor targeting due to the EPR effect.

A novel PGA-AGM-Dox conjugate family has been developed including conjugates with different drug linkers and drug ratios, that have been deeply characterized by different physicochemical techniques in order to elucidate structural and conformational features in solution as descriptors for qualitative determination of structural-activity relationships in biological settings. This conjugates showed the capacity of self-assemble in aggregates around 100 nanometers in aqueous solution, showing differences in either their critical aggregation concentration and shape as evidenced by DLS, SANS and cryo-TEM respectively. *In vitro* evaluation allowed a screening for the best candidates achieving drug synergism in both MCF-7ca and 4T1 cell lines. The conjugates showing the greatest *in vitro* activity, were chosen for *in vivo* evaluation in an orthotopic 4T1 murine tumor model. In summary, we demonstrated that structural and conformational features in solution of polymer-drug conjugates may play an active role, leading to differences in the biological performance[6].

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S10: *Química en la Frontera con la Biología*

CARACTERIZACIÓN DE DÍMEROS DE TUBULINA ACTIVADOS POR FORMACIÓN DE ADUCTOS CON ZAMPANOLIDA

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Palabras Clave: *Tubulina, Microtúbulos, Zampanolida, Taxol*.

El cáncer es una grave enfermedad que constituye un enorme problema de salud pública en la actualidad. El tratamiento de esta enfermedad se basa la utilización de compuestos dirigidos a diversas dianas terapéuticas, entre las que se encuentran la α,β-tubulina y sus polímeros los microtúbulos. Los agentes estabilizantes de microtúbulos (MSAs) son compuestos que bloquean la despolimerización de GDP-Tubulina, bloqueando la segregación cromosómica en la anafase mitótica. El primer MSA descubierto fue el Paclitaxel, capaz de interaccionar reversiblemente con la tubulina en el sitio de taxol.

Zampanolide (ZMP) y su análogo natural Dactylodide (DAC) son dos novedosos MSAs que, en contraste con Paclitaxel y sus derivados interaccionan covalentemente en el sitio de taxol [1]. El aducto tubulina-ZMP induce cambios en la conformación de la hélice M, estructura secundaria de la tubulina y así favoreciendo las interacciones laterales con protofilamentos de tubulina para la formación de microtúbulos. [2]

En el presente trabajo, se ha caracterizado la relación estructura-actividad de ZMP empleando análogos modificados en la cadena lateral *N*- acyl- hemiaminal, esencial en la interacción con la hélice M [3] y en el anillo tetrahidropirano. Estas modificaciones alteran el acoplamiento del compuesto a su lugar de unión, previo al establecimiento de un enlace covalente y que por ello determina su potencia. También se investigaron las propiedades de los dímeros de tubulina activados establemente por la unión covalente de estos compuestos con el fin de determinar el efecto de la activación de la tubulina en la afinidad de unión de otros fármacos a diferentes sitios de unión.

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S10: *Química en la Frontera con la Biología*

(-)-SHIKIMIC ACID, A PROMISING SCAFFOLD FOR NEW DRUGS

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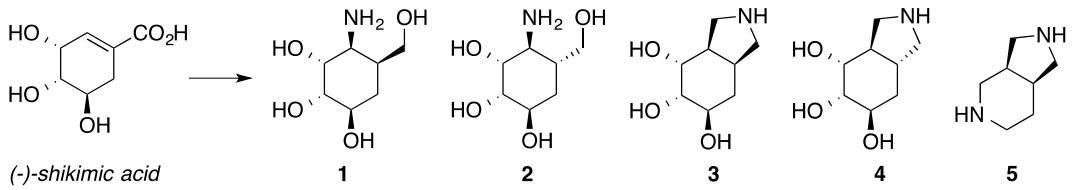
Key words: *amino alcohols, octahydro-1H-isoindoles, octahydro-1H-pyrrolo[3,4-c]pyridines, glycosidase inhibitors*

(-)-Shikimic acid is a natural compound that acts as a key intermediate in the biosynthesis of amino acids. Consequently, this derivative is widely present in many plants and has interesting biological properties. But besides the pharmacological relevance of shikimic acid itself, it is also an intermediate in the synthesis of many drugs, being the most relevant the antiviral agent oseltamivir (TamifluTM).[1]

(-)-Shikimic acid includes several relevant structural subunits: a cyclohexane ring, an α,β-unsaturated ester moiety and three hydroxy groups attached in a defined spatial orientation. Accordingly, it offers an atractive alternative to sugars for the preparation of highly functionalized molecules.[2]

Our research group is involved on a project aimed at the exploration of new synthetic possibilities offered by this promising and attractive starting material.[3] We will present our studies on the targets stated in Scheme 1.



Scheme 1

Interest of the novel compounds **1**, **2**, **3, 4** and **5** lies on their biological and pharmacological interest.

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S10: *Química en la Frontera con la Biología*

PHOTOSENSITIZED REACTIONS OF 5 *tert*-BUTYLURACIL

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Keywords: *DNA, photosensitization, (6-4) PPs*

Formation of **pyrimidine (Pyr) dimers** in DNA is associated with the carcinogenic effect of UV irradiation. Indeed, **cyclobutane pyrimidine dimers (CPDs) and pyrimidine (6-4) pyrimidone photoadducts (6-4 PPs)** represent 80% and 20% respectively, of the total UV-induced damage in the double helix [1]. As a consequence, a number of studies have been performed in order to understand the involved photochemistry. In spite of the extensive mechanistic knowledge gained in the last years, some aspects need to be clarified [2,3].

In the present study, a 5-*tert*-butyluracil derivative (Fig. 1A) has been synthesized to investigate the influence of a bulky substituent at C5 in the photochemistry and photophysics of thymine. Special attention has been devoted to its photosensitization by benzophenone, acetone and xanthone (Fig. 1B).

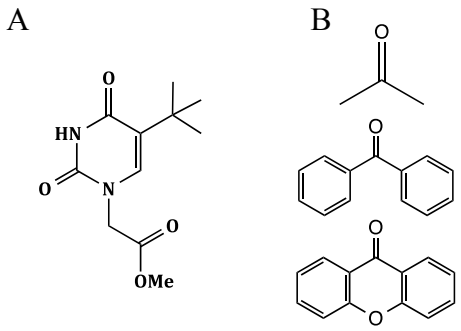

Fig. 1: Structures of A) 5-*tert*-butyluracil derivative and B) photosensitizers employed.

The results clearly show that CPDs are not formed in this case; conversely oxetane derivatives are obtained from a Paternò- Büchi photosensitized reaction, although it is slower than in that of thymine.

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S10: *Química en la Frontera con la Biología*

CARACTERIZACIÓN DE DOS SITIOS DE INTERACCIÓN LANGERINA-HEPARINA POR RMN, DOCKING Y ENTRECRUZAMIENTO

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Palabras Clave: *Interacciones Proteína-Carbohidrato, Glicosaminoglicanos, Langerina, Espectroscopía de RMN, STD-RMN*

Langerina (Lg) es una lectina de tipo C presente en las células de Langerhans que está involucrada en la captura de patógenos mediada por carbohidratos para neutralizarlos en unos orgánulos celulares denominados gránulos de Birbeck donde son procesados constituyendo una barrera natural frente a la infección por HIV. Además de la interacción de carbohidratos neutros conteniendo manosa y/o fucosa, se han descrito interacciones dependientes de Ca^{2+} con oligosacáridos derivados de manosa sulfatados. También, se ha demostrado la interacción en ausencia de calcio de Lg y fragmentos de heparina en disolución en un nuevo sitio de interacción. Basados en estos datos hemos realizado un estudio de la asociación de análogos de heparina de pequeña longitud. En primer lugar hemos realizado un estudio de entrecruzamiento con microparticulas de heparina para comprobar el sitio de asociación independiente de Ca^{2+}, como una hendidura formada al trimerizar la Langerina. Posteriormente hemos estudiado y validado el sitio de asociación dependiente de Ca^{2+} empleando una quimioteca de ocho compuestos con patrones de sulfatación variables y determinado por STD su modo de interacción. Mediante experimentos de NOESY transferido, cuantificación de la transferencia de saturación y docking combinado con simulaciones de dinámica molecular hemos determinado el modo de unión al sitio dependiente de Ca^{2+}. Este está caracterizado por la coordinación de los dos hidroxilos en disposición trans diequatorial (4 y 3) de la glucosamina del extremo no reductor al átomo de Ca^{2+}. y por la participación del carboxilato del residuo adyacente de iduronato. Por último, se ha estudiado mediante STD la interacción con Lg de un hexasacarido sintético prototipo de la región regular de heparina, con un sulfato adicional en la posición 4 del extremo no reductor de la cadena. Este grupo dirige la interacción al sitio independiente de Ca^{2+} al impedir la asociación en el sitio dependiente de Ca^{2+}.[1]

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S10: *Química en la Frontera con la Biología*

DESIGN OF NOVEL LIGANDS WITH HIGH AFFINITY AND SELECTIVITY FOR LECTINS

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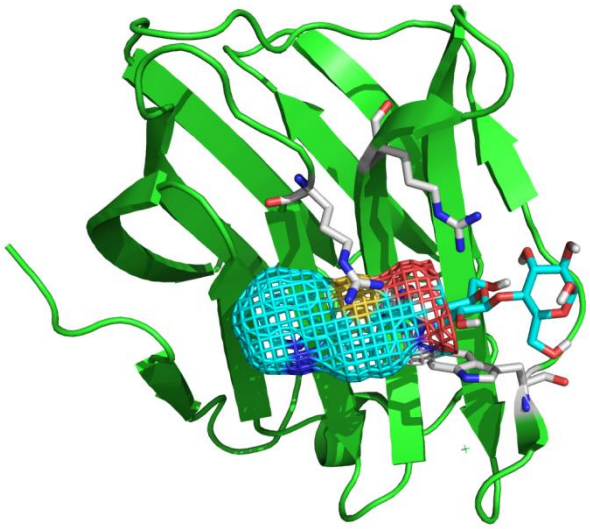
Key words: *lectin, docking, virtual screening, drug design.*

Lectins are proteins that bind carbohydrates and are involved in physiological processes like cell adhesion, signal transduction or membrane lattice generation, and pathological processes such as cancer metastasis and inflammation.[1] Due to the wide range of processes involving lectins, access to ligands able to modulate the activity of these proteins would improve the prognosis of various diseases.[2] In this work we used computational techniques, such as docking and virtual screening, to design different lectins binders based on the carbohydrate core specifically bound by the lectin. Our calculations predict improved affinity and selectivity towards different lectins in comparison to reported ligands. These carbohydrate-based compounds may have putative biological applications.[3]



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CHEMISTRY BEHIND THE IMMUNE RESPONSE FOR THE T_N ANTIGEN: THE ROLE OF THE PRESENTATION AND CHEMICAL NATURE OF THE PARTNERS

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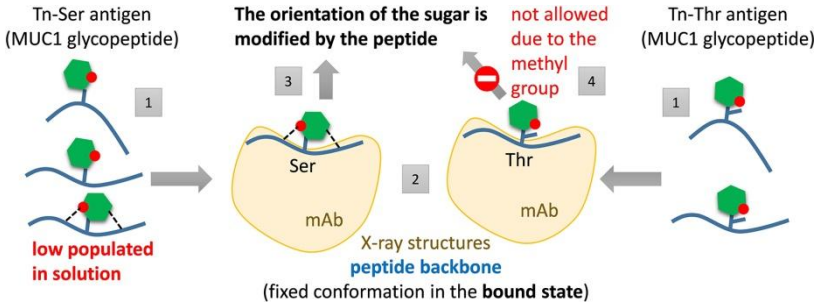
Keywords: *glycopeptides • antibodies • molecular recognition • X-ray diffraction • conformation analysis*

The Tn antigen (α-*O*-GalNAc-Ser/Thr) is one of the most specific human tumor-associated structures.[1] Consequently, it has found widespread use as biomarker and as potential therapeutic target against cancer. The Tn antigen is referred to *N*-acetylgalactosamine (GalNAc) α-*O*-linked to serine or threonine, not discriminating the amino acid to which GalNAc is linked.[2]

In this work, the structural features of two MUC1-derived glycopeptides bearing the Tn antigen in complex with an anti-MUC1 antibody are reported at atomic resolution. The study reveals significant differences in the conformational behavior of both glycopeptides in the bound state (see Figure). For the α-*O*-GalNAc-Ser derivative, the glycosidic linkage adopts a high-energy conformation stabilized by hydrogen bonds between the peptidic fragment and the sugar. This conformation seems unfeasible in the α-*O*-GalNAc-Thr containing glycopeptide due to the more limited flexibility of the side chain. Our data demonstrates the non-equivalence of Ser and Thr *O*-glycosylation points and provides insights on the occurrence in Nature of the PDTRP epitope for anti-MUC1 antibodies. From the chemical perspective, this features should be considered for developing novel antibodies and biosensors for these important antigens.



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RATIONAL DESIGN OF A SYNTHETIC MODEL OF THE DOPAMINE D3 RECEPTOR (D3R)

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Keywords: *Dopamine D3 receptor, eticlopride, synthetic model, docking*

Dopamine is one of the most important neurotransmitters in the central nervous system: it is involved both in physiological and pathological processes, exerting its effects through interaction with G protein-coupled receptors (GPCRs) [1]. The crystallization of the dopamine D3 receptor (D3R) forming a complex with the specific antagonist Eticlopride [2] has stimulated *in silico* studies of the ligand-receptor interactions in the binding pocket with the aim of designing a synthetic D3R model which can act as mimic of the natural receptor *in vitro* studies or as biosensor in biological fluids [3].

For the purpose of gaining atomistic detail of the binding pocket, we have carried out docking simulations of 8 antagonists (Eticlopride, Moperone, Paliperidone, S33084, Octoclothepin, Pimozide, Spiperone and Tefludazine) and 6 agonists (Lisuride, Pramipexole, 7-OH-DPAT, BP-897, PD128907 and Quinelorane), selected according to their affinity and selectivity for D3R, besides the native ligand, dopamine. VAL107^{III}, ASP110^{III}, SER182^{ECL2}, ILE183^{ECL2}, VAL189^{V}, SER192^{V}, SER196^{V}, TRP342^{VI}, PHE345^{VI} are highlighted as the main amino acid residues responsible for the interaction with agonists, differentiating them from those that interact with antagonists.

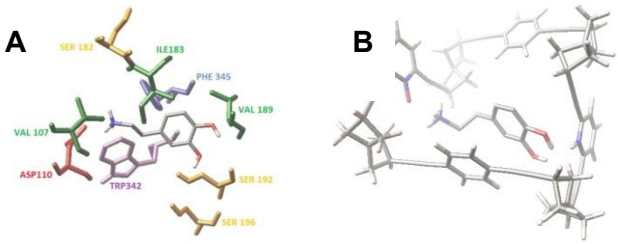

Image 1: **(A)** Resiudes responsible for the agonist-D3R interaction and **(B)** proposed macrocyle

Acid group in ASP which establishes an ionic bond with protonated amine of dopamine is emulated by the pyridine-N-oxide in the proposed macrocycle. Aromatic groups in TRP and PHE are emulated by benzene groups, which could stablish pi-pi interactions with the aromatic ring of dopamine, alcohol in SER is emulated by pyridine which can establish hydrogen bonds with alcohol groups of dopamine and chiral spiranes give hydrophobic regions as aliphatic chains in ILE and VAL do in the natural receptor D3R.

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S10: *Química en la Frontera con la Biología*

TARGETING G-QUADRUPLEX STRUCTURES WITH SMALL METALLO-ORGANIC MOLECULES

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Keywords: *quadruplex DNA, metal complexes, phen, DNA-ligand interactions*

The discovery of quadruplex structures has illuminated new roles of DNA in biology. The emergence of these four-stranded nucleic acid architectures has fuelled a very prolific area of investigation, mainly focused on the search of their potential uses in medicine, although applications are currently expanding to the fields of biotechnology and nanotechnology as well.[1-3] G-quadruplex DNA, in particular, has attracted much attention in the last years, because it is present in many regions of the human genome, such as the telomeres and few of the most commonly targeted oncogene promoters.[4,5]

In this communication we will present our recent work on the synthesis and G-DNA interactions of several metallo-organic molecules, as well as other organic derivatives, designed to specifically recognize G-quadruplexes. Structurally speaking, these small molecules are based either on polyaromatic Cu(II) or Pt(II) complexes, diquaternized 1,10-phenantroline derivatives, or carbohydrate-metal complex conjugates. In many cases, despite the relatively small size of the parent phen ligand, we have found that the compounds studied are able to recognize different G-DNA structures with good affinity and modest selectivity. We expect to use these results as a starting point towards the development of other multivalent molecular conjugates endorsed with a higher G-DNA binding selectivity, as required in most therapeutic applications.

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PROTEOMIC STUDY OF MESENCHYMAL STEM CELLS DURING AGEING BY iTRAQ

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Keywords: *proteómica cuantitativa, Itraq 8-plex, células madre mesenquimales*

Mesenchymal Stem Cells (MSCs) are of highly relevant for regeneration of mesenchymal tissues such as bone and cartilage. The promising role of MSCs in cell-based therapies and tissue engineering appears to be limited due to a decline of their regenerative potential with increasing donor age. This study pretends to establish a framework for future comparative and functional studies. Proteins from MSCs of rat bone marrow (BM-MSCs) of animals at different ages - newborn, infant, young, pre-pubertal, pubertal and adult- were digested in trypsine and marked by isobaric target relative absolute quantification (iTRAQ- 8 plex). Firstly were fractionated by basic reverse chromatography using 1200 HPLC (Agilent) and acid reverse chromatography using nano TempoSystem (Eksigent) acoplated to SunCollect (SunChrom) and introduced in 4800 MALDI-TOF/TOF (ABSciex). The data were analyzed with the Protein Pilot software for peptide matching, protein identification, and quantification. A total of 1047 proteins were identified of which 67 were differentially expressed in the different age groups studied. The proteins differentially expressed were implicated in several metabolic pathways using the String software but we classified all these proteins in three physiological processes (pluripotency, proliferation and energy metabolism). Several of differentially expressed proteins were validated by Western blotting; superoxide dismutase mitochondrial (over-expressed in pre-pubertal) and Laminin A (over-expressed in adult) relationated with proliferation; vimentin (over-expressed in pre-pubertal) involved in pluripotency and and vinculin (over-expressed in pre-pubertal) was validated by real-time polymerase chain reaction (RT-PCR). Also were performed kinetics assays of activity enzymatic of lactate dehydrogenase and glucose 6-phosphate (over- expressed in adult) for their implication in metabolic process. We concluded that group of pre-pubertal is the most pluripotent and proliferative and because of results obtained in this study this group is the most appropriate for its use in functional studies.

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ADAMANTANE AND 11-βHSD1: A PERFECT MATCH?

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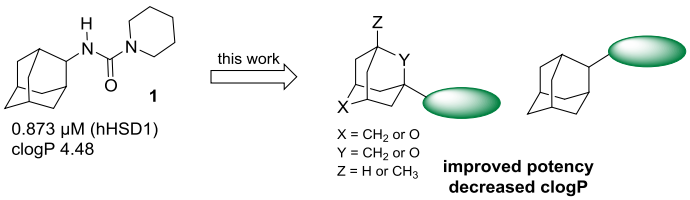
***Keywords**: 11β-HSD1, enzyme inhibitors, adamantane, metabolic syndrome*

It is well known that systemic glucocorticoid excess causes insulin resistance and central obesity. [1] Recent advances have demonstrated that local glucocorticoid levels can be regulated in the tissue level by inhibiting 11β-hydroxysteroid dehydrogenase 1 (11β-HSD1), which converts inert cortisone into active cortisol. In fact, knock-out 11β-HSD1 rodent models have been shown not only to protect against diet induced obesity, but also to improve insulin sensitivity. [2]

Since several groups and investigations have reaffirmed these findings, substantial activity in the academia and pharmaceutical industry has led to the discovery of numerous classes of non-steroidal 11β-HSD1 inhibitors. [3] Given that the enzyme active site includes a hydrophobic pocket to accommodate bulky lipophilic groups, our group is currently focused on the design and synthesis of new 11β-HSD1 inhibitors taking advantage of our expertise in polycyclic compounds.

Our starting point was based on the urea **1**, which exhibit potency and selectivity against 11β-HSD1. [4] Based on these results, we initiated a molecular modelling-guided medicinal chemistry program to optimize drug-likeness profile of the adamantane scaffold while improving potency. We have studied the effect of introducing an oxygen atom in the adamantane and of the position attachment to try to answer if is the adamantane the perfect match for 11β-HSD1.



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S10: *Química en la Frontera con la Biología*

SYNTHESIS OF A SELECTIVE MOLECULAR RECEPTOR FOR PHENYLALANINE

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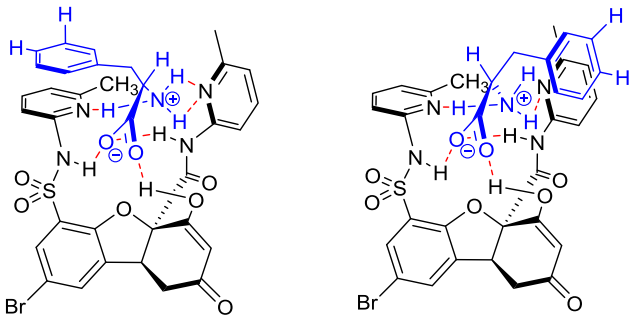
Keywords: *phenylalanine, racemic mixture, enantiomer, enantioselectivity*

Phenylalanine shows a lot of applications such as nutritional supplement, since it is an essential amino acid, antidepressant and analgesic.[1] Moreover, this amino acid is used in the industrial synthesis of the aspartame, an artificial sweetener.

In this communication, we present the preparation of a host based on a benzofurane scaffold [2] which simulates an oxyanion hole, similar to that present in many enzymes. This receptor has permitted us to carry out the resolution of a racemic mixture of phenylalanine by the formation of an associate in which several hydrogen bonds between the guest and the active groups of the oxyanion hole are present. Previously, the resolution of the racemic mixture of receptor itself was achieved by preparative chromatography on silicagel impregnated in *L*-phenylalanine.



Scheme 1. Geometries proposed for both associates between the receptor with *L*-phenylalanine and *D*-phenylalanine.

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S10: *Química en la Frontera con la Biología*

NANOTUBOS DE CARBONO COMO SOPORTE PARA LA INMUNIZACIÓN CON HAPTENOS

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Palabras Clave: *Nanotubo de carbono, hapteno, inmunización, anticuerpo, penthiopyrad.*

Los anticuerpos son biorreceptores moleculares con un gran número de aplicaciones biotecnológicas gracias a su elevada capacidad de reconocimiento hacia sus antígenos. La metodología clásica de producción de anticuerpos capaces de reconocer una pequeña molécula orgánica consiste en la síntesis de derivados funcionalizados (haptenos) y su anclaje a proteínas para hacerlos inmunogénicos. [1] Sin embargo, no siempre es posible disponer de la cantidad de hapteno funcionalizado necesaria para preparar suficiente inmunógeno para un procedimiento de inmunización convencional.

Nuestro objetivo en este proyecto fue el estudio de nanotubos de carbono como vehículos alternativos para la inmunización con haptenos. Para ello se emplearon nanotubos de multicapa (MWNT), los cuales tras ser activados en microondas fueron funcionalizados con un hapteno sintético derivado del fungicida penthiopyrad [2] (NT-PPm) o bien con un conjugado del mismo hapteno con seroalbúmina bovina (NT-BSA-PPm). Estos constructos inmunogénicos se inocularon en conejos New Zealand siguiendo diferentes pautas. El análisis de los antisueros obtenidos tras las inmunizaciones reveló que, como era de esperar, el protocolo de inmunización basado exclusivamente en dosis del constructo NT-PPm, es decir sin mediación proteica, no desencadenó una respuesta inmune potente. Sin embargo, cuando dicho protocolo fue precedido por una primera dosis del constructo con proteína (NT-BSA-PPm), se generó una respuesta inmune equivalente en cantidad y calidad a la obtenida con los conjugados tradiciones sin nanotubos, incluso empleando dosis de hapteno hasta 300 veces menores de lo habitual. Estos resultados ponen de manifiesto que es necesaria la participación del complejo mayor de histocompatibilidad (MHC) en la respuesta inmune primaria, el cual reacciona a inmunógenos derivados de proteínas. Por el contrario, es posible desencadenar una respuesta inmune secundaria, y por tanto de maduración de los linfocitos B productores de anticuerpos de elevada afinidad, utilizando cantidades muy pequeñas de antígeno sin necesidad de proteína, es decir sin la participación del MHC. Asimismo, se ha observado que los MWNTs poseen cierto carácter adyuvante siempre que su funcionalización se realice con conjugados proteicos, lo que permitiría eliminar el uso de aceites minerales altamente irritantes.

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S10: *Química en la Frontera con la Biología*

MODULATION OF THE INTERNAL PROPERTIES OF ANTIMICROBIAL CYCLIC PEPTIDES. A MOLECULAR DYNAMICS STUDY

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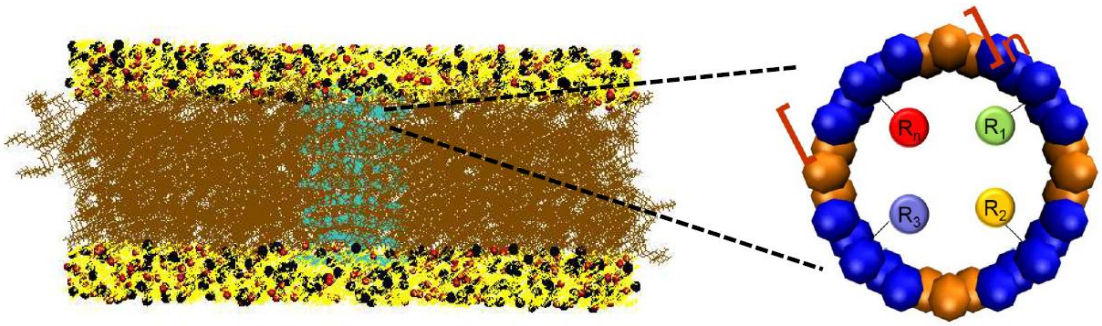
Keywords: *Peptide nanotubes, Lipid membrane, Molecular Dynamics*

Cyclic peptides (CPs) have emerged as good antimicrobial candidates due to their robust secondary structure and high activity. [1] α,γ-SCPN (Self-assembling Cyclic Peptide Nanotubes), composed of cyclic peptides alternating D-α-aminoacids and (1S,3S)-3-aminocycloalkanecarboxylic acids (γ-Acas), dispose each ring in antiparallel orientation between each two sub-units and the side chains of the amino acids are oriented outside of the nanotube.[2]

The modulation of the external properties of SCPNs determines the response caused in the lipid membrane, changing their permeability and resistance properties. [3] In this communication we will show that the control of the properties of the inner cavity could also lead to a modulation of the response caused by the CPs therein. Using Molecular Dynamics simulations we have studied the effect of introducing a variable number of γ-Acas, modified in C2, leading to inner-functionalized CPs with new and unknown stability and transport properties. Our preliminary findings open the door, at least conceptually, to another mechanism of interaction of CPs with cell membranes, different from those known up to the moment, and based on the control of the interior of the pore.



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S10: *Química en la Frontera con la Biología*

CYCLIC PEPTIDE SELF-ASSEMBLING MODULATED BY INTERNAL RECOGNITION

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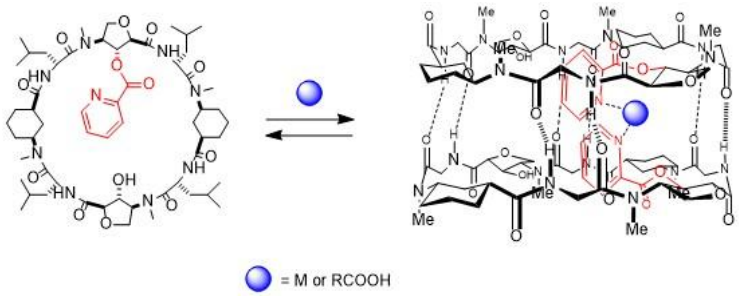
Keywords: *Amino acids, cyclic peptides, dimerization, self-assembly.*

Our research group is involved in the design and synthesis of supramolecular structures derived from peptides that contain γ-amino acids [1]. Regarding to this, we have demonstrated that cyclic peptides made of α and γ-amino acids of alternating chirality can adopt a flat conformation that allows stacking to form dimers or nanotubes [2,3]. The key feature of these structures is the presence of the β-carbon of each γ-amino acid projected towards the cavity of the ensemble that, after its selective functionalization, would allow to change the pore properties without interfering in the self-assembling properties [4]. With this idea, we have prepared a new γ-amino acid with a hydroxyl group in the β position [5] and incorporated into octapeptides in order to study their self-assembling properties. We have prepared different substituted cyclic peptides and studied the recognition properties of different guests.



This work was supported by the Spanish Ministry of Economy and Competitivity (MEC) [CTQ2010-15725, and CTQ2013-43264-R] and by the Xunta de Galicia (GPC2013-039 and EM2014/011). N. R.-V. also thanks the MEC for her FPU fellowship.

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S10: *Química en la Frontera con la Biología*

SYNTHESIS OF CELL PENETRATING PEPTIDES WITH TOPOLOGICAL CONTROL

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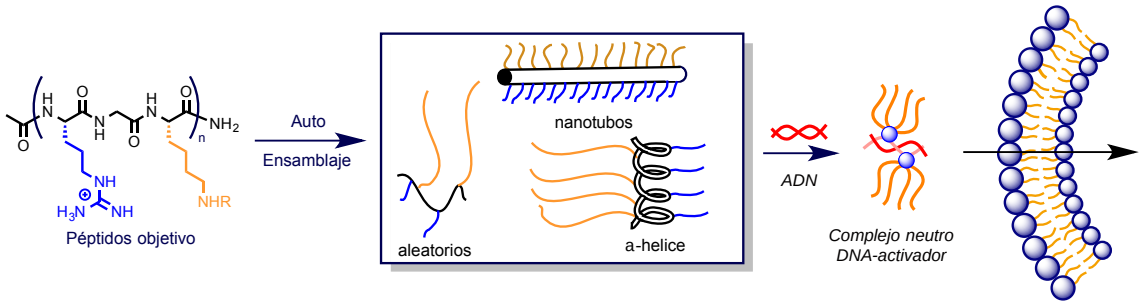
Keywords: *supramolecular chemistry, cell penetrating peptides, amphyphilic, solid phase synthesis.*

Cell penetrating peptides (CPPs) are short cationic molecules that cross biological membranes and that can be use in the delivery of universal cargos.[1] However, CPPs suffer from important limitations like toxicity, low stability and low selectivity. In this project we will try to overcome all these limitations and improve the synthetic design of CPPs. Our hypothesis is based on the importance of the secondary structure of the peptides in order to penetrate the cell membrane. The critical idea of our proposal is that the molecular shape of the peptides modulates the biochemical functionality. So, our general objective is focused on the control over the folding and aggregation of penetrating peptides in order to identify the minimum structural requirements that govern the translocation activity.



We will approach this challenge by the synthesis, characterization and internalization of cationic peptides bearing hydroxylamine residues that will be reacted with hydrophobic aldehydes.[2] This strategy will produce libraries of amphiphilic peptides with programed folding. In the near future, we will study the combination of these penetrating peptides with biologically interesting cargos such as nucleotides.[3]

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S10: *Química en la Frontera con la Biología*

CGH ARRAY ANALYSIS IN PEPTIDOMIMETICS AND DEPSIPEPTIDOMIMETICS $\alpha_v\beta_3$ RECEPTOR INHIBITION

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Keywords: *RGD, angiogenesis, genetic expression, depsipeptides*

Angiogenesis, the sprouting of new blood vessels from pre-existing vessels, is a remarkable feature of tumours growth and metastasis. The in vivo inhibition of this receptor by cyclic peptides containing RGD sequence may be used to selectively suppress these disease[1].

Our research group has developed a new methodology[2] for the evaluation of new antiangiogenic compounds, based in the genetic expression analysis using CGH array system.

The RGD mimetics activity can be modified by the presence of ester-bond[3], Therefore, we decided to prepare some depsipeptides analogous to the RGD-β-lactam compounds and evaluate their activity performing a genetic expression analysis.

We also have evaluated the activity of open-chain compounds without RGD formal structure.

The cyclic depsipeptides have demonstrated a very effective inhibitory activity. In the other hand the open-chain compounds have a surprising behavior, demonstrating a similar gene activation. This way, we call into question the essential need of RGD sequence to have an interaction between ligand and the receptor of the integrin[4, 5].

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S10: *Química en la Frontera con la Biología*

PEG-POLYACETAL-CURCUMIN CONJUGATE IN THE RESCUE OF ACUTE RAT SPINAL CORD INJURY

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Keywords: *drug delivery, nanomedicine, regenerative medicine*

Spinal cord injury (SCI) is a major cause of paralysis with currently no effective therapies [1]. Acute stages after trauma involves a fast inflammatory response with activation of a degenerative cascade process with multiple and massive neuronal and glial death. Curcumin, a naturally-occurring anti-inflammatory component of *Curcuma longa*, has already shown neuroprotective effects in acute and systemic administration in rodent SCI. However, the hydrophobic nature of curcumin together with the disruption of the blood-spinal cord barrier involves an important limitation for a proper systemic treatment[2,3].

Herein, the integration of curcumin in the mainchain of a PEG-Polyacetal [4,5] was used to achieve a family of pH-responsive conjugates with different total drug loading ranging from 1.8 to 5.7 %w/w to be used in intrathecal administration in SCI. In vitro cell viability assay was performed using rat ependymal-precursor cell derived from adult SC 1 week after suffering SCI (epSPCi). Free curcumin favors cell viability at low doses (up to 1 µM), however, higher doses (5 or 10 µM) were significantly toxic for the cells. The use of equivalent concentrations of any of the curcumin conjugates did not show any toxic effect up to 10 µM. The best performance was observed for the conjugate with a 3.8 %w/w curcumin loading. For *in vivo* analysis of the potential neuroprotective effect the selected conjugate (3.8%w/w PA-PEG-Curcumin) was used for intrathecal admin. after severe SCI in adult rats. A Cy5.5-derivatized conjugate was synthesized and use for *in vivo* monitoring. Interestingly, PEG-PA-Curcumin intrathecal single administration significantly improved locomotor activity after SCI compared with vehicle (PA-PEG control) treated animals. The functional improvement, analyzed by using the BBB scale Open field test was significantly improved from the first week after curcumin treatment. In order to disclose the mechanisms involved in PEG-PA-Curcumin efficiency, histological, immunofluorescence and Western Blotting analysis were performed. Diminished in apoptotic cell markers and increased neuronal stainings indicated a preferential neuroprotective role of the conjugate treated animals. Our findings clearly show a functional activity of PEG-PA-Curcumin conjugate on the rescue of locomotion activity preserving neural cell survival.

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S10: *Química en la Frontera con la Biología*

CONFORMATIONALLY RESTRICTED SUBSTRATE ANALOGS OF SHIKIMATE KINASE ENZYME AS NEW ANTITUBERCULAR AGENTS

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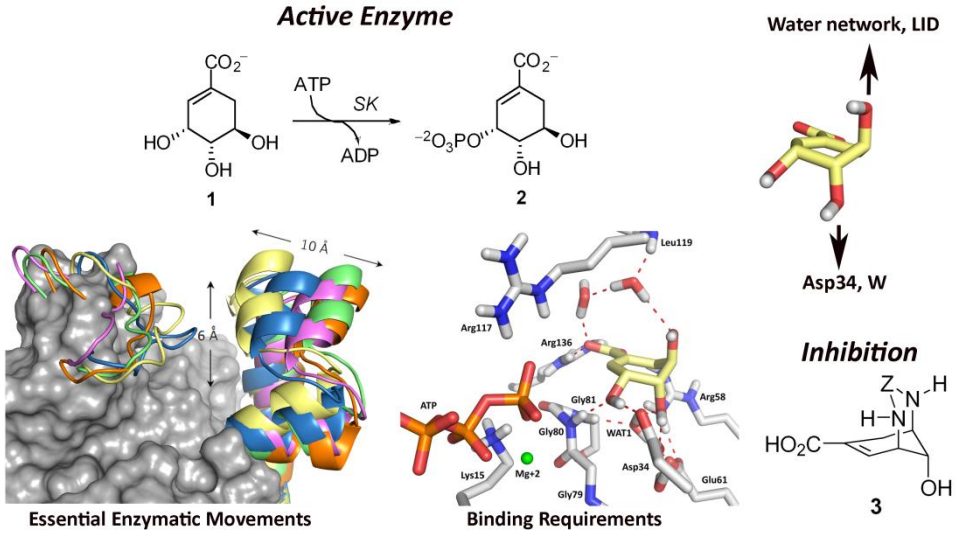
Keywords: *inhibitors, essential enzymes, tuberculosis, antibiotics*

Shikimate kinase is an essential enzyme in several pathogenic bacteria and it does not have any counterpart in human cells, thus making it an attractive target for the development of new antibiotics.[1] Based on the key interactions of the substrate and product binding and the enzyme movements that are essential for catalytic turnover of the *Mycobacterium tuberculosis* shikimate kinase enzyme (*Mt*-SK) that have been investigated by structural and computational studies,[2] several substrate analogs were designed and synthesized. These studies reveal that the fixation of the diaxial conformation of the C4 and C5 hydroxyl groups recognized by the enzyme or the replacement of the C3 hydroxyl group in the natural substrate by an amino group is a promising strategy for inhibition because it causes a dramatic reduction of the flexibility of the LID and shikimic acid binding domains. Our recent results on this project will be presented.[3]



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S10: *Química en la Frontera con la Biología*

EXPLORING THE REDUCTION OF ENZYME FLEXIBILITY IN THE DESIGN OF INHIBITORS

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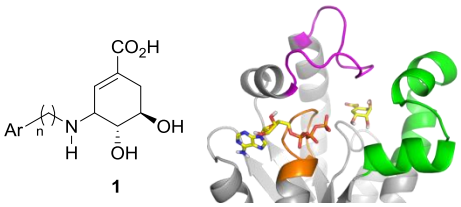
Keywords: *enzyme motion, catalytic turnover, inhibition*

Enzymes are proteins with substrate specificity and catalytic efficiency. Both properties derive not only from the chemistry of the active site, but also from its structure, i.e. the geometry and the environment of its functional groups and also from the possible conformational changes in the active site to afford the Michaelis complex that triggers the enzymatic reaction. For the latter, the active site is usually closed from the solvent environment and is subsequently opened for product release. Having in mind that this motion is essential for catalytic turnover, a good strategy for enzyme inhibition could be therefore to target the closing or opening motion. Based on this hypothesis, in the last years, we have achieved the efficient inhibition of the third enzyme of the shikimic acid pathway, type II dehydroquinase, for the possible development of new antibiotics [1,2]. We are exploring this strategy into the inhibition of another essential enzyme, shikimate kinase. Our recently reported studies of the dynamic behavior of the enzyme/product complex showed that Arg117 triggers the process by forming a strong electrostatic interaction with the C3 phosphate group in the product [3]. This causes destabilization of the product in the active center and a conformational change of the product occurs, which in turn leads a large opening (up to 10 Å) of the SB domain. To avoid this motion several analogs have been synthesized and tested. Our recent results on this project will be presented.



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Financial support from the Spanish Ministry of Economy and Competitiveness (SAF2013-42899-R), Xunta de Galicia (GRC2013-041) and the European Regional Development Fund (ERDF) is gratefully acknowledged. VP thanks the Spanish Ministry of Economy and Competitiveness for her FPI fellowship.

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S10: *Química en la Frontera con la Biología*

RNA SENSING BASED ON RECOGNITION-FOLDING PROCESSES

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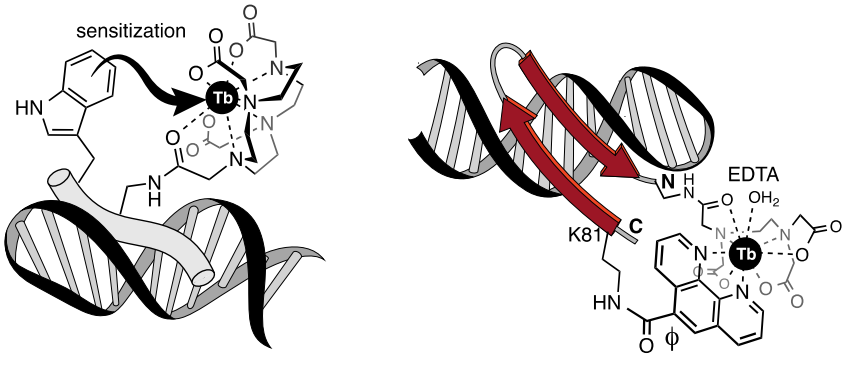
Keywords: *luminescent sensors, lanthanides, biomolecular recognition, peptides.*

Fluorescent technologies and biomolecular tagging strategies have revolutionized our understanding of protein location and function in live cells. In this context, it is of major interest the extension of these methodologies to study the localization, dynamics and regulation of the biological macromolecule that exhibits the most diverse range of functions: RNA.[1] [2]

We have recently demonstrated that the alfa-helical folding associated to the recognition of the *boxB* hairpin RNA by the protein N of bacteriophage P22 can be used for the development of a selective fluorescent sensor.[3] The sensor is based on a folding-induced intramolecular lanthanide sensitization, and results in a large increase in luminescent emission of a terbium chelate complex engineered near a tryptophan antenna.[4]

We have now applied an alternative sensing strategy for the development of a specific sensor of TAR RNA. Tat, an arginine-rich peptide that targets TAR, adopts a ß-sheet conformation upon binding to its target. We made a Tat derivative equipped with a coordinatively unsaturated EDTA chelating unit at the N-terminus of the Tat peptide, and a phenanthroline coordinating antenna at the C-terminus of the sequence. Fluorescence experiments in presence of a Tb (III) salt demonstrated that the peptide exhibit a very important increase in the luminescence upon binding to its target RNA.



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S10: *Química en la Frontera con la Biología*

SYNTHESIS, CHARACTERIZATION AND CYTOTOXICITY IN CACO-2 CELLS OF COPPER(I) COMPLEXES

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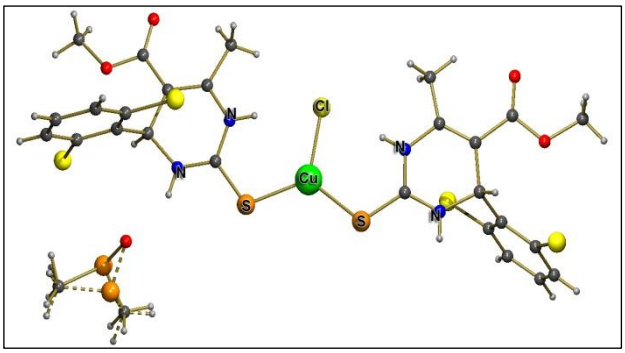
Keywords: *copper(I) complexes, X-Ray, Caco-2, colorectal cancer*

Following our previous studies about copper complexes linked to N,S-donor ligands with possible biological activity,[1] we have selected methyl 4-*R*-6-methyl-3,4-dihydropyrimidine-2(1*H*)-thione-5-carboxylates, where the *R* is 2,6-dichlorophenyl (HL^1), 4-*t*-butylphenyl (HL^2) and 4-hydroxy-3-methoxyphenyl (HL^3) as ligand.[2]



Three new copper(I) complexes were obtained through the reaction of the ligand with copper(II) chloride in 2:1 molar ratio. Structural characterization was carried out in solid and liquid state using different techniques allowing us to propose the formula $[CuCl(HL)_2]$ in all cases. As shown in the figure, $[CuCl(HL^1)_2]$ was recrystallized in dmso and the X-ray diffraction study revealed an almost perfect trigonal planar coordination geometry, solvated with one molecule of dmso.

Cytotoxicity reflected as (% of cell viability) of the copper complexes was assessed in the human colon carcinoma cell line (Caco-2) after 48 hours by the Vybrant MTT proliferation assay. The obtained half maximal inhibitory concentration (IC_{50}) values were very promising being 14.61 µM for $[CuCl(HL^1)_2]$, 26.60 µM for $[CuCl(HL^2)_2]$ and 86.98 µM for $[CuCl(HL^3)_2]$. Due to these interesting results, future studies including another colon cancer cell lines will be conducted to explore more in depth the antitumor activity of the cited copper complexes.

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S10: *Química en la Frontera con la Biología*

SPONTANEOUS PHOSPHOLIPID MEMBRANE GENERATION BY NATIVE CHEMICAL LIGATION

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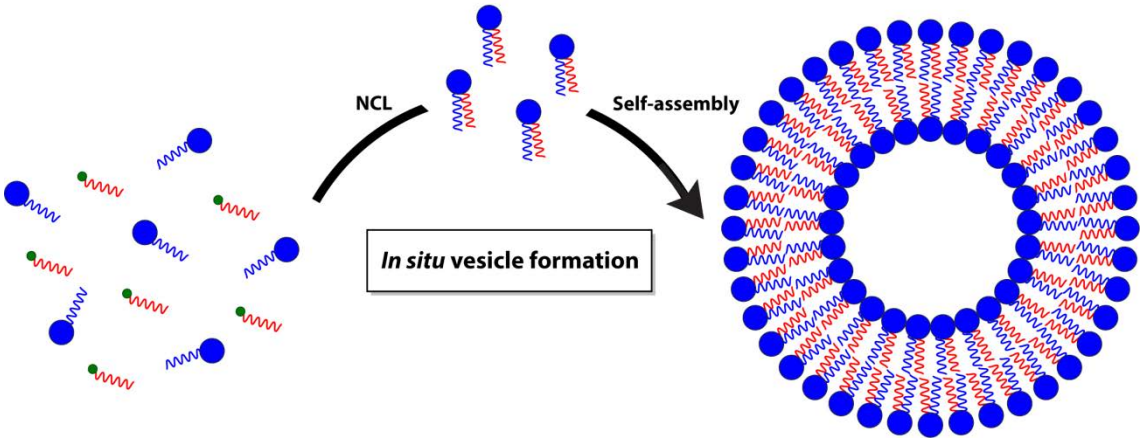
Keywords: *phospholipid, membrane, native chemical ligation, self-assembly*

Phospholipid membranes are employed in the study of protein-membrane interactions, drug-delivery, origin-of-life, and artificial reactors.[1] While the capability of phospholipids to self-assemble into membranes is well defined,[2] the *de novo* synthesis and formation of membranes from simple reactive precursors is poorly understood. Consequently, one of the major goals of synthetic biology is the development of self-assembling non-natural membranes, that will elucidate a range of new fundamental structural, dynamical and biochemical features on which nature builds living systems. Here we describe the use of native chemical ligation (NCL) to spontaneously generate phospholipid membranes from water-soluble starting materials.[3] NCL is one of the most popular tools for the synthesis of large peptides and small proteins. This non-enzymatic approach can be used to form phospholipids in a highly specific and chemoselective way. The lipids are capable of *in situ* self-assembly into vesicles that can grow to several microns in diameter. Moreover, the orthogonality, the high reaction rate, and the biocompatibility of this approach are key features that make it a powerful option for the efficient encapsulation and/or reconstitution of relevant biomolecules. We foresee future applications of NCL membrane assembly in advanced synthetic cell studies or in the construction of liposomal drug-delivery systems and bioreactors.



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S11. Polímeros para Aplicaciones Avanzadas (PAA) / Polymers for Advanced Applications

El simposio se centra en aspectos destacados del campo de los polímeros. La selección de conferencias invitadas y comunicaciones, pretende dar una visión actualizada de la posición estratégica que ocupan los materiales poliméricos en la exigente y dinámica sociedad moderna internacional.

The symposium focuses on the prominent aspects of the field of the polymers. The selection of the invited lectures and communications aims to give an updated vision about the strategic position occupied by the polymeric materials in the dynamic international modern society.

Organizadores:

Julio Sanromán (CSIC)

Mª Carmen Ramírez Gómez (UDC)

e-mails de contacto: jsroman@ictp.csic.es / cramirez@udc.es

Simposio patrocinado por el Grupo Especializado de Polímeros

Martes 21 de Julio 2015

08:40 – 09:40	**PL-3**	***Conferencia Plenaria*** (Común a todos los simposios) **Samuel I. Stupp** *"Supramolecular Materials Chemistry"*

Chairwoman: Carmen Ramírez

10:00 – 10:30	**S11-IL-01**	**Julio San Román** *"Aprendiendo de la Naturaleza la Formación de Estructuras Poliméricas Autoensambladas y sus Aplicaciones en Nanomedicina"*
10:30 – 10:45	**S11-OC-01**	**S. Campaña** *"Desarrollo de Nanopartículas Dendríticas Pegiladas para Aplicaciones Biomédicas"*
10:45 – 11:00	**S11-OC-02**	**M. Santos** *"Hydrogels and Surface Coating via "Clickable" Elastin-like Recombinamers for Cardiovascular Uses"*
11:00 – 11:30		Pausa Café

Chairman: Luis F. Barral

11:30 – 12:00	**S11-IL-02**	**Francisco M. Goycoolea** *"Biopolymer-Based Self-Assembled Nanocomplexes for Innovative Therapeutic Applications"*
12:00 – 12:15	**S11-OC-03**	**E. V. Lage** *"Polyoxamine Block Copolymer Micelles as Multi-responsive Drug Delivery Systems: An Interfacial Approach"*
12:15 – 12:30	**S11-OC-04**	**C. Vila-Sanjurjo** *"Interference with Bacterial Quorum Sensing Based Response by Sub-lethal Levels of Chitosan Nanoparticles"*
12:30 – 12:45	**S11-OC-05**	**M. Castro Cabado** *"Polycondensation Products of Polysaccharides and Polycarboxylic Acids by Thermal Processing: A Reliable Characterization Protocol"*
12:45 – 13:15	**S11-IL-03**	**Toribio Fernández Otero** *"Propiocepción Artificial de Músculos Poliméricos: Experimentos y Modelo (¿Pueden las Funciones Cerebrales ser Descritas por Ecuaciones Físico-Químicas?)"*
13:30 – 15:30		Comida

Martes 21 de Julio 2015

Chairwoman: Rebeca Bouza

15:30 – 15:45	**S11-OC-06**	**Ricardo Mallavia** *"Síntesis y Caracterización de Copolímeros de Fluoreno y Anilina vía Suzuki en Condiciones No Convencionales"*
15:45 – 16:00	**S11-OC-07**	**M. Cerrada** *"Development of Polar Polymorphs in PVDF Nanocomposites"*
16:00 – 16:15	**S11-OC-08**	**Y. Farrag** *"Synthesis of Polymeric Nanoparticles for Packaging Reinforcement Applications"*
16:15 – 16:30	**S11-OC-09**	**S. Malmir** *"Thermal and Morphological Characterization of Poly(3-hydroxylbutyrate-co-3-hydroxylvalerate) (PHBV) Bionanocomposites"*
16:30 – 17:00		Pausa Café

Chairman: Julio San Román

17:00 – 17:15	**S11-OC-10**	**L. Arboleda-Clemente** *"Evaluación del Incremento de la Conductividad Eléctrica y Térmica en Composites de Poliamida 12/Poliamida 6/nanotubos de carbono"*
17:15 – 17:30	**S11-OC-11**	**K. Cobos** *"Polímeros Helicoidales: Soldado Universal"*
17:30 – 17:45	**S11-OC-12**	**E. Suárez Picado** *"Polímeros Helicoidales como Sensores de Aminas"*
18:00 – 18:15	**S11-IL-04**	**Ricardo Riguera** *"Helical Polymers: Sensor and Aggregation Properties of Polyphenylacetylenes"*

18:30	***Sesión de Pósteres***

Comunicaciones Invitadas (IL)

S11: *Polímeros para Aplicaciones Avanzadas*

APRENDIENDO DE LA NATURALEZA LA FORMACIÓN DE ESTRUCTURAS POLIMÉRICAS AUTOENSAMBLADAS Y SUS APLICACIONES EN NANOMEDICINA

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La naturaleza nos brinda los modelos más evolucionados de distribución de materiales y su asociación o combinación para conseguir unas propiedades específicas, tanto desde el punto de vista fisicoquímico, como desde una perspectiva biológica. Este aspecto es de gran importancia cuando consideramos los componentes más importantes del organismo humano y desde la estructura morfología y propiedades de la membrana celular, hasta la distribución y orientación de sistemas celulares responsables de la comunicación y transmisión electrofisiológica (sistema nervioso central). Es fácil observar que la mayor parte de los sistemas en el organismo funcionan mediante mecanismos de auto asociación macromolecular, y considerando los sistemas poliméricos es de enorme importancia el balance entre componentes hidrofílicos e hidrofóbicos, responsables de la formación de sistemas micelares de enorme repercusión en todos los procesos de regeneración tisular y proliferación celular. Considerando estos principios se presentarán diferentes casos de sistemas poliméricos sintetizados mediante técnicas de polimerización tradicional, o metodologías más recientes como ATRP, RAFT que permiten diseñar y preparar sistemas de peso molecular bien definido y muy estrecha distribución de pesos moleculares. Este aspecto que de alguna manera biomimetiza lo que la naturaleza es capaz de diseñar y fabricar, proporciona una vía muy útil y elegante para la preparación de sistemas poliméricos autoensamblados que en condiciones fisiológicas se ensamblan para formar nanopartículas bioactivas de gran interés en la vectorización y liberación controlada de moléculas bioactivas, ya sea para activar un proceso de proliferación y regeneración tisular, como para limitar o inhibir la proliferación de determinadas líneas celulares específicas, aspecto este de gran trascendencia en el tratamiento específico de células tumorales. Se presentarán ejemplos concretos de sistemas desarrollados en los últimos años que presentan muy baja toxicidad y un buen control de procesos angiogénicos, regenerativos de tejido epitelial o bien para el tratamiento específico de tumores sólidos. La contribución de este tipo de sistemas al desarrollo de la Nanomedicina supone un avance de gran alcance para el tratamiento de enfermedades y lesiones de complicada y limitada solución, y abre posibilidades que parecían impensables tan solo hace 5-6 años. Considerando un esquema de desarrollo futuro, se puede considerar que el papel de sistemas poliméricos funcionales bien definidos desde el punto de vista estructural y tamaño macromolecular resultará definitivo en la evolución de este campo en los próximos años.

Los trabajos realizados en este campo han sido posibles gracias a la participación y financiación ofrecida por la red de excelencia CIBER-BBN.

S11: *Polímeros para Aplicaciones Avanzadas*

BIOPOLYMER-BASED SELF-ASSEMBLED NANOCOMPLEXES FOR INNOVATIVE THERAPEUTIC APPLICATIONS

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Polysaccharide, proteins and nucleic acids major constituent building blocks of biological systems and often occur as highly organized macromolecular architectures (e.g. the capsid of viruses). They can appear in the same or in different biological physiological environment interacting in specific or non-specific ways. When isolated and purified, these macromolecules can self-assembled (SA) into soft nanomaterials by non-covalent electrostatic complexation. The possibility to design materials with enhanced biological function and improved technological advantages, over those based on synthetic or inorganic components, has only started to be realized.

In this talk, I will address two main type of SA systems, namely polysaccharide-protein systems and polysaccharide-microRNA ones. Among the first type, we have studied alginate-lysozyme systems and found that they are extremely interesting to associate and release enzymes in a ionic-strength dependent manner; also, dextran sulfate-lysozyme complexation has been established as the key step to develop nanocapsules with capacity to inhibit the adhesion of *Helicobacter pylori* capsules to AGS stomach cells. This system is envisaged with great potential in antibiotic-free therapy. Among the second type, we have investigated electrostatic SA nanocomplexes (NCXs) comprising chitosan (CS) and miRNA and how the structure of CS (i.e. degree of acetylation -DA- and Mw) can influence the ability to obtain stable nanomaterials to deliver miRNA intracellularly into breast cancer cells (MCF-7). We have fully characterized the biophysical properties of these systems, namely their size (DLS), zeta potential and morphology (TEM). Binding studies using surface plasmon resonance and fluorescence quenching spectroscopy have also revealed that both CS´s DA and Mw have an influence in the formation of the NCXs and this is reflected in their transfection efficiency. The cytotoxicity of NCXs was found significantly lower than commercial transfecting agents. Transfection efficiency studies showed succesful downregulation of the target gene after treatment with CS-miRNA NCXs, thus indicating their potential use in breast cancer therapy.

S11: *Polímeros para Aplicaciones Avanzadas*

PROPIOCEPCIÓN ARTIFICIAL DE MÚSCULOS POLIMÉRICOS: EXPERIMENTOS Y MODELO (¿PUEDEN LAS FUNCIONES CEREBRALES SER DESCRITAS POR ECUACIONES FÍSICO-QUÍMICAS?) ARTIFICIAL PROPRIOCEPTION FROM POLYMERIC MOTORS

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Designers and engineers have been dreaming for decades with motors sensing, by themselves, working and surrounding conditions, as biological muscles do originating proprioception. The evolution of the working potential, or that of the consumed electrical energy, of electrochemical artificial muscles based on electroactive materials (intrinsically conducting polymers, redox polymers, carbon nanotubes, fullerene derivatives, grapheme derivatives, porphyrines, phtalocyanines, among others) and driven by constant currents senses, while working, any variation of the mechanical (trailed mass, obstacles, pressure, strain or stress) thermal or chemical conditions of work. They are linear faradaic polymeric motors: currents control movement rates and charges control displacements and muscle position. One physically uniform artificial device includes one chemically based motor and several sensors working simultaneously under the same driving reaction. Actuating (current and charge) and sensing (potential and energy) magnitudes are present, simultaneously, in the only two connecting wires and can be read by the computer at any time. From basic polymeric, mechanical and electrochemical principles a basic equation is attained. It includes and describes, simultaneously, the polymeric motor characteristics (rate of the muscle movement and muscle position) and the working variables (temperature, electrolyte concentration and mechanical conditions). By changing working conditions experimental results overlap theoretical predictions. The ensemble computer-generator-muscle-theoretical equation constitutes and describes artificial mechanical, thermal and chemical proprioception of the system. Proprioceptive tools and zoomorphic or anthropomorphic soft robots can be envisaged. If proprioception a, up to now, considered psychological property can be described by a physical-chemical equation, could brain other brain functions be described by similar equations? Some working lines will be presented.

ACKNOWLEDGMENTS: Authors acknowledge financial support from Spanish Government (MCI) Project MAT2011-24973, Jose G. Martinez acknowledges to the Spanish Education Ministry for a FPU grant (AP2010-3460).

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S11: *Polímeros para Aplicaciones Avanzadas*

HELICAL POLYMERS: SENSOR AND AGGREGATION PROPERTIES OF POLYPHENYLACETYLENES

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Keywords: *Polyphenylacetylenes, helical inversion and elongation, metal ion complexation, chiral nanoparticles, nanotubes and gels*

The design of helical polymers that respond to external stimuli by changing their helical sense or pitch has become a field of major interest in recent years. The helical structure of Polyphenylacetylenes has been used for the development of chiral sensors, molecular devices, chiro-optical switches, memory elements for information storage, chiral catalyst and conductive materials among other applications.[1] where switching the helicity/elongation of the chain by an external agent is the key.

In this talk I will described our results[2-8] on the design and properties of helical polyphenylacetylenes and show how polymers with helical sense and elongation sensitive to external stimuli acting on the conformational composition of the pendant can be obtained by careful selection of the pendant. Also, ways to selectively trigger the supramolecular aggregation of these polymers to produce macroscopically chiral nanospheres, nanotubes and gels is described.

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Comunicaciones Orales (OC)

S11: *Polímeros para Aplicaciones Avanzadas*

DESARROLLO DE NANOPARTÍCULAS DENDRÍTICAS PEGILADAS PARA APLICACIONES BIOMÉDICAS

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Palabras Clave: *Dendrímero, nanopartícula, tetrafenilmetano, PEG*

Los dendrímeros rígidos constituyen un subgrupo importante dentro de la química de dendrímeros, destacando entre otros los polifenilenos de Miller y Neenan [1] y de Mullen [2] y los poli(fenilenoetinileno)s de Moore [3]. En nuestro grupo de investigación hemos desarrollado dendrímeros rígidos con forma globular persistente basados en tetrafenilmetano [4]. Estas macromoléculas poseen cavidades interiores hidrofóbicas bien definidas y excelentes propiedades ópticas, pero la funcionalización periférica con grupos metoxilo limita su aplicabilidad.

Con la idea de utilizar estos nuevos dendrímeros en aplicaciones biomédicas, se ha llevado a cabo la síntesis de derivados funcionalizados en la periferia con oligoetilenglicoles (PEG). Partiendo de una unidad terminal funcionalizada con ésteres, se ha llevado a cabo el crecimiento de los dendrones mediante una ruta convergente basada en acoplamientos de Sonogashira. Una vez obtenidos los dendrímeros por acoplamiento de los correspondientes dendrones al núcleo, la hidrólisis de los ésteres terminales seguida de amidación con aminoPEGs utilizando una carbodiimida como agente acoplante proporciona dendrímeros decorados con oligoetilenglicoles en su superficie como nanopartículas esféricas luminiscentes con cavidades hidrofóbicas y excelente solubilidad en agua.

Agradecimientos: Este trabajo ha sido financiado por el MEC y FEDER (MAT2013-42425-R y la Xunta de Galicia (PGIDT/PGIDIT, 08TMT002209PR).

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S11: *Polímeros para Aplicaciones Avanzadas*

HYDROGELS AND SURFACE COATINGS VIA"CLICKABLE" ELASTIN-LIKE RECOMBINAMERS FOR CARDIOVASCULAR USES

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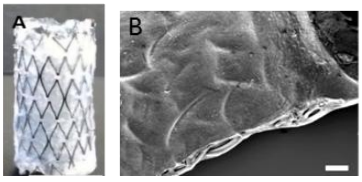
Key words: *Elastin-like Recombinamers, Hydrogel, Click chemistry, Stent*

Emerging technologies to obtain hydrogels by a cell friendly process are of great interest for biomedical applications. Elastin-like recombinamers (ELRs) are protein-based polymers obtained by recombinant DNA technologies, which means a total control over the aminoacidic sequence. Moreover, these ELRs can be design to include different bioactive domains.[1] In addition, they are biocompatible and possess self-assembly capability and responsiveness to different stimuli. ELR-based click hydrogels have been prepared at physiological conditions by covalent crosslinking via click chemistry. 1,3-Dipolar cycloaddition reaction between azides and alkynes is the most prominent example of click methodology.[2] This technology is compatible with most of the functional groups present in proteins and peptides, with no-toxic by-products and requires short reaction times. Chemical modification of both, a structural ELR and a biofunctionalized ELR-bearing RGD cell-adhesion sequence, to carry the reactive groups, azide and alkyne, is required to obtain click hydrogels. A new generation of catalyst-free click hydrogels, ELR-CFCGs, has been obtained when the recombinamer is functionalized with activated cyclooctine units.



These novel gels, ELR-CFCGs, have been applied in the field of tissue engineering at the cardiovascular area for coating not resorbable stents, in order to avoid in-stent restenosis. Proliferation of endothelial cells (HUVECs) on ELR-biostents with different bioactive sequences (REDV and RGD) has been tested. These ELR-biostents have resulted in a complete endothelialisation *in vitro* in a short time (10-15 days); and have shown high hemocompatibility after *in vitro* thrombogenicity assays. These results are a very promising starting point for future trials *in vivo*.

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S11: *Polímeros para Aplicaciones Avanzadas*

POLOXAMINE BLOCK COPOLYMER MICELLES AS MULTI-RESPONSIVE DRUG DELIVERY SYSTEMS: AN INTERFACIAL APPROACH

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Keywords: *Langmuir monolayers, poloxamine, Tetronic, drug delivery, smart polymers*

Low solubility of drugs in biological fluids is one of the most challenging pharmaceutical considerations nowadays. To solve this complication, nanosized association colloids have been long considered as rather suitable carriers for poorly water-soluble drugs. Among these colloidal vectors, amphiphilic block copolymer micelles are a promising strategy for drug delivery for their ability to modulate their self-assembly depending on their physicochemical environment. This intelligent behaviour lies in the fact that the chemical architecture of these polymer surfactants allows them to reversibly form and break micelles in response to several stimuli [1]. This would ultimately let the drug be properly delivered and optimally carry out its pharmacological action, which draws our attention to smart polymer-based systems.

Considering biocompatible polymers, poly(ethylene oxide)-poly(propylene oxide) block copolymers have been found to form aggregates with enhanced properties. A number of architectures are known for this kind of molecules, being more commonly used linear and X-shaped varieties. The latter, named poloxamines or Tetronic®, are built out of four PPO-PEO arms linked by a central ionisable ethylenediamine group. Varieties with different number of EO units and PO units and/or HLB value, such as the selected ones (Tetronics 904, 908, 1107 and 1307), are known to show different properties as surfactants [2].

In order to obtain information on their molecular arrangement when self-assembled, monolayers are very useful tools at mimicking aggregates in bulk solution. A study of these copolymers spread at the air/water interface was carried out at different conditions of temperature, pH and ionic strength. In this sense, high temperature as well as high values of ionic strength and pH have shown to favour micellisation.

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S11: *Polímeros para Aplicaciones Avanzadas*

INTERFERENCE WITH A BACTERIAL QUORUM SENSING-BASED RESPONSE BY SUB-LETHAL LEVELS OF CHITOSAN NANOPARTICLES

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Keywords: *Quorum Sensing, AHLs, chitosan, nanoparticles*

The quorum sensing (QS) hypothesis explains a type of bacterial cell-cell communication mediated by means of exocellular compounds that act as autoinducers (AIs). Among AIs, N-acyl-homoserine lactones (AHLs) in Gram (-) bacteria have received most of the attention. AHLs diffuse in and out of the cell where they bind to specific regulators of gene expression that control communal behaviours in a cell-density dependent manner. This phenomenon has profound implications in the control of many important bacterial traits (*e.g*. biofilm formation, secretion of virulence factors, etc.) [1]. Although several mathematical models proposed in recent years describe QS behavior, these are often beset by conceptual complexities [2] and lack rigorous experimental validation. We have developed a novel and simple conceptual framework upon which the formation of the AHL-based QS response can be mathematically modeled. Particularly, our model proposes an existence of a critical threshold of an AHL-activated state beyond which the QS response is triggered at the population level. Our model has been proven to explain the onset of the QS response in two AHL responding bacterial strains, namely a fluorescent *E. coli* reporter [3] and a mutant strain of *C. violaceum* [4]. Notably, *in silico* simulation, using a simple cubic lattice in a bacterial culture, agrees closely with the behavior measured *in vivo*. We anticipate that our model can be central to the development of smart anti-QS strategies based in biopolymer-based nanomaterials which displace the activation state of the cell below the threshold where QS response is triggered. Specifically, we have found the conditions in which sub-lethal levels of chitosan–derived nanoparticles (CS NPs) [5] drastically reduce the AHL-based response of a fluorescence *E. coli* reporter without compromising cell viability.

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S11: *Polímeros para Aplicaciones Avanzadas*

POYCONDENSATION PRODUCTS OF POLYSACCHARIDES AND POLYCARBOXYLIC ACIDS BY THERMAL PROCESSING. A RELIABLE CHARACTERIZATION PROTOCOL

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Key Words: *polycondensation; citric acid; polysaccharides;*

This work deals with the analysis of the polycondensation reaction between polysaccharides and polycarboxylic acids under thermal processing, by the use of three complementary analytical techniques: Fourier Transform Infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and rheometry. The approached has been thoroughly studied on a system comprising maltodextrin and citric acid. It has been proved that the polycondensation reaction of systems containing maltodextrin and citric acid is effectively produced by thermal treatment. The composition of the system has a big impact on the polycondensation behavior as well as on the resulting polycondensation product. FTIR has shown esterification covalent bonding upon thermal treatment but it has also proven the existence of strong hydrogen bond interactions between maltodextrin and citric acid. TGA allowed the determination of the polycondensation reaction temperature about 140 oC. The progress of the reaction could be estimated as from the weight loss associated to the release of water following the esterification. Similar reaction progress could be estimated by FTIR, as from the ration of absorption bands associated to C=O and free OH groups. The formation of crosslinked polymer upon thermal treatment could be studied by rheology. The evolution and cross-over of the curves for moduli G' and G'' has allowed to determine the gel time for composition with 40-60% of citric acid at 140 oC. The resulting crosslinked product has a greater thermal stability than the statting materials maltodextrin and citric acid, as evidenced by TGA. Overall, this study shows that the combination of FTIR, TGA and rheometry techniques is very useful for the characterization of polycondensation process between polysaccharides and polycarboxylic acids under thermal conditions carried out at industrial scale.

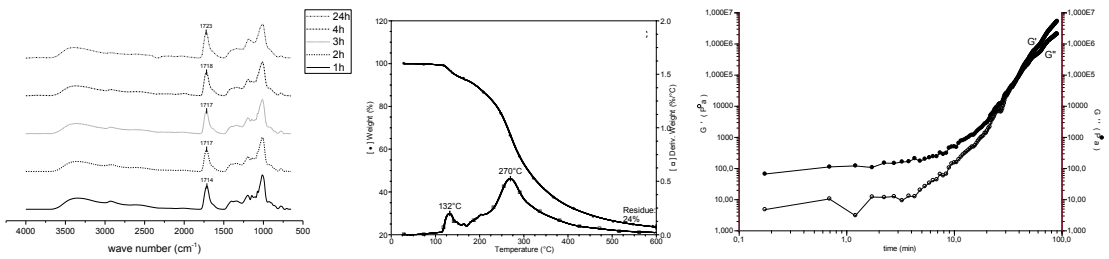

Figure 1. FTIR spectra of composition containing 40% citric acid at different heating times at 140ºC (left). TGA. and rheogram at 140ºC of compositions containing 40% citric acid (from left to right).

S11: *Polímeros para Aplicaciones Avanzadas*

SÍNTESIS Y CARACTERIZACIÓN DE COPOLÍMEROS DE FLUORENO Y ANILINA VIA SUZUKI EN CONDICIONES NO CONVENCIONALES

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Palabras Clave: *Polifluorenos, policondensación vía Suzuki, microondas, fluorescencia.*

Los polifluorenos han atraído un considerable interés a la comunidad científica principalmente por sus diferentes campos de aplicación y por su gran versatilidad sintética, tanto en la cadena lateral como en la principal, debido a que estas modificaciones estructurales inciden directamente en las propiedades del material [1]. Los polímeros π-conjugados con grupos aminos (-NH_2) en la cadena principal aromática no han recibido tanta atención si se compara con sus análogos conductores, las polianilinas. Además, desde el punto de vista sintético, la búsqueda de nuevos procesos de fabricación y obtención de polímeros conjugados de forma más eficaz en menor tiempo empleando métodos no convencionales constituye un reto adicional en la obtención de estos polímeros.

En este trabajo se presenta la preparación y evaluación de copolímeros de fluoreno y anilina (copoli-[9,9-bis(hexil-fluoren-2,7-diilo)-alt-co-(2/3-aminobenzen-1,4-diilo)]) via Suzuki en condiciones no convencionales. El estudio se ha realizado comparando el rendimiento y la distribución de pesos moleculares de las macromoléculas obtenidas, así como la regioregularidad de las díadas obtenidas (por emplear un monómero asimétrico) para cada una de las condiciones ensayadas. Los parámetros de síntesis asistida con microondas se han estudiado empleando diferentes métodos de control (potencia, presión y temperatura) y se han modificado las variables típicas de interés: volumen, catalizador (tipo y porcentaje), disolvente, temperatura y tiempos de reacción. Empleando esta metodología se alcanzan valores de rendimiento muy aceptables (>85%) con pesos moleculares promedios (aprox. 20kg/mol) en 20 minutos de reacción a 135 ºC, en tolueno empleando paladio cero al 3% como catalizador, mientras que, en condiciones clásicas, es necesario al menos 24 horas para obtener un resultado similar. Los copolímeros obtenidos han sido caracterizados mediante técnicas espectroscópicas clásicas de IR y RMN, así como técnicas específicas GPC y TGA. La caracterización óptica (excitación y emisión) de este copolímero no presenta diferencia entre distintos lotes fabricados, sin embargo, hay un claro efecto solvatocrómico en función de los disolventes probados y de su solubilidad. En definitiva, esta nueva metodología aplicada a la fabricación de polifluorenos nos permite alcanzar con buen rendimiento productos, de un tamaño apropiado para realizar ensayos biológicos minimizando los tiempos necesarios para conseguir estos polímeros y sus derivados.

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DEVELOPMENT OF POLAR POLYMORPHS IN PVDF NANOCOMPOSITES

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Keywords: *Polyvinylidene fluoride, polymorphs, electromagnetic interference, carbon nanotube.*

Polyvinylidene fluoride, PVDF, is a specialty plastic material belonging to the fluoropolymer family. It is used generally in applications requiring the highest purity, strength, and resistance to solvents, acids, bases and heat and low smoke generation during a fire event. Compared with other fluoropolymers, it has an easier melt processing because of its relatively low melting point at around 177 °C. Moreover, it has a low density (approximately 1.78 g/cm^3) compared with other fluoropolymers. PVDF shows excellent chemical resistance, good physical and thermal stability and a fascinating polymorphism [1 and refs. therein]. Depending on the crystallization conditions PVDF may present different well-known crystalline structures. The α phase is non-polar whereas the β, γ and δ phases are polar, the β one exhibiting improved pyroand piezoelectric properties [1] The existence of these polar crystalline structures confers a unique electric behavior to PVDF.

Recent investigations on either PVDF-copper or PVDF-aluminum nanoparticles hybrids display a promising attenuation of the electromagnetic radiation, enabling them as suitable materials for radiation protection [2, 3]. The polymorph developed in those nanocomposites was the α form, i.e., a non-polar crystalline cell. Carbon nanotubes promote the formation of the β polymorph and PVDF based composites with those carbon derivatives are now proposed to evaluate the importance of presence of the different crystalline structures on the final properties.

Agradecimientos: Se agradece la financiación de esta investigación al MINECO (proyecto MAT2013-47972-C2-1-P). The synchrotron experiments were performed in the BL11-NCD beamline at ALBA Synchrotron Light Facility with the collaboration of ALBA staff.

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SYNTHESIS OF POLYMERIC NANOPARTICLES FOR PACKAGING REINFORCEMENT APPLICATIONS

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Keywords: *Nanoparticles, PHBV, Starch.*

Polymeric nanoparticles have received an increasing scientific interests over the last years, developing of different techniques for synthesis, control of size and shape, characterization, and functionalization of nanoparticles allow a very wide range of applications for the nanoparticles in different areas like medicine, cosmetics, chemical catalysis etc. Our project is focusing on the synthesis and characterization of biodegradable, biocompatible polymeric nanoparticles from natural sources, being used afterwards in reinforcement of biodegradable films as main application.

Nanoparticles of Poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) and starch were synthesized via emulsification/solvent evaporation [1,2] and nanoprecipitation methods [3], different synthesis were performed changing some parameters of the reactions like the stabilizer, stabilizer concentration, way of solvent evaporation, polymer concentration and the solvents to study the effect of these parameters on the size, morphology and the yield of the reaction.

The size distribution and the morphology of the obtained nanoparticles were characterized using DLS and SEM.

The aim is to produce a high yield of proper sized nanoparticles via a process capable to be scaled up to industrial level production.

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THERMAL AND MORPHOLOGICAL CHARACTERIZATION OF POLY(3-HYDROXYBUTYRATE-CO-3-HYDROXYVALERATE)(PHBV) BIONANOCOMPOSITES

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Key Words: *PHBV, Bionanocomposite, Thermal Properties, Morphological Properties*

Substituting petroleum based conventional plastics with biodegradable and environment friendly polymers obtained from natural resources attracts topics of many recent investigations due to the advantages of this group of materials, e.g. biocompatibility and biodegradability. However, mentioned material suffering from some disadvantages like poor mechanical, thermal and barrier properties which can be solved by blending with other polymers or introducing suitable nanofillers. Incorporating of nanoparticles to PHBV matrix with the goal of improved thermal, mechanical, processing and barrier properties had been reported [1-3].

The purpose of this work is to study morphological and thermal properties of bionanocomposites of PHBV with different concentrations of carbon nanocellulose crystal (CNC) and carbon nanocellulose fiber (CNF) prepared by cast film method. In this regard, scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) will be used for morphological and thermal studies respectively.

ACKNOWLEDGMENT:

Financial support was provided from Ministerio de Economía y Competitividad (MAT2013-41892-R, Project NanoCompBioPol) and Xunta de Galicia Government (Autonomous Community Government) and FEDER: Program of Consolidation and Structuring Competitive Research Units (GRC 2014/036).

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EVALUACIÓN DEL INCREMENTO DE LA CONDUCTIVIDAD ELÉCTRICA Y TÉRMICA EN COMPOSITES DE POLIAMIDA 12/POLIAMIDA 6/ NANOTUBOS DE CARBONO

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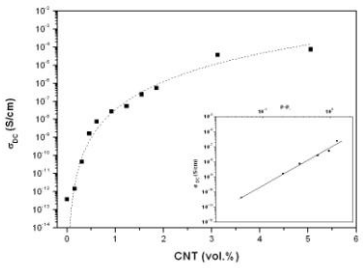
Palabras Clave: *nanotubos de carbono, poliamidas, conductividad eléctrica, conductividad térmica*

La obtención de nanocompuestos conductores, dispersando nanotubos de carbono (MWCNTs) en matrices poliméricas no conductoras es un tema de gran interés tanto desde el punto de vista científico como tecnológico. La introducción del nanorelleno conductor en una mezcla inmiscible como la poliamida 12/poliamida 6 (PA12/PA6) puede favorecer la disminución de la concentración umbral límite a partir de la cual se produce el fenómeno de percolación eléctrica [1].

Por otra parte, para muchos dispositivos electrónicos y circuitos integrados se requieren materiales que, además de unas determinadas propiedades eléctricas, permitan una buena disipación del calor indeseado que se genera durante su funcionamiento. Esto es un hándicap para la mayoría de las matrices poliméricas, aunque su aditivación con nanorellenos conductores podría mejorar sus propiedades térmicas [2].

En este trabajo, se han obtenido nanocompuestos poliméricos diluyendo una masterbatch con un 15% en peso de MWCNTs predispersos en una matriz de PA12, en una mezcla de PA12/PA6 con la misma proporción de poliamidas, mediante mezclado en fundido. Se han estudiado diferentes contenidos de nanotubos en la matriz (de 0 al 5% en volumen).



Finalmente, se han evaluado la conductividad eléctrica (figura 1) y conductividad térmica de los nanocompuestos en función del contenido de nanotubos, correlacionando dichos resultados con la morfología de los materiales.

Figura 1: σ_{dc} **frente a CNT (% vol.)**

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POLÍMEROS HELICOIDALES: SOLDADO UNIVERSAL

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Palabras Clave: *Polímeros helicoidales, polifenilacetilenos, sargento, soldado universal, amplificación de quiralidad.*

Los polifenilacetilenos (PPA) son polímeros helicoidales dinámicos en los cuales es posible modular el sentido de giro de la cadena polimérica a partir de estímulos externos[1]. Dentro de las propiedades que presentan, se encuentra un fenómeno de amplificación de quiralidad denominado *"**Efecto Sargentos y Soldados**"*, presente en copolímeros donde una pequeña fracción de unidad monomérica quiral es capaz de ordenar las unidades monoméricas aquirales presentes a lo largo de toda la cadena del copolímero[2]. En este trabajo, se estudia una variable del **clásico** *"**Efecto Sargentos y Soldados**"*[3] aplicado en copolímeros derivados de PPA con ambas unidades monoméricas quirales, donde la unidad monomérica que actúa como soldado universal (derivado del *ácido metoxifenilacético, MPA*)[4,5] obedece las ordenes de la unidad que actúa como sargento (derivado del *ácido 9-antril-metoxiacético, 9-AMA*), independientemente de la configuración absoluta que presente.

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POLÍMEROS HELICOIDALES COMO SENSORES DE AMINAS

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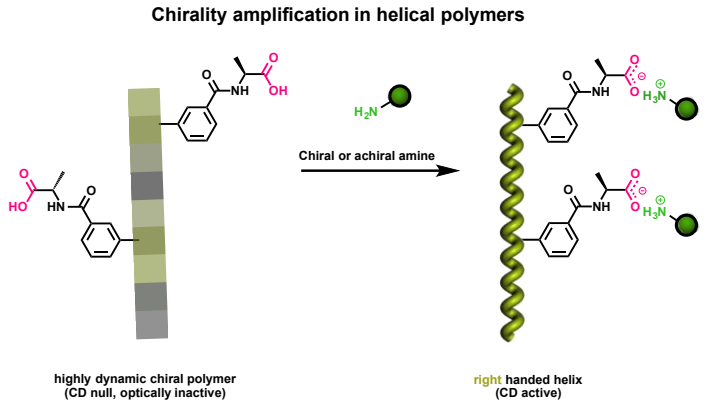
Palabras Clave: *polímeros helicoidales, polifenilacetilenos, amplificación de quiralidad, sensores.*

Los polifenilacetilenos son un tipo de polímeros flexibles y altamente dinámicos, lo que le confiere unas excelentes propiedades como sensores cuando se enfrentan a estímulos externos [1] [2] [3]. Esta característica se aprovechó para diseñar una serie de polímeros sustituidos en posiciones *para*- y *meta*- conteniendo dos aminoácidos distintos en sus "pendants", alanina y glicina. El empleo de estos aminoácidos nos permite estudiar el efecto del centro quiral y del tamaño del sustituyente en la estructura helicoidal.

Los aminoácidos de alanina y glicina están unidos al esqueleto fenilacetilénico a través del extremo *N*-terminal, quedando así libre el extremo *C*-terminal y por tanto, el grupo carboxilo del aminoácido. Dicho grupo funcional se emplea para posibles aplicaciones como sensores de moléculas orgánicas, iones, disolventes, pH…

En este trabajo se ha evaluado la capacidad sensorial de los polifenilacetilenos generados, así como el estudio de la interacción supramolecular ácido-amina que se lleva a cabo en disolvente orgánico prótico como MeOH y también en H_2O.



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SENCILLO TRATAMIENTO PARA LA OPTIMIZACIÓN IRREVERSIBLE DE LA CONDUCTIVIDAD ELÉCTRICA DE POLI(3,4-ETILENDIOXITIOFENO)

Margarita Sanchez-Jiménez,[1] Rafael S. Peres,[2,3] Francisco Casellas,[4] Carlos A. Ferreira,[3] Lourdes Franco,[2] Jordi Puiggalí,[2,5] Francesc Estrany,[1,5,*] and Carlos Alemán[2,5,*]

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Palabras Clave: *conductividad eléctrica, reorganización estructural, microcristales, mecanismo de percolación.*

Se propone un tratamiento cíclico de calentamiento-enfriamiento para mejorar irreversiblemente la conductividad eléctrica de films de PEDOT dopado con ClO_4^-, obtenido según estudios anteriores [1]. El ciclo consiste en aumentar la temperatura de las muestras (1 ºC/min) de 25 ºC a 70 ºC y enfriarlas hasta 25ºC de nuevo (0,5 ºC/min). Se usaron acetonitrilo y agua como medios de polimerización del PEDOT.

La resistencia eléctrica del PEDOT se midió por el método de dos puntas. El film recibe calor disipado en una resistencia por efecto Joule modulando la corriente que fluye a su través que proviene de una fuente de voltaje continuo. Así tenemos control gradual y continuo de la temperatura de la película. Las conductividades eléctricas de films preparados en acetonitrilo y agua aumentan $\times$1.8 y $\times$8.6 respectivamente.

Se realizaron análisis morfológicos (SEM), topográficos (AFM) y estructurales (XRD y DSC) para explicar la mejora de la conductividad. Ell ciclo térmico provoca re-disposiciones estructurales locales según la porosidad del PC. En acetonitrilo, promueve la reorganización de la estructura compacta inicial favoreciendo la formación de microcristales que reducen la orientación aleatoria de las cadenas[2]. Mientras en solución acuosa, promueve un mecanismo de percolación en que se forman agregados sub-micrométricos (detectados como partículas poliédricas en la superficie) junto a procesos de fusión-recristalización [3].

Las ventajas del tratamiento propuesto son simplicidad, irreversibilidad y efectividad de incrementos muy moderados de temperatura.

Agradecimientos

Este trabajo fue posible gracias a fondos MICINN-FEDER (MAT2012-34498 y MAT2012-3625) y de la Generalitat de Catalunya (XRQTC). Los autores también agradecen a las agencias gubernamentales brasileñas CNPq y CAPES (proceso BEX 457 13736124) para la beca de RS Peres.

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S11: *Polímeros para Aplicaciones Avanzadas*

ENHANCING THERMOELECTRIC CHARACTERISTICS OF POLYANILINES

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Keywords: *polyaniline, PANI, conducting polymer, electrical, thermal conductivity.*

There is currently an increasing interest in both the scientific community and society in general to design innovative thermoelectric materials able to improve the efficiency of clean energy generating devices. In this context, conducting composite materials based on polyanilines (PANI) with enhanced thermoelectric properties are worthwhile studying. As a first requirement, a worthy thermoelectric material should combine high electric conductivity while simultaneously decreasing or keeping low thermal conductivity [1].

To fulfil this objective, new synthetic methods for PANI have been assayed in order to attain a higher level of structural order of PANI molecules, in particular "nano-structured materials", as this new morphology improves the thermoelectrical properties. The preparation of PANIs has been adapted from the methods described by Dopico et al. [2] and Park et al. [3], which consist in emulsion polymerizations involving a monomer (aniline), an oxidant (ammonium persulfate) and a dopant, either organic (dodecylbenzensulfonic acid) or inorganic (HCl), with an excess of dopant in relation to aniline concentration. Three different types of synthesis have been performed: direct synthesis, "in situ-polymerization" of PANI/carbon nanotubes (CNTs) composites and an indirect route involving additional steps "undoping-redoping".

The synthesized PANIs have been characterized by several techniques: electrical and thermal conductivity (Table 1), thermal analysis, scanning electron and transmission microscopy, elemental analysis and FTIR.

Table 1. *Electrical and thermal conductivity results of PANI samples at 25□C.*

	Electrical conductivity range (S/cm)	Thermal conductivity range (W/m·K)
PANI direct synthesis	0.7- 9.6	$8.9 \cdot 10^{-2}$-0.159
PANI/CNTs composites	16.7- 24.3	0.253-0.265
PANI undoping-redoping	5.5-17.3	0.220

The above results show that the modified PANIS comply with the basic properties of promising thermoelectric materials.

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EMPLEO DE POLÍMEROS DE IMPRESIÓN MOLECULAR (MIPs) PARA LA PURIFICACIÓN DE EXTRACTOS NATURALES DE APLICACIÓN EN LA COSMÉTICA NATURAL

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Palabras Clave: *Polímeros molecularmente impresos, polifenoles, cosmética natural*

La cosmética natural se ha convertido en los últimos años en una alternativa a la cosmética convencional no sólo para las personas que padecen algún tipo de enfermedad, sino también para quienes prefieren utilizar productos de origen natural para el cuidado de la piel, cabello, etc. Las plantas contienen principios activos altamente efectivos que pueden ser utilizados en la formulación de distintos productos cosméticos. Entre estos principios activos se encuentran los polifenoles, metabolitos secundarios presentes en todas las plantas vasculares que poseen una elevada capacidad antioxidante. Los polifenoles se caracterizan por contener en su estructura uno o varios anillos de benceno y uno o varios grupos hidroxilícos. Esta estructura hace que tengan una gran capacidad para donar electrones o protones, lo cual permite que puedan captar especies moleculares de oxígeno activo como radicales superóxido o hidroxilo, peróxido de hidrógeno, entre otros [1].

Este trabajo, enmarcado en el proyecto CosmetInnova, se ha centrado en el desarrollo y puesta a punto de una metodología que permita purificar y concentrar polifenoles presentes en estractos naturales (té verde, rooibos, alcachofa, bagazo de uva, etc…) mediante la utilización de MIPs. Como primera aproximación y dado que se trata de un grupo diverso de sustancias, los estudios se han llevado a cabo con un material no impreso molecularmente (NIP), formulado con hidroxi-etil-metacrilato (HEMA) como monómero, dimetacrilato de etilenglicol (EGDMA) como agente entrecruzante, como iniciador el 2,2'-azo-bis-isobutirilnitrilo (AIBN) y acetona como disolvente. Sobre la base de estudios previos [2], se utilizó como método de purificación y concentración la dispersión de matriz en fase sólida. Como disolventes de elución se han probado agua, agua acidificada e hidróxido amónico a distintas concentraciones.

El método ensayado ha permitido la separación selectiva de los polifenoles seleccionados en los distintos extractos naturales estudiados, obteniéndose porcentajes de elución elevados utilizando agua acidificada como disolvente de elución. Asimismo, ha sido posible obtener extractos líquidos enriquecidos en polifenoles.

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DESARROLLO DE UNA METODOLOGÍA DE EXTRACCIÓN EN FASE SÓLIDA CON POLÍMEROS DE IMPRESIÓN MOLECULAR PARA LA PURIFICACIÓN Y CONCENTRACIÓN DE TETRAHIDROCANNABINOL EN ORINA

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Palabras Clave: THC, *MIP, especificidad, selectividad, MISPE*

Los polímeros de impresión molecular (MIPs) son materiales sintéticos altamente específicos y selectivos, propiedades que los han convertido en la alternativa ideal a los adsorbentes convencionales empleados en las técnicas de preparación de muestra. De ellas, la extracción en fase sólida con MIPs (MISPE) es la más utilizada. El auge de su uso se debe principalmente a su simplicidad, rapidez, eficacia, reproducibilidad, posibilidad de automatización y bajo coste[1].

La eficacia del reconocimiento molecular de un MIP depende directamente de la estabilidad del complejo formado entre la molécula plantilla (analito) o análogo estructural (mimic) y el monómero de funcionalidad complementaria en un disolvente apropiado[2]. Aunque otros aspectos relativos a la síntesis, como el propio disolvente (porógeno), el agente entrecruzante responsable de la formación de la red polimérica o las condiciones de polimerización (térmicas o fotoquímicas) influyen en las propiedades de enlace del MIP; así como el tipo de técnica preparativa de MIP ('bulk', polimerización por precipitación, etc.) e incluso la naturaleza de la muestra. Para lograr un buen rendimiento en MISPE, es imprescindible la optimización de todas estas variables[3].

Este trabajo describe la puesta a punto de una metodología MISPE para la determinación de la principal sustancia psicoactiva indicadora del consumo de cannnabis, el tetrahidrocannabinol (THC), en muestras de orina[4]; desde el proceso de diseño del MIP a través de ensayos de unión post-polimerización en NIPs (polímeros no impresos, preparados en ausencia de plantilla) y de la modelización molecular, hasta la optimización del procedimiento MISPE (adsorción-desorción), pasando por la caracterización química del polímero (perfil cinético, selectividad cruzada…).

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ANÁLISIS DE LA DEGRADACIÓN DEL PLGA PARA IMPLANTOLOGÍA ORAL

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Palabras Clave: *PLGA, DSC, odontología, regresión no lineal, statistical learning*

Para adaptarse a la demanda funcional dentro de la medicina regenerativa y, en concreto, de la cirugía maxilofacial, es crucial partir de una adecuada selección de los materiales, efectuada de acuerdo a criterios relacionados con la variación de sus propiedades con respecto al tiempo. Conocer y estimar la evolución de estas propiedades, sujetas a la acción de factores de degradación física, química, biológica y biomecánica, es fundamental para una correcta aplicación [1].

El objetivo de este trabajo es estimar el ciclo de vida de biopolímeros poli(D,L-lactida-co-glicolico), PLGA comerciales, aplicados en medicina regenerativa así como evaluar la influencia de diversos factores (como el peso molecular) en su degradación. Para este propósito, se han medido con respecto al tiempo diversas propiedades críticas para la calidad del PLGA (50:50), obtenido a 3 pesos moleculares (17000, 44000 y 153000 g/mol). Éstas son, por un lado, la temperatura de transición vítrea (T_g) obtenida por calorimetría diferencial de barrido (DSC) y, por otro, la pérdida de masa y el *pH* medidos en ensayos de degradación in vitro, en disolución salina (SBF) y a 37ºC.

Se ha modelizado mediante regresión no lineal con función logística [2] las relaciones existente entre el pH, la masa perdida y la T_g con respecto al tiempo, estimando el camino de degradación de cada material. Igualmente, se ha definido la relación entre la T_g y el *pH* mediante un modelo de regresión logística. Se ha evaluado la influencia del peso molecular en la masa perdida, variación de *pH* y T_g mediante modelos estadísticos de análisis de la varianza (ANOVA) uni- y multivariantes [2]. Se ha establecido una relación entre el tiempo de vida debido a envejecimiento térmico [3] y el tiempo de vida debido a procesos de hidrólisis.

La modelización estadística de los datos de degradación ha permitido relacionar la composición del PDLG con la variación de sus propiedades, su degradación y tiempo de vida. Los resultados obtenidos permiten elaborar un criterio de selección de este tipo de materiales según las aplicaciones.

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NEW POLYURETHANES FOR BIOMEDICAL APPLICATIONS

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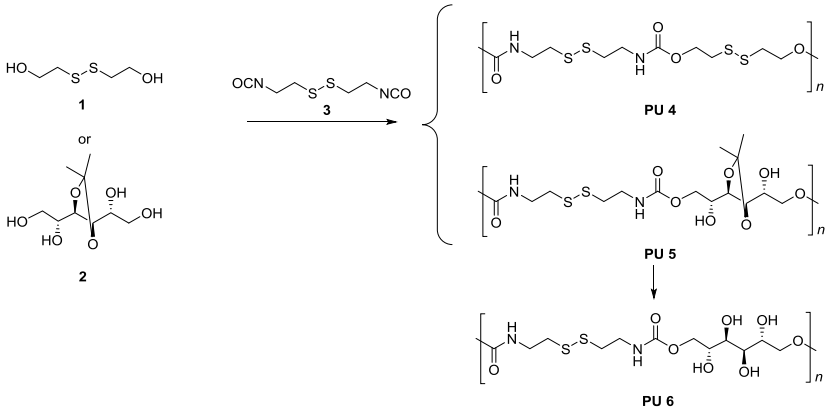
Keywords: *carbohydrate-based polyurethanes, biodegradable polymers, biomedical applications*

Carbohydrates stand out as readily available raw materials for the synthesis of biodegradable and biocompatible polymers [1]. Furthermore, the presence of disulfide bonds along the polymer chains will ensure the biodegradation of the polymers under reductive conditions. Thus, we have prepared a series of polymers containing disulfide bonds and carbohydrate moieties to be evaluated as colon-specific drug delivery systems (CDDS).



Scheme 1

We now describe the synthesis of polyurethanes (PU) (Scheme 1) by the polyaddition reaction of 2,2'-ditihiodiethanol (**1**) or 3,4-di-*O*-isopropylidene-D-mannitol (**2**) and bis(beta-isocianatoethyl) disulfide (**3**). Hydrolysis of the *O*-protecting groups of PU **5** afforded the corresponding fully polyhydroxylated PU. Further crosslinking reaction of PU **5** or PU **6** with **3** will be also described. Rheological characterization of PU **4** showed good compression characteristics based on its Carr index and inter-particle porosity results (28% and 1.07, respectively) [2]. Preliminary studies of multiparticulate systems coated with PU **4** for CDDS are under course.

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NEW POLYTRIAZOLES FOR BIOMEDICAL APPLICATIONS

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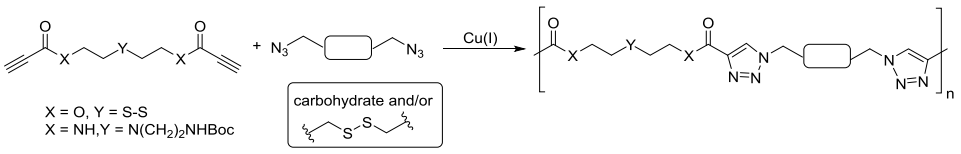
Keywords: *carbohydrate-based polytriazoles, biodegradable polymers, biomedical applications*

Synthetic carbohydrate-based polymers have shown to be biodegradable and biocompatible materials [1]. On the other hand, positively-charged biodegradable polymers are being studied as non-viral vectors in gene therapy [2]. In addition to this, cationic polymers containing disulfide bonds promote DNA release under reductive conditions [3].

In order to combine the above mentioned features, we now describe the synthesis of carbohydrate-based polytriazoles by 1,3-dipolar cycloaddition reactions in the presence of Cu(I) (Scheme 1). First, we prepared the appropriate monomers: diazido-carbohydrate derivatives, diazido derivatives containing disulfide bonds, and dialkyne terminal monomers containing protonable amino groups or disulfide bonds.



Scheme 1

These polytriazoles were obtained in good yields, molecular weights in the range 24,000-84,000 g/mol, and narrow polydispersities (1.1-1.2). Deprotection of the amino pendant groups leads to polycationic polymers. Physicochemical characterization of the new polymers will be described.

Acknowledgements: We thank the Ministerio de Economía y Competitividad of Spain and the Junta de Andalucía for the financial support.

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NUEVOS POLÍMEROS AROMÁTICOS CON CAPACIDAD DE ENTRECRUZAR POR VÍA FOTOQUÍMICA PARA MEMBRANAS DE SEPARACIÓN DE GASES CON PRODUCTIVIDAD MEJORADA

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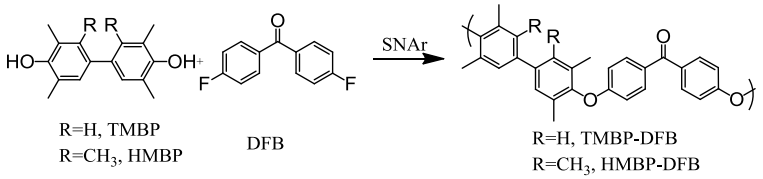
Palabras Clave: *PEEKs, separación de gases, entrecruzamiento UV.*

Se ha sintetizado una familia de poliéter cetonas, PEEKs (Esquema1), mediante reacción entre dioles aromáticos rígidos y difluorobenzofenona. De este modo, se han obtenido polímeros amorfos de altos pesos moleculares, con elevada resistencia térmica y altas Tg, capaces de entrecruzar mediante radiación UV. Ambos polímeros formaron películas con excelentes propiedades mecánicas que pudieron ser probados como membranas de filtración de gases.



Polímero	Tg (ºC)	Densidad (g/cm3)	η_{inh} (dL/g)
TMBP-DFB	270	1,1179	1,34
HMBP-DFB	270	1,1007	0,64

Esquema 1. *Estructuras y propiedades de las polieter cetonas de este trabajo.*

Los resultados obtenidos muestran que el efecto del entrecruzamiento UV de las membranas produjo una disminución considerable en la permeabilidad de los gases He, O_2, N_2, CH_4 y CO_2, junto con un aumento muy apreciable de la selectividad. La productividad de las membranas entrecruzadas para la pareja O_2/N_2 resultó excelente, superando claramente el límite de Robeson de 1991 y acercándose al límite de 2008, como puede verse en la Figura 1.

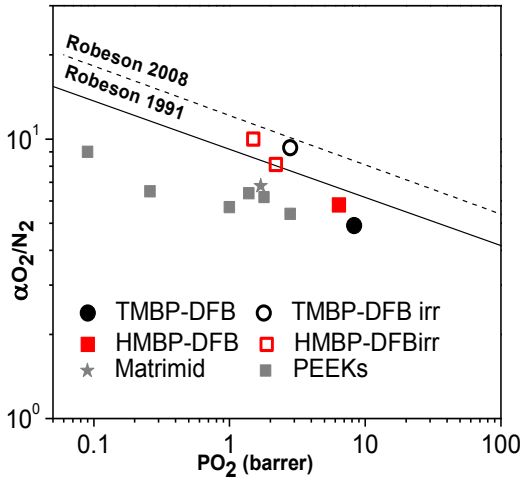


Figura 1. *Gráfico de Robeson para la pareja de gases O_2/N_2*

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REUTILIZACIÓN DE PEBD Y CELULOSA PROCEDENTES DEL SECTOR BANANERO ECUATORIANO PARA LA OBTENCIÓN DE ECO-MATERIALES COMPUESTOS

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Palabras Clave: *PEBD. Raquis de Banano. Análisis Térmico*

La industria bananera de Ecuador utiliza un elevado porcentaje de materiales poliméricos durante el proceso de producción de banano que son desechados al medio o tratados por incineración.

En este trabajo se pretende iniciar el proceso de reutilización de las fundas de polietileno de baja densidad (PEBD) desechadas en el cultivo de banano para darles un uso alternativo en la obtención de eco-materiales compuestos (E-MC). [1]

Se llevaron a cabo las caracterizaciones de los E-MC obtenidos a partir de PEBD y la fibra celulósica de raquis de banano (FCRB), fabricados en diferentes proporciones por medio del mezclado por extrusión. [2]

Como simulador de las fundas utilizadas, se seleccionó un PEBD comercial (Lupolen 1840 H) de la empresa BVVBA Basell poliolefinas, en forma de pellets de 6.5 mm de largo y 2 mm de diámetro, con densidad de 0.919 g/cm^3 a 23ºC y una velocidad de fusión de masa (MFR) 1.59 g/10 min. Este PEBD se mezcló con fibra de celulosa obtenida a partir de los desechos del raquis de banano. El raquis fue tratado en dos procesos; uno mecánico, consistente en selección, secado y molienda, y otro cualitativo en el que se aplicó un tratamiento químico para la extracción de la celulosa. El material resultante fue sometido a un proceso de secado en estufa a 40ºC durante 24 horas.

Se prepararon diferentes proporciones de PEBD y fibras celulósicas (0-30% en peso). Los E-MC obtenidos por extrusión se analizaron mediante calorimetría diferencial de barrido (DSC) y análisis termogravimétrico (TGA).

AGRADECIMIENTOS: Este trabajo ha sido financiado por la Xunta de Galicia y cofinanciado con fondos FEDER, a través del Programa de Consolidación y Estructuración de las Unidades de Investigación Competitivas del Sistema Universitario de Galicia (GRC 2014/036).

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A CONTRIBUTION TO THE STRUCTURAL AND SYNTHETIC STUDY OF PEPTIDES BASED ON POLYHYDROXYLATED CYCLOPENTANE AND CYCLOPENTENE β-AMINOACIDS

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Keywords: *sugars, amino acids, peptides*

Peptides play a crucial role in biology. However, their use as therapeutic agents suffers from their poor metabolic stability and transport properties together with their limited structural diversity, which is related to the limited number of secondary structures and backbones resulting from the small number of proteinogenic amino acids. Accordingly, a great deal of work has been carried out in recent years aimed at the synthesis of non-natural amino acids. This represents the first step for the introduction of elements of diversity for the development of peptidomimetics with high levels of diversity and the capability to generate highly ordered structures that may act as new drugs and overcome the pharmacological limitations of proteins.[1]

Cyclic β-amino acids, became a hot topic in synthetic and medicinal chemistry as a result of their present interest as stabilizers of peptide conformations, a property that has been related to the high tendency of their homopolymers to fold in rigid secondary structures in short peptide sequences.[2]

As a part of an ongoing project aimed at the synthesis of polyhydroxylated cicloalkane β-amino acids, we will present two complementary protocols involved in the synthesis of the polysubstituted cyclopentane and cycloptene β-amino acids satated in Figure 1. Preliminary studies on the incorporation of β-amino acids **1** and **4** into peptides will also be reported.

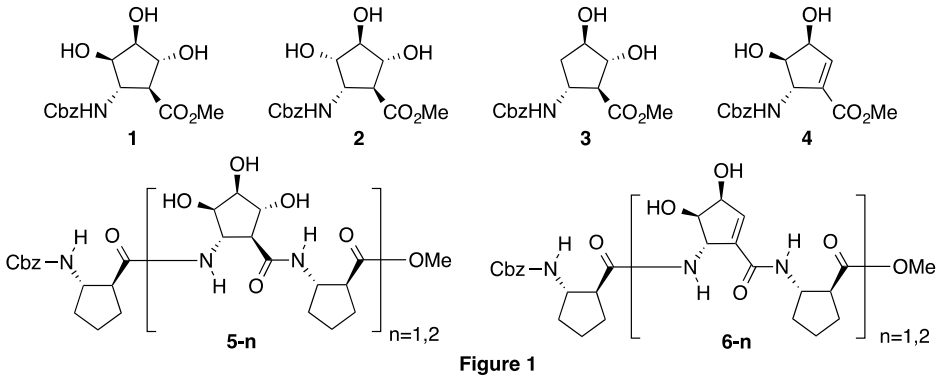

Figure 1

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S11: *Polímeros para Aplicaciones Avanzadas*

DESARROLLO DE HIDROGELES Y NANOPARTÍCULAS FLUORESCENTES

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Palabras Clave: *ELR*, *hidrogel, fluorescencia, EGFP*

Los recombinámeros tipo elastina (ELRs, en inglés), han estado involucrados en el desarrollo de diferentes dispositivos biomédicos, como hidrogeles biocompatibles y bioactivos utilizados como soportes que simulan las propiedades de la matriz extracelular, con una temperatura de transición (sol-gel) inferior a la fisiológica, lo que permite su uso como material inyectable [1].

Su origen recombinante permite la fusión de secuencias de aminoácidos bioactivas que permiten la utilización de estos ELRs en distintas aplicaciones de ingeniería de tejidos. Con el objeto de mejorar la trazabilidad del material al ser implantado o inyectado en un organismo, se ha fusionado la proteína verde fluorescente mejorada (EGFP) [2] a un SELR [3] con la capacidad de auto-ensamblarse para formar nanopartículas (NPs) a bajas concentraciones, pudiendo ser recubiertas con un ELR con secuencias de adhesión celular, e hidrogeles inyectables a otras más altas.

El material fue caracterizado por distintos métodos, incluyendo el análisis de las NPs y de los hidrogeles. La Tt fue determinada por calorimetría diferencial de barrido (DSC), siendo de 16.8ºC en solución fisiológica (PBS), mientras que los resultados de dispersión de luz (DLS) mostraron una distribución de tamaños de partícula amplia, pero estable. Se observaron altos niveles de fluorescencia, tanto cuantitativa como cualitativamente, e incluso se observaron bacterias *E. coli* de expresión fluorescentes por microscopía. Las partículas resultantes de la combinación de ELRs fueron de mayor tamaño que las originales, y con carga superficial positiva, algo muy favorable para la adhesión e internalización celular. Esta capacidad fue analizada y confirmada mediante ensayos celulares *in vitro*. Los hidrogeles fueron formados a 37ºC y se determinó cualitativamente su estabilidad y su fluorescencia.

En conclusión, se ha desarrollado satisfactoriamente un material gelificable y fluorescente. Sus características lo hacen un potencial candidato a ser incluido en dispositivos biomédicos mejorando la trazabilidad del hidrogel y permitiendo determinar su biodegradabilidad y posible migración. Futuros estudios incluirán experimentos de medida de fluorescencia *in vivo* que permitan corroborar su utilidad en biomedicina.

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S11: *Polímeros para Aplicaciones Avanzadas*

DESARROLLO DE BIOCOMPOSITES BASADOS EN ALMIDÓN TERMOPLÁSTICO REFORZADO CON MICROCELULOSA: EFECTO DEL PLASTIFICANTE Y DEL RELLENO

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Palabras Clave: *almidón termoplástico, biocomposites, biopolímero, celulosa microcristalina, glicerol, sorbitol.*

El problema cada vez mayor de los residuos generados por los plásticos derivados del petróleo, así como la escasez de los recursos fósiles, ha estimulado la investigación sobre los biopolímeros renovables. Entre los candidatos a biopolímero para aplicaciones de vida corta, como el envasado, destaca el almidón; debido principalmente a su gran disponibilidad, bajo coste y biodegradabilidad. El almidón no es un verdadero termoplástico, pero en presencia de plastificante, temperatura y cizalla, es capaz de fundir convirtiéndose en almidón termoplástico (TPS), cuyas propiedades se ven influenciadas por el tipo y cantidad de plastificante empleado [1]. El almidón termoplástico, sin embargo, presenta importantes desventajas, como son, su alta afinidad al agua y sus pobres propiedades mecánicas, las cuales además varían con el tiempo debido a la tendencia del almidón a retrogradarse. Una estrategia para solventar estos inconvenientes es mediante la adición de un relleno como refuerzo del TPS. La celulosa microcristalina se presenta como un posible relleno válido, debido a que posee una estructura de polisacárido similar a la del almidón [2].

El objetivo de este trabajo es el desarrollo y estudio de biocomposites de almidón de trigo plastificado con dos polioles de diferente peso molecular y reforzado con celulosa microcristalina, investigando el efecto del tipo de plastificante y de la cantidad de relleno sobre las propiedades térmicas y dinamomecánicas, la cristalinidad y la absorción en agua de los materiales.

Se examinaron tres tipos de plastificantes: glicerol, sorbitol y una mezcla glicerol-sorbitol (1:1); y la cantidad del refuerzo de microcelulosa se varió del 0 al 10% en peso. Los materiales plastificados con sorbitol fueron los que mostraron una mayor estabilidad térmica, menor absorción en agua y mayor rigidez a temperatura ambiente, pero resultaron ser más frágiles.

Ayuda financiera del Ministerio de Economía y Competitividad (MAT2013-41892-R, Project NanoCompBioPol) y la Xunta de Galicia y FEDER; Programa de Consolidación y estructuración de las Unidades de Investigación (GRC 2014/036).

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S11: *Polímeros para Aplicaciones Avanzadas*

RECOMBINAMERO TIPO ELASTINA COMO SISTEMA MUCOADHESIVO DE LIBERACION DE FÁRMACOS

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Palabras Clave: *ELR, elastin-like, mucoadhesión, hidrogel, liberación, fármaco*

El objetivo de este trabajo es el desarrollo de un sistema de liberación controlada de fármacos a través de la mucosa intestinal. La mucosa es un tejido que recubre las paredes de órganos que están en contacto con el exterior y desempeña funciones de protección, secreción y absorción. Para facilitar su función protectora, la mucosa se encuentra recubierta de un gel formado principalmente por mucina, agua y sales. Dado que un sistema mucoadhesivo establece un íntimo contacto con la mucosa, es un sistema ideal para la dosificación de fármacos, pues permite un largo tiempo de permanencia en el lugar de dosificación. Los recombinameros tipo elastina (ELRs) son polímeros proteicos basados en la repetición de pentapéptidos presentes en la elastina natural, diseñados y construidos mediante técnicas de ADN recombinante y bioproducidos en *E.coli*.

Se diseñó un ELR con dos partes y funciones distintas: una cuya función es la de formar geles físicos en respuesta al aumento de temperatura y otra cuya función es la de establecer la interacción con la mucina. La formación de geles en respuesta a la temperatura fue evaluado mediante reología oscilatoria mientras que la interacción ELR con la mucina fue evaluada utilizando diferentes técnicas: variación del ángulo de contacto[1] para medir la capacidad de esparcimiento ELR-mucina, sinergismo reológico[2] que permite cuantificar el aumento de las propiedades reológicas que derivan de la interacción ELR-mucina, así como técnicas de dispersión de luz como la turbidimetría[3] o la variación en la distribución de tamaños de las partículas de mucina[4], variación en la carga superficial de las partículas de mucina (potencial Z)[3], etc... Técnicas que nos permiten determinar si un material es mucoadhesivo o no.

Los resultados obtenidos nos permiten confirmar que el ELR diseñado forma geles físicos reversibles en respuesta a los cambios de temperatura y que el diseño es eficaz a la hora de interaccionar con la mucina. Podemos afirmar pues, que el ELR diseñado es sistema mucoadhesivo candidato a ser utilizado como sistema de liberación de fármacos vía mucosa gastrointestinal.

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S11: *Polímeros para Aplicaciones Avanzadas*

SYNTHESIS OF PEDOT/DWCNT NANOCOMPOSITES FOR THERMOELECTRIC APPLICATIONS

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Key words: *DWCNT, nanocomposites, thermoelectric efficiency*

Thermoelectric devices as an energy source and temperature alternatives have been deeply investigated in the last years. As an alternative to the traditional inorganic materials used as thermoelectric materials, conducting polymers due to their promising thermoelectric properties, such us poly (3,4-ethylenedioxythiophene) can offer great advantages such as low cost of production, easy chemical modification and abundance. The main problem of conducting polymers is that by themselves they are not efficient. Presently, the incorporation of conducting nanofillers, such as CNTs, has increased the thermoelectric properties [1]. The thermoelectric efficiency (TE) of these materials is measured by the dimensionless parameter $ZT=\sigma S^2 T/\kappa$; σ and κ being the electrical and thermal conductivities, respectively, and S the Seebeck coefficient [2]. The usual methods to obtain these nanocomposites have many problems such as: big amount of impurities, heterogeneity and stability. For this reason, the aim of this work was to develop a new method to obtain PEDOT/DWCNT nanocomposites by electrochemical polymerization for thermoelectric applications. Double-walled carbon nanotubes was used such working electrode. They have been previously suspended in aqueous media using cationic surfactant such as cetyl thrimethyl ammonium bromide (CTAB) [3].

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S12. Más Allá de la Química del Grafeno y sus Aplicaciones (BGCA) / Beyond Graphene Chemistry and Applications

Las excepcionales propiedades del grafeno han generado grandes expectativas sobre sus aplicaciones, dando lugar, por ejemplo, a tecnologías emergentes. Este simposio es un foro nacional único para revisar la situación actual, los últimos desarrollos y, no menos importante, las futuras perspectivas, todo ello tanto a nivel de investigación fundamental como de aplicaciones avanzadas, cubriendo no sólo facetas experimentales, si no también teóricas.

The exceptional and unsurpassed properties of graphene have generated great expectation about its applications, giving rise, for example, to emerging technologies. This symposium is a unique national forum to review the present status, the latest developments and, but not least, future prospects, at both fundamental investigation and advanced applications levels, covering not only the experimental side, but also theoretical aspects.

Organizadores:

Ángela Sastre (UHM)

Fernando Langa (UCLM)

José Manuel Pingarrón (UCM)

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Miércoles 21 de Julio 2015

08:40 – 09:40	**PL-4**	***Conferencia Plenaria*** (Común a todos los simposios) **Luis Liz-Marzán** *"Chemical Growth of Metal Nanoparticles: Why and How?"*

Chairman: Fernando Langa

		Nazario Martín
10:00 – 10:30	**S12-IL-01**	*"Modifying Graphene with Electroactive Systems: Towards New Properties?"*
		Enrique Ortí
10:30 – 10:40	**S12-OC-01**	*"Concave Donors as Supramolecular Partners for C_{60} and C_{60} Fragments"*
		Enrique Maroto
10:40 – 10:50	**S12-OC-02**	*"Enantiospecific cis-Trans Isomerization in Chiral Fulleropyrrolidines: Hydrogen-Bonding Assistance in the Carbanion Stabilization in $H_2O@C_{60}$"*
		Mª Antonia Herrero
10:50 – 11:00	**S12-OC-03**	*"Chemical Modification of the CNTs to Modulate their Function"*
11:00 – 11:30		Pausa Café

Chairwoman: Ángela Sastre-Santos

		Paolo Samori
11:30 – 12:00	**S12-IL-02**	*"Taming Functional Complexity in 2D Materials Mastering the Supramolecular Approach"*
		Gema de la Torre
12:00 – 12:10	**S12-OC-04**	*"Dyeing Graphene: Hybrid Ensembles with Phthalocyanines"*
		Mª José Gómez-Escalonilla
12:10 – 12:20	**S12-OC-05**	*"Cicloadición de Nitriliminas a Grafeno. Confirmación Teórica y Experimental"*
		Marina Garrido
12:20 – 12:30	**S12-OC-06**	*"Modificación Supramolecular de Grafeno con Moléculas Electroactivas"*
		Luis Martín Gomis
12:30 – 12:40	**S12-OC-07**	*"Supramolecular Perylenediimide-Graphene Systems as Donor-Acceptor Nanoensembles"*
		Verónica León
12:40 – 12:50	**S12-OC-08**	*"Few-Layer of Graphene from Ball-Milling of Graphite with Triazine Derivatives"*
		Myriam Barrejón
12:50 – 13:00	**S12-OC-09**	*"N-Funcionalizacion de Grafeno N-Dopado"*
		Araceli G. Campaña
13:00 – 13:10	**S12-OC-10**	*"Bottom-Up approach towards Distorted Nanographenes containing Seven-Membered Carbocycles"*
		Sabela Quiroga
13:10 – 13:20	**S12-OC-11**	*"Synthesis and Properties of Nanographenes by Solution Chemistry"*
		Moisés Canle
13:20 – 13:30	**S12-OC-12**	*"Functionalization of Carbon Surface through Photoinitiated Reactions"*
13:30 – 15:30		Comida

Miércoles 21 de Julio 2015

Chairman: José Manuel Pingarrón

15:30 – 16:00	**S12-IL-03**	**Hermenegildo García** *"Metal-Free Catalysts: Graphenes as Sustainable Catalysts"*
16:00 – 16:10	**S12-OC-13**	**Romina Lorca** *"Novel Click Reaction Catalyst based on Gold Nanoparticules and Oligonucleotides for Preparation of Hybrid Nanostructures"*
16:10 – 16:20	**S12-OC-14**	**Marta Puche** *"Inmovilización del Catalizador de Jacobsen en Superficies de Grafenos Dirigida a la Epoxidación Enantioselectiva de Olefinas"*
16:20 – 16:30	**S12-OC-15**	**Ana Primo** *"Copper Nanoparticles Supported on Doped Graphenes as Catalyst for the Dehydrogenative Coupling of Silanes and Alcohols"*
16:30 – 17:00		Pausa Café

Chairman: Nazario Martín

17:00 – 17:10	**S12-OC-16**	**José M. Pingarrón** *"Graphene Grafted with Water-Soluble Polymers for Electrochemical Biosensors"*
17:10 – 17:20	**S12-OC-17**	**Enrique Díez-Barra** *"Graphene Quantum Dots: an Eco-friendly Preparation"*
17:20 – 17:30	**S12-OC-18**	**Gonzalo Martínez-García** *"Inmunosensor Electroquímico para la determinación de Péptido YY en Suero Humano basado en la Química del Diazonio sobre Óxido de Grafeno Reducido"*
17:30 – 17:40	**S12-OC-19**	**Araceli Gónzalez-Cortés** *"Novel Electrochemical Inmunosensor Prepared from Reduced Graphene Oxide-carboxymethylcellulose Hybrid. Application to the Determination of Adiponectin"*
17:40 – 17:50	**S12-OC-20**	**Israel Temprano** *"Epitaxial Growth of Few-layer MoS_2(0001) on FeS_2{100}"*
17:50 – 18:00	**S12-OC-21**	**David Rodríguez-San Miguel** *"Preparation of Corrugated and Porous N-Doped Graphene from Controlled Pyrolysis of Metal-Funcionallized Covalent Organic Frameworks Based on Imine and its Evaluation as Supercapacitors"*
18:00 – 18:30	**S12-IL-04**	**Amaia Zurutuza** *"Impact of Graphene's Properties in Applications"*

18:30	***Sesión de Pósteres*** ***Entrega de Premios GE NaNoMatMol***

18:30	**Reunión del GE de "Nanociencia y Materiales Moleculares"**

Comunicaciones Invitadas (IL)

S12: *Más Allá de la Química del Grafeno y sus Aplicaciones*

MODIFYING GRAPHENE WITH ELECTROACTIVE SYSTEMS: TOWARDS NEW PROPERTIES?

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Keywords: *Electroactive molecules, supramolecular chemistry, graphene.*

Graphene is playing a major role in today's science and technology due to its outstanding mechanical and electronic properties.[1] In particular, this material offers promising opportunities for electronic devices and chemical sensors. The development of new functional structures from different electroactive units and this promising material, able to transform sunlight into electrical or chemical energy are important features for the fabrication of innovative optoelectronic devices. However, to overcome the drawbacks of low solubility and re-aggregation found in solution processes involving graphene layers, covalent or supramolecular chemical derivatization is a requirement prior to their transfer to solid substrates.[2] In this communication, we will present our results on the synthesis of new graphene-based nanohybrids involving different electron-donor moieties, namely exTTF and cyanines, connected through covalent and supramolecular chemical linkages.[3] The detailed characterization of the new chemical nanostructures will be thoroughly discussed. Furthermore, graphene's surface is an excellent scenario to play with a variety of electroactive molecules.[4]

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S12: *Más Allá de la Química del Grafeno y sus Aplicaciones*

TAMING FUNCTIONAL COMPLEXITY IN 2D MATERIALS MASTERING THE SUPRAMOLECULAR APPROACH

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Keywords: *supramolecular chemistry, graphene, nanocomposites, self-assembly.*

Supramolecularly engineered hybrid materials containing graphene are key multifunctional systems for applications in (opto)electronics and energy. However, their practical use requires the optimization of the processing, self-assembly at surfaces using non-conventional methods, their controlled manipulation and responsiveness to external stimuli, and the quantitative study of various physico-chemical properties at distinct length- and time-scales. My lecture will review our recent findings on:

(i) The harnessing of the yield of exfoliation of graphene in liquid media by mastering the supramolecular approach via the combination with ad-hoc functional molecules possessing high affinity for the graphene surface, leading ultimately to the bottom-up formation of optically responsive graphene based nanocomposites for electronics. [1]

(ii) The tuning of the graphene properties by combining them with organic semiconductors as a strategy both to promote hole mobility in an otherwise electron transporting material and to exploit the tunable ionization energy of thermally annealed liquid phase exfoliated graphene to modulate the transport regime as well as to fabricate new memory devices.[2]

(iii) The local thermal reduction of graphene oxide using a laser writer in order to develop very smooth, ultra thin, highly transparent and extremely conducting reduced graphene oxide patterns that can operate as highly sensitive ozone sensor.

Our approaches provide a glimpse on the chemist's toolbox to generate nanocomposites with ad-hoc properties for science and technology of 2D materials.

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S12: *Más Allá de la Química del Grafeno y sus Aplicaciones*

METAL-FREE CATALYSTS: GRAPHENES AS SUSTAINABLE CATALYSTS

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Keywords: *graphene, catalysis, metal-free catalysts.*

Catalysis is dominated by the use of metals that are responsible for the active sites in Lewis acids, oxidation and reduction centers and for coupling reactions. Frequently, precious metals or critical metals are required as catalysts. Critical metals are those of which there exist limited resources, frequently localized in a few geographical areas. Hydrogenation of multiple C-C by Pt or Pd catalysts or naphtha reforming by Pt and Ir are typical process of oil refining and petrochemistry that are carried out at multi-billion ton scale and that make use of noble metals. Due strategic reasons, EU launched in 2011 a program to decrease the European dependency on critical metals, catalysis being named as one of the areas extremely sensitive. For the sake of sustainability, it would be desirable to replace metal catalysts by other materials non containing metals, particularly by carbon-based catalysts. Carbon allotropes have defined structures compared to conventional active carbons and offer an excellent platform to introduce active sites. Among the various carbon nanoforms, graphenes have several advantages as catalysts including availability and sustainability since they can be obtained by pyrolysis from biomass wastes.[1] In the presentation I will discuss the nature of possible active sites introduced in graphenes as defects (Figure 1) and the state of the art and targets in the field.

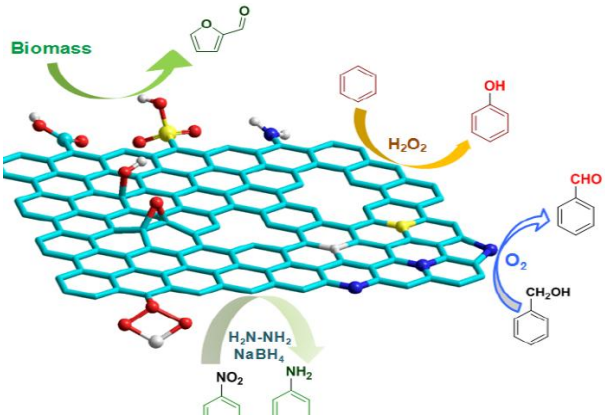

Figure 1. Illustration of possible active sites that can be present on a graphene sheet as consequence of defects, including dangling bonds at the periphery, oxygenated functional groups, doping heteroatoms, holes on the sheet and impurities. The figure also indicates those reaction types that have been reported using graphenes as carbocatalyst.

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S12: *Más Allá de la Química del Grafeno y sus Aplicaciones*

IMPACT OF GRAPHENE's PROPERTIES IN APPLICATIONS

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Keywords: *graphene, thermal properties, applications.*

Graphene has been shown to have remarkable properties such as high charge carrier mobility, high electrical conductivity (when doped), high thermal conductivity, flexibility, transparency and mechanical strength. However, for these properties to be translated into industrial applications many technological challenges and influencing factors have to be overcome.[1] Furthermore, the term graphene covers a family of materials and as a consequence depending on the type of graphene the properties of the material will be different. During this talk I would like to focus on the thermal properties of graphene and the impact that graphene's structure can have on this particular property.[2] More specifically the thermal properties of chemically exfoliated graphene (graphene oxide) and the effect of restoring back the sp^2 structure via thermal treatment.

In addition, I will cover some of the progress that has occurred in graphene applications such as composites,[3,4] biomedical applications (photothermal therapy, biosensors)[5,6] and lighting (OLEDs) where graphene has the advantage of added flexibility but has to guarantee performance similar to that of ITO.[7]

Finally, I should mention that graphene is currently at a research stage and that it will still require a number of years to be industrially relevant.[1]

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Comunicaciones Orales (OC)

S12: *Más Allá de la Química del Grafeno y sus Aplicaciones*

CONCAVE DONORS AS SUPRAMOLECULAR PARTNERS FOR C_{60} AND C_{60} FRAGMENTS

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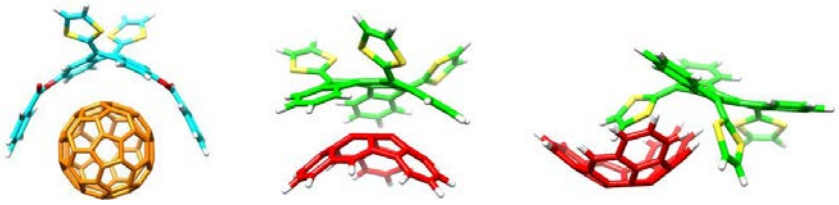
Keywords: *Supramolecular complexes, fullerenes, donor-acceptor, theoretical calculations*

π-Extended tetrathiafulvalene (TTF) derivatives with concave structures have been employed in the construction of non-covalent supramolecular entities involving C_{60} as the electron acceptor. Among these sulfur-containing derivatives, the 9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (exTTF) and the truxene-TTF (trux-TTF) electron-donating systems have been successfully applied in the C_{60} recognition with very high affinities.[1] The trux-TTF fragment (trux-TTF), which absorbs light efficiently in the visible region, has been used, for the first time, as an adequate host to bind a fullerene fragment (hemifullerene $C_{30}H_{12}$).[2] The supramolecular complex formed show charge transfer processes upon photoexcitation.

The nature and strength of the intermolecular interactions determining the formation of the supramolecular associates are investigated using DFT calculations including dispersion correction terms. The structures and absolute binding energies are computed for a series of host compounds involving exTTF derivatives of increasing complexity and trux-TTF. The predicted trends are rationalized in terms of the different intermolecular interactions (π-π, n-π, and CH···π) taking place in the associate. Two different types of conformers are found to compete in energy in forming the supramolecular trux-TTF·$C_{30}H_{12}$ aggregate: concave-convex dimers, dominated by π-π interactions, and staggered assemblies, controlled by CH-π and n-π forces (see Figure)



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ENANTIOSPECIFIC *CIS-TRANS* ISOMERIZATION IN CHIRAL FULLEROPYRROLIDINES: HYDROGEN-BONDING ASSISTANCE IN THE CARBANION STABILIZATION IN $H_2O@C_{60}$

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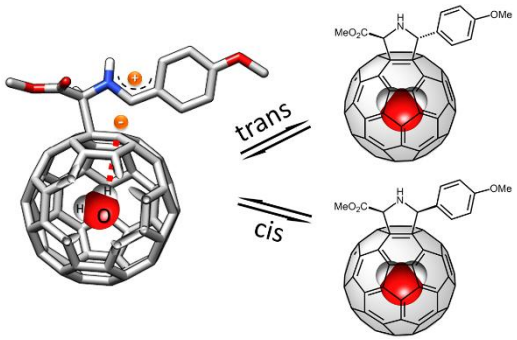
Keywords: *isomerization, fullerenes, endohedral, stereospecificity*

Rearrangement and retrocycloaddition processes on fullerenes have attracted much attention since they reveal the amazing reactivity of these highly strained curved molecules.[1] Thus, fullerene derivatives can, under certain conditions, undergo kinetically controlled retrocycloaddition reactions that have proven their worth in several protection−deprotection protocols.[2] However, despite the interest of the aforementioned chemical transformations, their stereochemical studies have not been properly addressed and still remain as a significant scientific demanding task.

Herein, we report the first *cis−trans* isomerization reaction from enantiomerically enriched fullerene derivatives. The experimental findings and theoretical DFT calculations reveal that this process operates on a completely stereospecific manner.[3] Furthermore, the *cis−trans* isomerization also works efficiently in higher fullerenes and the less-explored endohedral fullerenes, namely $H_2O@C_{60}$. In this regard, we report on an unprecedented behavior of the inner water molecule in assisting the stabilization of the carbanion formed during the isomerization process through hydrogen-bonding (H-bonding) involving a water H atom.



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CHEMICAL MODIFICATION OF THE CNHs TO MODULATE THEIR FUNCTION

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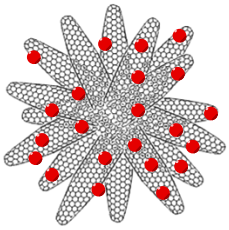
Keywords: *Carbon nanohorns, chemical modification, different applications…*

This communication focuses on the various chemical transformations used for selective modification of CNHs. Carbon nanohorns[1] (CNHs) are horn-shaped tubular structures (similar in structure to single-walled carbon nanotubes) capped with a conical tip. Individual nanohorns tend to cluster and form a globular structure between 80 and 100 nanometres in diameter with the tips of individual nanohorns projecting outward from the centre in all directions. The high purity and the lack of metal particles of produced CNHs is their major advantage compared to carbon nanotubes. These nanomaterials have interesting properties such as chemical and mechanical stability. These properties make them suitable for a high range of applications.



Functionalized material

The main handicap of these nanostructures is the lack of solubility, therefore in order to integrate them in different fields, they should be modified. Our group is focused on the design of very versatile new synthetic approaches[2] for the modification of CNHs. These methodologies allow us to modify the new materials in order to apply them in different fields such as catalysis, materials science, biomedicine….The different systems could be modulated in the search of a wide range of applications based on an appropriate surface modification. Future applications require a better understanding of the structure-property correlations. For this reason, a whole set of techniques such as AFM, TEM, TGA and NMR are often used in our group to characterize the structure of these ensembles. Therefore, in this communication we report our latest development on the functionalization of CNHs, with overview at the most important applications, such as materials and medicinal science.

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DYEING GRAPHENE: HYBRID ENSEMBLES WITH PHTHALOCYANINES

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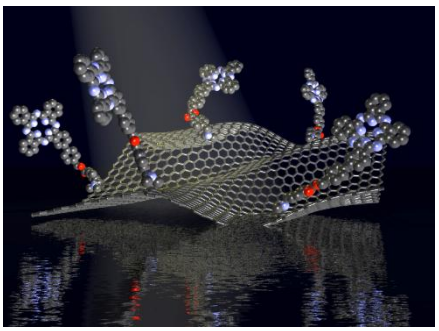
Keywords: phthalocyanines, single-walled nanotubes, graphene

Graphene has attracted extensive attention in recent years due to its striking mechanical, optical and electrical properties.[1] This single-atom-thick material is a gapless semiconductor with electron mobilities reaching 10 000 cm^2 V^{-1} s^{-1} at room temperature, which render it a competitive alternative, among others, in photovoltaic applications, either as a transparent conducting electrode or as active component in combination with appropriate organic counterparts such as conjugated polymers. Chemical functionalization of graphene with visible-light harvesting chromophores can be also envisaged as a useful approach for solar cell applications. In this context, there have been a number of articles describing the preparation of graphene-porphyrin nanohybrids.[2] Phthalocyanines are also ideal for this purpose, since they can might be considered superior to porphyrins in terms of light harvesting and electron donation. In fact, phthalocyanine-SWNTs nanohybrids have recently proved to be excellent candidates to nanoscale photovoltaic applications.[3]

Here we describe the preparation of a covalent phthalocyanine-graphene hybrids prepared from graphene layers obtained by liquid exfoliation of graphite, and its structural and photophysical characterization.



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CICLOADICIÓN DE NITRILIMINAS A GRAFENO. CONFIRMACIÓN TEÓRICA Y EXPERIMENTAL.

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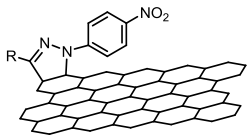
Palabras Clave: *grafeno, band-gap, cicloadición 1,3-dipolar, nitrilimina*

El descubrimiento del grafeno ha implicado un gran interés debido a sus extraordinarias propiedades térmicas, mecánicas y electrónicas. Para muchas de sus múltiples aplicaciones, la modulación de las propiedades electrónicas del grafeno mediante funcionalización química, así como el control sobre la apertura de su ancho de banda son de gran interés, debido al potencial de este material para una amplia gama de aplicaciones. [1] Debido a la menor reactividad de grafeno, en comparación con otras nanoestructuras de carbono, el abanico de reacciones disponibles para la modificación de este material es menor que en el caso de fullerenos o nanotubos de carbono. Mientras que la mayoría de los estudios que implican la funcionalización de grafeno, ésta se ha realizado por amidación de los grupos carboxílicos o mediante el uso de sales de diazonio, [2] también se ha descrito algún ejemplo de cicloadición 1,3-dipolar de iluros de azometino [3], pero no existen ejemplos en la literatura de cicloadición de otros dipolos menos reactivos como nitriliminas u óxidos de nitrilo.

Por otra parte, en la mayoría de reacciones de cicloadición a [60] fullereno, el LUMO del fullereno se desplaza a valores más altos alrededor de 0,15 eV respecto al del fullereno pristino. Sin embargo, en nuestro grupo hemos demostrado previamente que, en la cicloadición de nitriliminas a fullerenos, el LUMO del C_{60} no se desplaza a valores más altos debido al carácter aceptor del anillo de pirazolina. [4,5] Por lo tanto, la extensión de esta reacción a grafeno puede ser una herramienta útil para controlar el ancho de banda del grafeno funcionalizado. En este trabajo describimos la viabilidad de la cicloadición 1,3-dipolar de nitriliminas a grafeno mediante un estudio teórico y experimental.



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MODIFICACIÓN SUPRAMOLECULAR DE GRAFENO CON MÓLECULAS ELECTROACTIVAS

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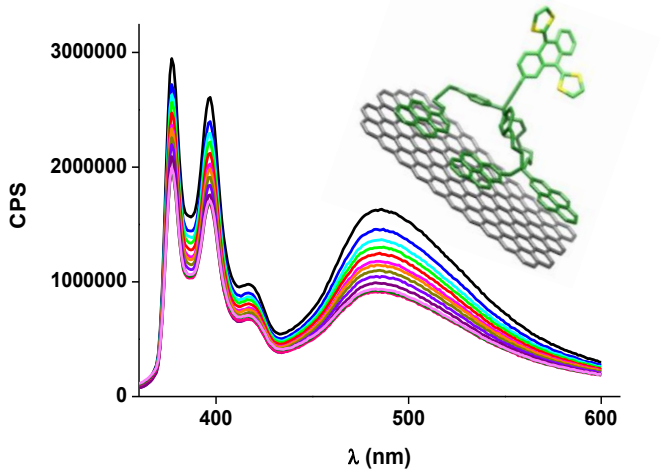
Palabras Clave: *grafeno, química no covalente, moléculas electroactivas*

El grafeno es probablemente el nanomaterial basado en carbono más estudiado desde su descubrimiento, debido a sus excepcionales propiedades electrónicas, mecánicas y térmicas. Sin embargo, presenta varios inconvenientes para su aplicación tecnológica, sobre todo en lo que a prestaciones electrónicas se refiere, debido a su band-gap cero y a la gran tendencia a agregarse que presenta, como consecuencia de las fuertes interacciones π-π entre distintas láminas.

La modificación química, tanto covalente como no covalente, [1, 2] es una herramienta que permite modular el band-gap del grafeno y, por tanto, sus propiedades electrónicas, facilitando la manipulación de este material. [3]

En esta comunicación presentaremos la funcionalización no covalente de grafeno con distintas moléculas electroactivas, como derivados de tetratiafulvaleno π-extendido (π-exTTF), porfirina o fullereno, y distintos modos de anclaje. Se presentará la caracterización llevada a cabo mediante diversas técnicas (en la figura se muestra por ejemplo una valoración mediante espectroscopia de fluorescencia) y se compararán las propiedades de los materiales sintetizados.



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SUPRAMOLECULAR PERYLENEDIIMIDE-GRAPHENE SYSTEMS AS DONOR-ACCEPTOR NANOENSEMBLES.

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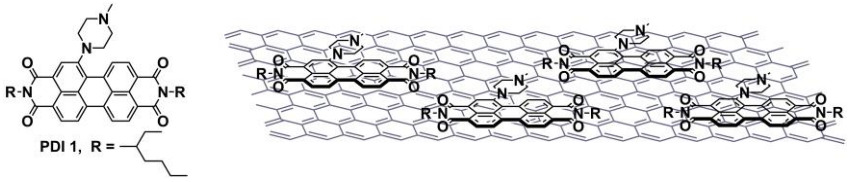
Keywords: *Perylendiimide, supramolecular, graphene.*

Perylenediimides are a family of aromatic flat organic molecules, which have been extensively used, in combination with many carbon nanoforms, to form hybrid materials with excellent optoelectronic properties, and have found applications as artificial photosynthetic systems [1] and in photovoltaic devices.[2]

On the other side, it is undeniable that the utilization of high quality graphene, or graphene-based materials, has become a reality in contemporary materials science, but doping of graphene materials with electroactive molecules needs still to be optimized. In this context the use of flat organic compounds facilitating graphite exfoliation, while at the same time acting as electroactive non-covalent dopants, is a smart and convenient way to obtain graphene-based hybrid materials without disrupting its novel electronic structure.[3]

Here we present the synthesis and characterization of an electron-donor PDI 1, bay-substituted with one piperazine append, and its successful use as exfoliating agent for graphite. PDI 1 has the ability to supramolecularly interact with exfoliated graphene sheets, stabilizing them and preventing their reassembly. Preliminary photophysic measurements show effective electronic communication between PDI and graphene flat surface and a potential application as active material in a new generation of graphene based photovoltaic devices.[4]

This research was financially supported by the Spanish Ministry of Economy and Competitiveness (Mineco) of Spain (CTQ2011-26455 and CTQ2014-55798-R) and Generalitat Valenciana (PROMETEO 2012/010).



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FEW-LAYER OF GRAPHENE FROM BALL-MILLING OF GRAPHITE WITH TRIAZINE DERIVATIVES

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Keywords: *graphene, ball milling, triazine*

The emergence of graphene has recently opened up a new field in the science and technology of two-dimensional nanomaterials with continuously growing interest. Graphene exhibits unique properties arising from its strictly single atomic layers of sp2-bonded carbon atoms densely packed in a honeycomb crystal lattice. These properties generate huge interest from different application fields, [1] however they are also highly dependent on the number of layers of graphene. Unless well separated from each other, graphene sheets have a natural tendency toward re-stacking in order to re-establish the graphitic structure through Van der Waals interactions. [2] Therefore, stable dispersion of individual graphene sheets, in convenient media, is essential for the material to be fully exploited in the different application fields.

Our research group has developed a scalable and easy methodology for the exfoliation of graphite sheets through interactions with melamine (2,4,6-triamine-1,3,5-triazine) by ball milling processes in solvent free conditions. Once graphite is exfoliated, the graphene layers can be dispersed in water and organic solvents at room temperature, by means of soft sonication conditions. Moreover melamine can be removed by filtration and graphene samples are redispersed in fresh solvents forming stable dispersions during weeks. [3]
This procedure has several interesting aspects as regards the preparation of non-covalently modified graphene, where derivatives of aminotriazines can be designed to form extensive hydrogen-bond 2D networks on the graphene surface with the aim of manipulating their electronic and chemical properties. [4]

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S12: *Más Allá de la Química del Grafeno y sus Aplicaciones*

N-FUNCIONALIZACION DE GRAFENO N-DOPADO

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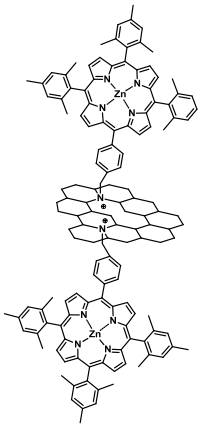
Palabras clave: *N-grafeno, N-funcionalización*

En los últimos años, el grafeno ha atraído un gran interés debido a su estructura única y a sus espectaculares propiedades que lo hace un candidato extraordinario para un gran número de aplicaciones. Son muchos los esfuerzos que se han realizado para modular las propiedades electrónicas de este material. Entre las diferentes posibilidades existentes para modificar grafeno, el dopaje con nitrógeno ha sido una forma muy efectiva para aumentar su conductividad electrónica, mejorar sus propiedades electro-donadoras y aumentar la facilidad de modificación del grafeno. [1]

Además de los métodos conocidos de modificación de grafeno, mediante funcionalización de la estructura carbonada, el grafeno N-dopado [2] podría ser modificado por reacciones específicas sobre el heteroátomo, lo que permitiría incorporar de modo selectivo en el Nitrógeno sustituyentes con funcionalidades específicas.

En esta comunicación presentamos por primera vez la funcionalización de grafeno N-dopado; para ello hemos elegido reacciones de N-alquilación. Con el fin de confirmar esta funcionalización se han llevado a cabo un detallado estudio mediante TGA, XPS, FTIR y espectroscopia Raman, así como estudios de AFM que han proporcionado información sobre la topografía de la muestra.



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BOTTOM-UP APPROACH TOWARDS DISTORTED NANOGRAPHENES CONTAINING SEVEN-MEMBERED CARBOCYCLES

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Keywords: *nanographene, graphene defects.*

Graphene samples exhibit unique electronic and mechanical properties. However, structural defects, which may appear during growth or processing, can significantly modify its properties.[1] Thus, the synthesis and study of carbon nanostructures with topological defects may help understanding graphene itself and also in the construction of new materials based on the controlled inclusion of imperfect nanographenes into graphene lattice.[2]

Within this context, we have designed a versatile route to construct nanographenes of different sizes incorporating a single heptagon. Key synthetic steps include Co(0)-mediated intermolecular cyclotrimerization reaction and cyclodehydrogenation reactions.
In this way, we obtained compounds **1** and **2**, presenting a **seven**-membered ring core partially surrounded in a hexagonal lattice (Figure 1). X-Ray crystal structures confirmed the distortion caused by the odd-membered ring, enhancing solubility drastically. Both compounds also showed very promising optical and electronical properties. Moreover, compounds **1** and **2** are strategically functionalized to extend the polycyclic π-framework in two different directions following two different approaches: **i)** nucleophilic addition to the ketone moeity; **ii)** application of recently developed Ni(0)-catalyzed cross-coupling reactions using methoxy groups as electrophiles.[3] In both cases, subsequent cyclodehydrogenation reactions lead to differently expanded distorted nanographenes. By combining both strategies we are constructing a variety of distorted aromatic structures containing a 7-membered carbocycle.

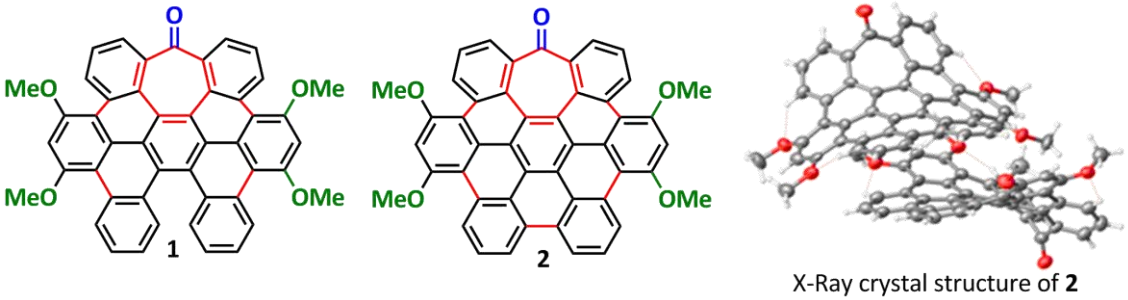

Figure 1

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SYNTHESIS AND PROPERTIES OF NANOGRAPHENES BY SOLUTION CHEMISTRY

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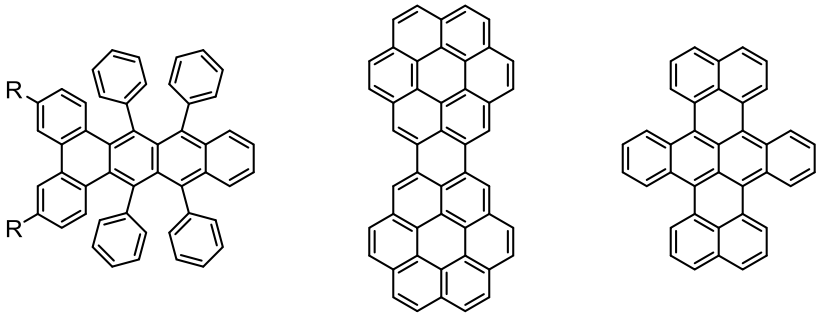
Keywords: *nanographene, polycyclic aromatic hydrocarbon (PAH), arynes.*

In the last decade, graphene has astonished the scientific community, mainly due to its unique properties and potencial applications in the field of material science. We are probably dealing with the emergence of a new technology based on this material.[1]
From a structural point of view, graphene can be considered as a large polycyclic aromatic hydrocarbon (PAH). Therefore, classical methods to prepare PAHs by solution chemistry has become an useful method to prepare well-defined nanographenes.[2] These bottom-up approaches avoid the structural inhomogeneity implicit in top-down methods, and they provide access to nanographenes with different topologies and peripheries, a crucial feature to control the properties of these carbon-based material.
In this contribution we describe our efforts to prepare graphene molecules by chemical synthesis in solution, in particular dibenzorubrenes (**1**), dicoronylene (**2**) and dibenzoterrylene (**3**).



1 **2** **3**

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FUNCTIONALIZATION OF CARBON SURFACES THROUGH PHOTOINITIATED REACTIONS

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Keywords: *graphene, carbon nanotubes, carbon surfaces functionalization, photoinitiated reactions*

We have devised a simple method to functionalize carbon surfaces with a variety of organic moieties, from small molecules to proteins or enzymes. The method involves UVC and/or Vis light irradiation of heterogeneous solutions of the solid in the presence of the molecules to be inserted, and has been tested on different carbonaceous materials: graphite, carbon nanotubes, graphene.

Relevant differences have been found between using oxidized and reduced surfaces. The nature of the functionalized surface has been characterized through different techniques, such as TCA, TGA/FTIR, XPS and SS-NMR.

Here, we will give some examples of the obtained results: kinetics, chemical and spectroscopic characterization, and a proposal of a suitable mechanism for the process.

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NOVEL CLICK REACTION CATALYST BASED ON GOLD NANOPARTICULES AND OLIGONUCLEOTIDES FOR PREPARATION OF HYBRID NANOSTRUCTURES

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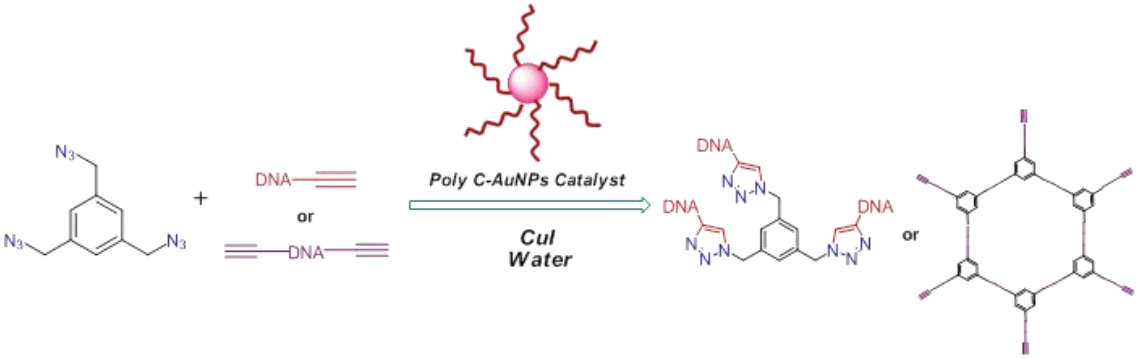
Keywords: *oligonucleotides, click reaction, gold nanoparticles,*

The development of nanomaterials and biomaterials with precise control in composition, architecture and functionality has generated great advances in various fields, such as, biomedicine and materials science [1, 2]. In this regard, the standard Click reaction has proven very useful for the preparation of a variety of materials. This reaction implies the cycloaddition between an azide and alkyne moiety catalysed by Cu^{+} and has been applied in the orthogonal ligation of a variety of biomolecules, including oligonucleotides for preparation of hybrid nanostructures based on DNA [3, 4]. In this sense we have development a novel catalyst based on gold nanoparticles modified with DNA sequences (Poly C-AuNPs), which improve the cycloaddition reaction in water of the azide group present in a derivative of benzene and oligonucleotides bearing an alkyne group, the use this catalyst, not only improves the efficiency of the reaction, but also can be reused and protects the DNA from degradation. Using this methodology we have prepared different hybrid structures.



Synthesis of hybrid nanostructures via Click Reaction using a novel catalyst.

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INMOVILIZACIÓN DEL CATALIZADOR DE JACOBSEN EN SUPERFICIES DE GRAFENOS DIRIGIDA A LA EPOXIDACIÓN ENANTIOSELECTIVA DE OLEFINAS

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Palabras Clave: *manganeso, salen, catálisis enantioselectiva, epoxidación, inmovilización, grafeno.*

Los complejos de Mn(III) coordinados a ligandos salen (*N,N'*-etilenobis(salicilimino)) quirales, descritos por los grupos de Jacobsen y Katsuki, son bien conocidos como catalizadores eficientes en la epoxidación asimétrica de olefinas.[1,2] La inmovilización de estos complejos en diversos soportes sólidos, tales como silicatos mesoporosos, materiales poliméricos, etc., ha permitido estudiar tanto la actividad y estabilidad del catalizador, así como su recuperación y reciclaje. Sin embargo, la inmovilización de estos complejos en materiales deslaminados ha sido menos explorada. [3]

En los últimos años, el elevado interés manifestado en el desarrollo de materiales híbridos basados en grafeno ha potenciado su estudio y aplicación tanto a nivel académico como industrial. De entre muchas de las características de los materiales basados en el grafeno, destacan su estructura laminar, su elevada área superficial y su accesible modificación química, lo que resulta especialmente atractivo a la hora de inmovilizar complejos, clústeres o nanopartículas de metales de transición. Recientemente, se ha descrito la inmovilización covalente de un complejo de Mn (III)-salen quiral en la superficie del óxido de grafeno y su actividad catalítica.[4]

El objeto de nuestro estudio consiste en modificar químicamente la superficie de grafeno con el fin de favorecer el anclaje de complejos de Mn(III)-salen quirales mediante inmovilización coordinativa o axial. En la siguiente comunicación se presentarán la síntesis y caracterización de los materiales híbridos obtenidos, así como los resultados de la actividad catalítica y enantioselectividad en la epoxidación de alquenos proquirales.

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COPPER NANOPARTICLES SUPPORTED ON DOPED GRAPHENES AS CATALYST FOR THE DEHYDROGENATIVE COUPLING OF SILANES AND ALCOHOLS

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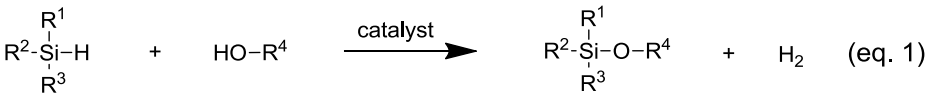
Keywords: *copper nanoparticles, graphene, catalysts*

We will describe the synthesis of catalysts based on copper nanoparticles supported on a series of undoped and doped graphenes and their high catalytic activity for the dehydrogenative coupling of silanes with alcohols (see eq. 1). [1]



Alcoxysilanes are high added-value commodity reagents for surface and for preparation of hybrid organic-inorganic materials. It was reported that these reagents can be obtained using supported gold nanoparticles as heterogeneous catalysts. One line of research of continued interest aims at replacing gold and precious metals by abundant and affordable base metals as copper. Our catalysts combine the activity of copper nanoparticles with the use of graphene or doped graphenes. Graphenes as supports have favorable properties such as very large specific surface area of about 2500 m^2g^{-1} totally accessible and extended π orbitals on G that can interact strongly with the empty d orbitals of transition metal atoms at the interface. Herein, we will report an innovative procedure for the synthesis of these catalysts that simultaneously leads to the preparation of Cu NPs on G by carbonization of natural biopolymers. An additional advantage is that the procedure allows doping or co-doping of the G sheet with heteroatoms. The interaction of metal NPs with heteroatoms on doped G is a tool to control the activity of G. The resulting graphitic material, after exfoliation, is constituted by a single layer or few-layers graphene as it can be seen by AFM. The catalyst contains a 17 wt% of Cu nanoparticles with the average NP diameter of 24 nm. Cu on graphene exhibits high activity for the dehydrogenative coupling of silanes with alcohols. The presence of dopant elements exhibits a remarkable influence on the catalytic activity, the most efficient catalyst being Cu-(B)G followed by Cu-G.

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GRAPHENE GRAFTED WITH WATER-SOLUBLE POLYMERS FOR ELECTROCHEMICAL BIOSENSORS

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Key words: *graphene functionalization, modified electrodes, electrochemical biosensors*

The rational design of electrochemical biosensors with improved bioanalytical performance and robustness is currently expedited by the preparation of novel nanostructured transduction elements based on advanced hybrid nanomaterials with well-defined properties. In this context, graphene has emerged as one of the most promising nanomaterials due to its unique properties. However, the high hydrophobicity and the absence of chemical functionalities in graphene restrain the direct application of this nanomaterial in bioelectroanalytical applications.

The present work describes several original approaches to overcome these limitations by grafting water-soluble polymers bearing reactive functional groups to reduced graphene oxide nanosheets. In the first method, graphene oxide was initially grafted with silane groups bearing epoxy or primary amino groups, which were then employed as modification points for the covalent cross-linking with ethylendiamine core polyamidoamino G-4 dendrimers and O-carboxymethylcellulose. The second approach was based on the introduction of thiol groups on the graphene oxide basal plane by azo-grafting with *p*-mercaptoaniline or treatment with (3-mercaptopropyl)trimethoxysilane. These reactive thiol groups were then employed for the chemisorptions of Au nanoparticles, which were further decorated with low molecular weight dextrans end-group activated with thiol groups. These novel hybrid nanomaterials showed high stability in aqueous suspensions and were employed as scaffolds for the covalent immobilization of redox enzymes and oligonucleotides on electrode surfaces. The nanostructured electrodes were successfully used to design electrochemical enzyme [1-3] and DNA biosensors [4] which were characterized by their excellent analytical performance and high stability.

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GRAPHENE QUANTUM DOTS: AN ECO-FRIENDLY PREPARATION

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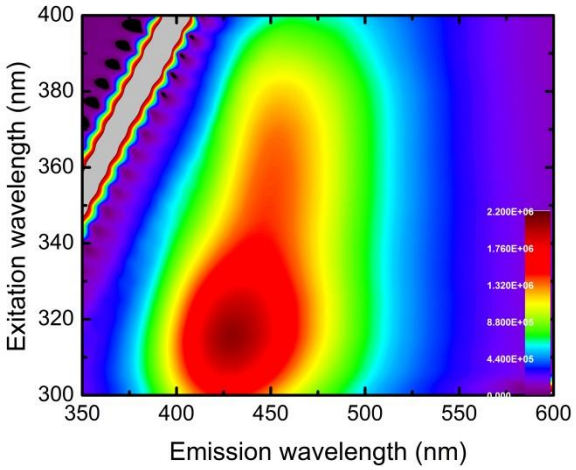
Keywords: *graphene, quantum dots, mecanochemistry*

We report a cheap, easy and eco-friendly means to obtain graphene quantum dots (GQDs): ball-milling for the fragmentation of graphite in the presence of sodium percarbonate as solid oxidant. This approach is related to the mechanochemical methodology reported by us for the preparation of few-layered graphene from graphite [1] and carbon fibers [2]. In contrast to the conventional techniques used for the synthesis of graphene, and now for graphene quantum dots, the ball-milling process avoids the use of strong minerals acids, high temperatures and high vacuum chambers, while the solvents, if used, can be recovered and recycled. In addition, the protocol is quite simple, making it possible to set up the experiment in a few minutes.

As it is known, photoluminescence (PL) is the most valued property of quantum dots and the wavelength of emission in deeply related to the size of the QD as a consequence of the quantum confinement of the excitons [3]. The PL spectra of the obtained graphene quantum dots solutions are indicative of a homogeneous size distribution. In addition large Stokes displacement, 125 nm (λex=315; λem=430), are observed.



A complete characterization will be presented.

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S12: *Más Allá de la Química del Grafeno y sus Aplicaciones*

INMUNOSENSOR ELECTROQUÍMICO PARA LA DETERMINACIÓN DE PEPTIDO YY EN SUERO HUMANO BASADO EN LA QUÍMICA DEL DIAZONIO SOBRE ÓXIDO DE GRAFENO REDUCIDO

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Palabras Clave: *Peptido YY, inmunosensor electroquímico, grafeno.*

El Peptido YY (PYY) es un potente anorexígeno producido en el intestino. Es secretado en el torrente sanguíneo tras la ingesta de alimentos, produciendo un efecto de saciedad [1]. Este comportamiento ha hecho que el PYY pueda considerarse un agente terapéutico para controlar el apetito y la cantidad de calorias ingeridas.

En este trabajo se describe la preparación del primer inmunosensor para PYY. El diseño se basa en la preparación de una plataforma electródica de óxido de grafeno reducido (rGO), sobre el que se inmoviliza el anticuerpo específico de captura (anti-PYY). Para la reducción de GO se aplicó un método novedoso con ácido ascórbico, que evita el uso de reactivos como la hidrazina, tóxicos y más caros. Sobre la superficie electródica se redujo electroquímicamente la sal de diazonio del ácido 4-aminobenzoico (ver Figura 1), formándose el radical 4-carboxifenilo que permite la unión covalente del anticuerpo anti-PYY. La determinación de PYY se realiza mediante voltamperometría diferencial de impulsos estableciendo un inmunoensayo competitivo entre PYY y PYY biotinilado, con estreptavidina marcada con fosfatasa alcalina y 1-naftilfosfato como sustrato de la reacción enzimática.

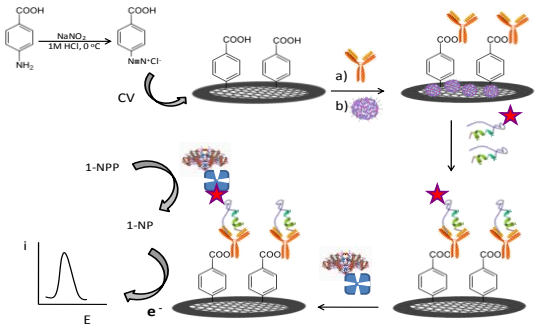

Figura 1. Preparación y funcionamiento del inmunosensor

El método desarrollado permite la determinación de PYY en el intervalo de concentraciones de 10^{-4} - 10^{2} ng/mL, con un límite de detección de 0.01 pg/mL y una buena reproducibilidad entre electrodos, con RSD = 5.5% (n=5).

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S12: *Más Allá de la Química del Grafeno y sus Aplicaciones*

NOVEL ELECTROCHEMICAL IMMUNOSENSOR PREPARED FROM REDUCED GRAPHENE OXIDE-CARBOXYMETHYLCELLULOSE HYBRID. APPLICATION TO THE DETERMINATION OF ADIPONECTIN

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Keywords: *graphene, adiponectin, immunosensor, carboxymethyl cellulose*

Graphene has largely proven to be an extremely suitable and versatile material for electroanalytical applications [1]. Minor drawbacks as the high hydrophobicity of graphene nanosheets, the low solubility, and the tendency to form agglomerates were found in the practical use of this material. However, in the field of biosensors, a major obstacle is the absence of functional moieties on graphene surface that really limits the possibility of easy immobilization of biomolecules. Nevertheless, this problem can be avoided by applying strategies for chemical derivatization, although these should be appropriate to prevent damage the structure of graphene and the consequent loss of its excellent properties. A convenient alternative consists of preparing graphene-polymer hybrids using macromolecules such as carboxymethylcellulose (CMC). CMC-rGO hybrids combine the properties of both materials, with the result of a high conductive, hydrophilic, and biocompatible product. A method for the preparation of CMC-rGO hybrids by covalent binding of oxidized CMC to graphene oxide layers followed by chemical reduction with sodium borohydride, was recently developed by our group, and the resulting oxygen-rich conducting nanostructures was used for the fabrication of a tyrosinase enzyme biosensor [2].

Taking advantage of the excellent electrochemical behavior observed for CMC-rGO hybrids, these were used for the first time to prepare an electrochemical immunosensor. Moreover, in order to ensure the stable and oriented binding of antibodies, a novel strategy was implemented using Mix&Go™. This is a commercial polymeric coating that contains metallic complexes to bind proteins. The combination of CMC-rGO hybrids and Mix&Go™ resulted in a very suitable alternative that could be used as the general route for preparing point-of care devices. Following this strategy, the first immunosensor for adiponectin (APN) was developed. APN is a cytokine involved in glucose and lipid metabolism, with a central role in regulation of insulin resistance. It has been proposed as a biomarker for metabolic syndrome. Anti-APN antibody was immobilized by means of Mix&Go™ polymer onto a CMC-rGO-modified screen-printed carbon electrode (SPCE), and a sandwich-type immunoassay with biotinylated-anti-APN and HRP-Strept was established. The determination of APN was performed by addition of hydrogen peroxide in the presence of hydroquinone and measurement of the current signal at -200 mV. The method has a great sensitivity with a detection limit as low as 61 ng/mL.

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S12: *Más Allá de la Química del Grafeno y sus Aplicaciones*

EPITAXIAL GROWTH OF FEW-LAYER MOS_2(0001) ON FES_2{100}

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Keywords: *2D materials, CVD, Surface science*

Graphene is currently the most widely studied two-dimensional material due to its many extraordinary electronic properties. However, pristine graphene does not have a bandgap, a property that is essential for many electronic applications[1]. Single-layer MoS_2 has arisen as a possible alternative to graphene due to a natural large intrinsic bandgap of 1.8 eV (1.2 eV in bulk MoS_2) and thermal stability up to 1100 ºC, whilst MoS_2 is widely used in industry for its tribological properties (e.g. lubricant) and catalytic properties (e.g. hydrodesulphurization). Recent studies have indeed demonstrated the capabilities of 2D MoS_2 in applications such as field effect transistors, low power switches, optoelectronics, and spintronics[2].

Few-layer MoS_2 is most commonly obtained by top-down methods such as lithium intercalation, micro mechanical exfoliation, or liquid-phase exfoliation. Bottom-up synthesis methods for 2D materials, such as CVD or self-assembled monolayers have already showed promise in delivering high quality graphene. A few attempts to grow high-quality MoS_2 layers via CVD on different surfaces have yielded very different results so far[3]. Whilst large area MoS_2 atomic layers were produced by evaporating pure sulphur on a Mo precovered SiO_2 surface, MoS_2 nanoclusters were found to form by depositing Mo on Au{111} and HOPG under a pressure of H_2S. In this work, we report the facile formation of a highly ordered MoS_2(0001) film, of the order of 1 nm thick, on the {100} surface of a FeS_2 (iron pyrite) substrate[4-6] under ultra-high vacuum (UHV) conditions.

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S12: *Más Allá de la Química del Grafeno y sus Aplicaciones*

PREPARATION OF CORRUGATED AND POROUS N-DOPED GRAPHENE FROM CONTROLLED PYROLYSIS OF METAL-FUNCIONALLIZED COVALENT ORGANIC FRAMEWORKS BASED ON IMINE AND ITS EVALUATION AS SUPERCAPACITORS

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Keywords: *Graphene, Covalent Organic Framework, Supercapacitor.*

Supercapacitors have drawn great attention in the industry as energy storage devices because of their high performance in terms of reversibility, life cycles and high energy and power densities. The electrodes are critical in this type of device and, in this context, graphene, and especially highly corrugated porous graphene is an exceptional candidate. Currently, this type of graphene is obtained by procedures using MgO templates, graphene oxide cooling with liquid nitrogen, or a combined method of ion exchange and activation with NaOH [1]. These processes are expensive and complex, therefore, there is a growing interest in having scalable, cost-effective and simple synthetic methods for their industrial implementation.

Herein, we present a new method for synthesizing highly corrugated porous graphene with excellent supercapacitive properties. The method consists of calcination at moderate temperatures of 2D Covalent Organic Frameworks with adsorbed metals. The effectiveness of the obtained graphene supercapacitive electrode, which exceeds the performance of any related carbonaceous material [2], is caused by its high surface area and uniform pore size distribution. The structure, morphology and configuration of the precursor promotes the generation of hierarchical porosity in the final material not needing to use MgO templates or ion exchange resins and NaOH. The method also allows the incorporation of heteroatoms, such as nitrogen, in the graphene structure.

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Presentaciones Póster (PP)

Listado de presentaciones póster

VERSATILE FLUORESCENCE SYSTEMS BASED ON GRAPHENE QUANTUM DOTS

A. Martín

AgNPs/SiO_2/rGO HYBRIDS AS ELECTROCHEMICAL PLATFORMS FOR THE PREPARATION OF IMMUNOSENSORS: DETERMINATION OF ETHINYLESTRADIOL IN BIOLOGICAL SAMPLES

G. Martínez-García

S12: *Más Allá de la Química del Grafeno y sus Aplicaciones*

VERSATILE FLUORESCENCE SYSTEMS BASED ON GRAPHENE QUANTUM DOTS

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Keywords: *fluorescence, graphene quantum dots, sensors*

Graphene quantum dots (GQDs) can be used as sensors of numerous analytes and also as targeting systems, due to their photoluminescence (PL) properties. For instance, using these cabon nanoforms, Cu (II) cations [1] or Au (III) and glutathione [2] can be detected. In addition, some organic molecules have a strong interaction with these nanoforms, inducing changes in the fluorescence intensity: quenching (signal-off) or enhancement (signal-on). Electrostatic interactions, π-π stacking and hydrogen bonding are some of the interactions that could modify their PL spectra.

For these purposes, we have developed an eco-friendly, easy and cheap way to prepare graphene quantum dots by mechanochemical activation [3]. A ball-milling treatment is applied to graphite in absence of solvent. The GQDs prepared by this methodology have high water solubility and can be easily modified on the surface to improve their solubility in organic solvents and/or introduce the required molecule for the final application. This strategy makes the system specific to different analytes, an ideal carrier and, at the same time, avoids aggregations between each GQD.

Graphene quantum dots are fully-characterized by different techniques such as PL, TEM, UV-NIR, TGA, RAMAN… Final results will be presented.

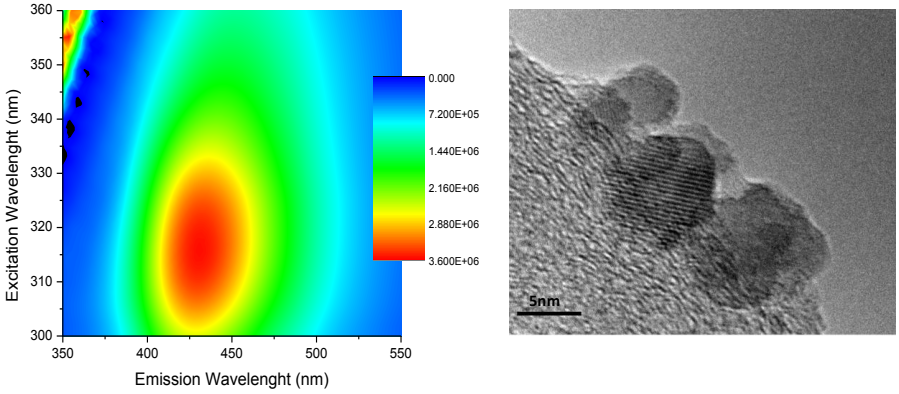

Figure 1: a) PL spectra of the GQDs and b) TEM image of prepared GQDs.

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S12: *Más Allá de la Química del Grafeno y sus Aplicaciones*

AgNPs/SiO_2/rGO HYBRIDS AS ELECTROCHEMICAL PLATFORMS FOR THE PREPARATION OF IMMUNOSENSORS: DETERMINATION OF ETHINYLESTRADIOL IN BIOLOGICAL SAMPLES

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Keywords: *silver nanoparticles, ethynylestradiol, immunosensor, graphene.*

Hybrid materials prepared from graphene and SiO_2 constitute excellent substrates for the development of electrochemical sensors. The huge conductivity, high surface area, biocompatibility and robustness of graphene, coupled with the physical and chemical resistance of silica, the hydrophilicity, chemical inertness, and the high surface area/volume ratio, all contribute to increase the electroactive surface, thus enhancing sensitivity [1]. Furthermore, metallic nanoparticles are characterized by their electrocatalytic ability together with the capacity for adsorption of biomolecules, biocompatibility and high conductivity. Also it has been found that functionalization of graphene with SiO_2 allows anchoring metal nanoparticles securely onto graphene support with a high dispersion and enhancing the catalytic performance [2]. Despite their properties, only few examples can be found in the literature regarding the application of metallic nanoparticles / silica / graphene hybrids to the preparation of electrochemical (bio)sensors.

This work describes the preparation of an electrochemical immunosensor for ethinylestradiol (EE2) based on the surface modification of a glassy carbon electrode with AgNPs/SiO_2/ graphene oxide hybrids followed by grafting of 4-aminobenzoic acid and immobilization of anti-EE2 by covalent binding. EE2, one of the most potent synthetic estrogenic hormones, is an essential constituent of oral contraceptives widely prescribed to prevent pregnancy in women. Adverse effects of EE2 include accelerated coagulation and fibrinolysis. Moreover, use of combined hormonal contraceptives has shown to be associated with increased risk of venous thrombosis depending on estrogen concentration. EE2 is excreted in urine and feces as glucuronide and sulphate metabolites. A major challenge is the presence of residues of EE2 and its derivatives in the environment coming from excretions, where can produce negative impact on the reproductive system in wildlife and human.

A competitive immunoassay for the determination of the hormone using peroxidase-labeled ethinylestradiol (HRP-EE2) and measurement of the amperometric response at −200 mV in the presence of hydroquinone (HQ) as redox mediator was developed. Calibration curves for EE2 exhibited a linear range between 0.1 and 50 ng/mL, with a detection limit of 65 pg/mL.

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S13. Productos Naturales en la Señalización Química en Sistemas Biológicos (PNSQ) / Chemical Signaling Mediated by Natural Products in Biological Systems

El simposio se centra en aspectos que involucren la Química de Productos Naturales (PN), incluyendo: 1) Estudio de nuevas moléculas naturales de origen terrestre y marino. Bioactividad. 2) Síntesis de Productos Naturales y derivados. 3) Nuevos métodos de extracción y separación. 4) Desarrollo de bioensayos y técnicas analíticas para la rápida identificación de PN, técnicas de derreplicación, metabolómica y nuevas aproximaciones de bioprospección. 5) Avances en la Elucidación Estructural de PN. 6) Biosíntesis de PN. 7) Química Ecológica. 8) Biotransformaciones y Biocatálisis. 9) Biotecnología de PN: Producción y Aplicaciones. 10) Utilización de PN en síntesis de compuestos de aplicación.

The symposium is focus to all aspects of research having to do with natural products chemistry (NP), including: 1) Study of new natural molecules of terrestrial and marine origin - bioactivity. 2) Synthesis of natural products and their derivatives. 3) New extraction and separation methods. 4) Dereplication, metabolomics, and rational approaches to bioprospecting. 5) Advances in structural elucidation. 6) Biosynthesis of natural products. 7) Chemical Ecology. 8) Biotransformation and biocatalysis. 9) Biotechnology of NP: Production and applications. 10) Use of NP in the synthesis of compounds with applications.

Organizadores:

Javier José Fernández Castro (ULL)

Carlos Jiménez González (UDC)

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Simposio patrocinado por el Grupo Especializado de Química de Productos de Naturales

Lunes 20 de Julio 2015

08:40 – 09:40	**PL-2**	***Conferencia Plenaria*** (Común a todos los simposios) **Tomás Torres Cebada** *"Phtalocyanines: Old Dyes, New Molecular Materials"*

Chairman: Jaime Rodríguez

10:00 – 10:30	**S13-IL-01**	**Greg Challis** *"Exploiting Microbial Genomics for Discovery of New Natural Products and Biosynthetic Pathways"*
10:30 – 10:45	**S13-OC-01**	**J. Javier Fernández**, "*Bioactive Metabolites from Dinoflagellates"*
10:45 – 11:00	**S13-OC-02**	**Guillermo Tarazona** "*Linking Stereoclusters by DFT Studies: Halioxepine B, a New Cytotoxic Terpene from the Indian Ocean Sponge Haplosclerida*"
11:00 – 11:30		Pausa Café

Chairman: Manuel Norte

11:30 – 12:00	**S13-IL-02**	**Isidro G. Collado**, "*Genomic Inspired Synthesis of Hybrid Molecules as Antifungal Agents against the Phytopathogen Fungus Botrytis cinerea***"**
12:00 – 12:15	**S13-OC-03**	**Fernando Reyes** *"A Novel Family of Isocyanide Antibiotics with Broad Spectrum against Gram-Negative Pathogens Produced by Cultures of The Fungus Ophiosphaerella korrae"*
12:15 – 12:30	**S13-OC-04**	**Carlos Urda** "*Determination of the Stereochemistry of Bistratamide N*"
12:30 – 12:45	**S13-OC-05**	**Belén Vaz** "*Structural Studies of Chlorophyll C Pigments*"
12:45 – 13:30		**Entrega de los Premios de Investigación REDPRONAT 2014**
13:30 – 15:30		Comida

Lunes 20 de Julio 2015

Chairman: Miguel Carda

15:30 – 16:00	**S13-IL-03**	**Martin E. Maier** *"Natural Product Analogs: Other than Trial and Error?"*
16:00 – 16:15	**S13-OC-06**	**María Pérez** *"Nitraraine, an Alkaloid with an Unresolved Structure"*
16:15 – 16:30	**S13-OC-07**	**David Díez** *"Sulfonyl Nazarov Reagents as cis-Decalins Precursors"*
16:30 – 17:00		Pausa Café

Chairman: Alejandro F. Barrero

17:00 – 17:30	**S13-IL-04**	**Ángel Rodríguez de Lera** *"Synthesis of Natural Epigenetic Modulators"*
17:30 – 17:50	**S13-OC-08**	**Mercedes Álvarez** "*New Results in the Synthesis of Phormidolides B-C*"
17:50 – 18:30		**Asamblea General del Grupo Especializado de Productos Naturales de la RSEQ**

18:30	***Sesión de Pósteres***

Comunicaciones Invitadas (IL)

S13: *Productos Naturales en la Señalización Química en Sistemas Biológicos*

EXPLOITING MICROBIAL GENOMICS FOR DISCOVERY OF NEW NATURAL PRODUCTS AND BIOSYNTHETIC PATHWAYS

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Bacteria belonging to the *Streptomyces* genus are renowned for their ability to produce bioactive natural products. Indeed, more than two thirds of natural antibiotics in clinical use originate from *Streptomyces* species. Remarkably, however, analyses of genome sequences for several well-characterised members of this genus have suggested that they have a far greater potential to produce bioactive metabolites than has been uncovered by classical bioactivity-guided isolation approaches. A likely explanation is that many of the biosynthetic gene clusters for such metabolites are not well expressed under laboratory growth conditions.

An overview of cryptic biosynthetic pathways (i.e. those with the potential to assemble hitherto undiscovered metabolites) encoded by the genomes of several *Streptomyces* species, such as *Streptomyces coelicolor*,[1] *Streptomyces ambofaciens*,[2] *Streptomyces scabies* and *Streptomyces venezuelae* will be given. Strategies for identifying the products of such cryptic pathways will be discussed,[3] including rational methods for inducing the expression of gene clusters that are expressed poorly, or not at all, under laboratory growth conditions.[4] Several examples of the discovery of novel metabolic products of cryptic gene clusters will be presented,[5-10] and insights into the biological functions and biosynthetic pathways of these metabolites will be described.

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S13: *Productos Naturales en la Señalización Química en Sistemas Biológicos*

GENOMIC INSPIRED SYNTHESIS OF HYBRID MOLECULES AS ANTIFUNGAL AGENTS AGAINST THE PHYTOPATHOGEN FUNGUS *BOTRYTIS CINEREA*

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Keywords: *genomic, synthesis, clovane, amides, amidines, Botrytis cinerea.*

Botrytis cinerea is the causal agent of the grey mould disease that affects more than 200 ornamental and agriculturally important plant species. This fungus produces important commercial losses around the world, especially on red fruits, grapes and wines.

The recent availability of the *B. cinerea* genome, at the Genoscope and at the Broad Institute, revealed an abundance of novel biosynthetic gene clusters and provided the opportunity to investigate secondary metabolism gene clusters.[1]

To study them, in the last years we have undertaken different approaches: chemical- and molecular-based epigenetic studies, comparative genomic study, and gene inactivation. As a result, new molecules with novel structures were found. Additionally, the biosynthesis of the two main families of toxins secreted by this phytopathogen fungus, botrydial and botcinic acid derivatives, involved in the infection mechanism, has been established by our research group.[2,3]

By reverse genetic, it was established that the *B. cinerea* double mutant, which had deleted the genes involved in the biosynthesis of sesquiterpene botrydial and the polyketides botcinic acid and botcinins did not displayed virulence and pathogenicity.[4]

These results prompted us to undertake the synthesis of hybrid molecules, which bear inhibitors of the sesquiterpene cyclase and the polyketide synthase involved in the biosynthesis of both toxins.

In this communication, we will describe the synthesis, inspired by genomic, of hybrid molecules as potential fungicides to control the infection produced by this phytopathogen fungus in commercial crops.

So, among other results, we will report the use of tin triflate as a catalyst in the selective one pot synthesis, via a Ritter-type three components reaction, of *N*-(hydroxyclovanyl)alkyl/aryl-amides and *N*-(hydroxyclovanyl)-*N'*-alkyl/aryl-amidines. Additionally, hybrid amides and amidines molecules, bearing a rearranged clovane skeleton as potential sesquiterpene cyclase inhibitors will be reported.

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S13: *Productos Naturales en la Señalización Química en Sistemas Biológicos*

NATURAL PRODUCT ANALOGS: MORE THAN TRIAL AND ERROR?

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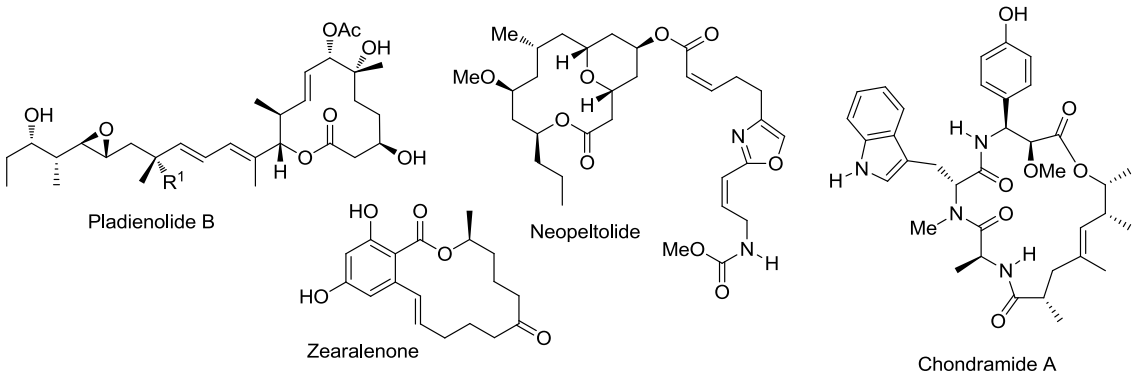
Keywords: *natural product synthesis, macrolactones*

Natural products (NPs) are fascinating not only because of their unique molecular architectures but also because of their biological activity and mode of action. The observed downward trend in new chemical entities (NCEs) in the last decade, makes it worthwhile to reconsider NP chemistry. The obvious advantage of NPs over non-natural molecules is that during their biosynthesis they already have interacted with different enzymes and proteins. Accordingly, their core scaffolds can be considered privileged structures. Thus, NPs are good starting points for analog synthesis and various concepts to generate NP analogs are known in the literature [1].

This talk briefly summarizes the most important strategies in this regard and highlights examples from our own group illustrated with the NPs shown in the Scheme.



In most of the cases simply opportunistic strategies were used where the type of analogs in part was determined by the synthetic strategy. For some of the cases we based the design of analogs on biosynthetic considerations.

It can be concluded that as long as virtual screening is not significantly improved, the synthesis of natural product analogs will largely rely on trial and error as well as serendipity.

Acknowledgements. This work was supported by the DFG and the state of Baden-Württemberg. Parts of it were carried out within the framework of COST Action CM 0804.

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S13: *Productos Naturales en la Señalización Química en Sistemas Biológicos*

SYNTHESIS OF NATURAL EPIGENETIC MODULATORS

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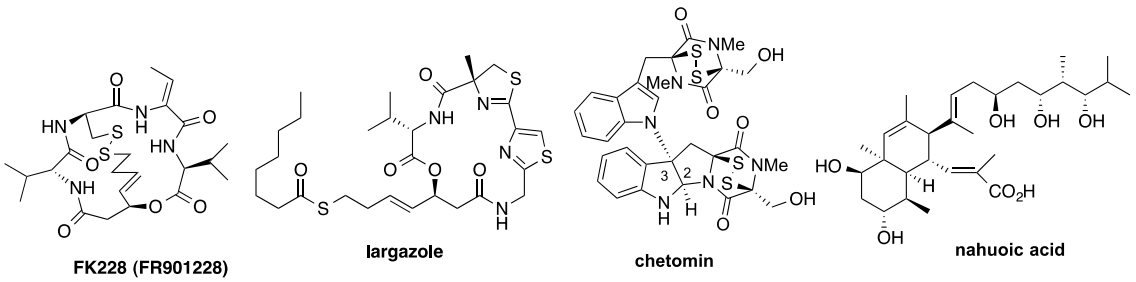
Keywords: *Epigenetics, natural products, total synthesis*

Epigenetic modifications, which are heritable changes in phenotype that do not involve alterations in the DNA sequence, are of current biological and pharmaceutical interest. Epigenetic mechanisms include DNA methylation, post-translational modifications of histones (primarily methylation and acetylation of lysine and histidine residues), and effects of non-coding RNAs. Biological and functional data link the alteration of the epigenetic machineries to the development of diseases, including cancer, inflammatory, autoimmune, metabolic and neurological disorders. Five drugs targeting epigenetic enzymes have been approved for the treatment of cancer. One of them, romidepsin (FK228), a natural product produced by *Chromobacterium violaceum* No. 968, is used in the clinic for the treatment of cutaneous T-cell lymphoma (CTCL) and peripheral T-cell lymphoma (PTCL).

Recent progress on the synthesis of selected natural epigenetic modulators, which feature a diversity of scaffolds with high stereochemical and functional group complexity, will be presented. Nature has evolved not only a variety of enzymes with a superb mechanistic richness for the deposition and removal of epigenetic marks on chromatin, but also biosynthetic machineries for the generation of secondary metabolites that regulate the activity of these proteins and, as a consequence, the biological and physio(patho)logical pathways in which they are implicated. The field of epigenetics is no exception to the unmatched and inexhaustible role of natural products as inspiration for the discovery of novel chemotypes and the development of the corresponding pharmacophores and drugs.



FK228 (FR901228) largazole chetomin nahuoic acid

Comunicaciones Orales (OC)

S13: *Productos Naturales en la Señalización Química en Sistemas Biológicos*

BIOACTIVE METABOLITES FROM DINOFLAGELLATES

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Keywords: *Dinoflagellates, marine toxins, DSP toxins, Prorocentrum*

Dinoflagellates are an important source of bioactive marine compounds. Some toxic species of these microalgae are responsible of the "Harmful Algal Blooms" (HABs) also known as red tides. HABs are great interests for their environmental impact and involve potential risk for public health by entering toxins into the food chain by contaminated seafood, through marine aerosols or by direct contact with the toxic metabolite in the sea [1]. These toxins have very complex structures and their structural elucidation has became a challenge within the natural products research area and showed an extraordinary value to study intracellular processes [2]. The genus *Prorocentrum* is recognized as co-responsible for the toxic syndrome Diarrethic Shellfish Poisoning (DSP). This genus has been described as producer of many secondary metabolites with remarkable structural diversity, including linear polycyclic compounds, macrolide and polyhydroxy compounds of high molecular weight [3,4]. As a result of our search for new bioactive products in artificial cultures, this communication describes structural and biological studies of metabolites isolated from cultures of *Prorocentrum belizeanum (hoffmannianum)* [5].

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LINKING STEREOCLUSTERS BY DFT STUDIES: HALIOXEPINE B, A NEW CYTOTOXIC TERPENE FROM THE INDIAN OCEAN SPONGE HAPLOSCLERIDA

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Keywords: *Halioxepine, terpene, marine natural products, NMR-DFT, sponge*

As part of our continuing program to identify metabolites with anticancer properties, a sample of the Indonesian sponge *Haliclona sp.*, collected off the coast of East Timor, was studied. Bioassay-guided fractionation resulted in the isolation of a new derivative, halioxepine B, together with the known meroditerpene halioxepine [1]. Halioxepine B showed moderate cytotoxicity against different cancer cell lines [2].

The stereochemical relationships among the different chiral centers were determined by ROESY and *J*-based analysis [3], as well as by comparison with the literature models [4]. The relative configuration between two stereoclusters placed in A and B rings could not be solved only by NMR measurements. Therefore, it was established by calculation of theoretical NMR chemical shifts by DFT studies and comparison to experimental values (Figure 1) [5].The absolute configuration will be resolved by application of Mosher's method or by Electronic Circular Dichroism and DFT calculations.

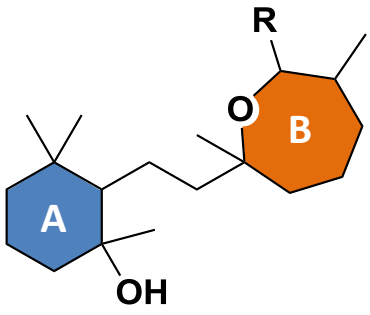

Figure 1.- Stereoclusters linked in halioxepine B established by NMR-DFT.

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A NOVEL FAMILY OF ISOCYANIDE ANTIBIOTICS WITH BROAD SPECTRUM AGAINST GRAM-NEGATIVE PATHOGENS PRODUCED BY CULTURES OF THE FUNGUS *OPHIOSPHAERELLA KORRAE*

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Key words: *isocyanide antibiotics,* Ophiosphaerella korrae*, structural elucidation*

Emergence of bacterial resistance represents a major issue for all classes of antibiotics and the identification of new treatments is urgently needed. The complex plastic architecture of Gram-negative bacteria enables a wide diversity of antibiotic resistance mechanisms and the development of new drugs active against these pathogens has become a major medical concern. Natural products have played a pivotal role over the last 50 years in the discovery of new antibacterial agents and most of the antibiotics currently in clinical use can be traced back to a natural origin [1,2].

Within the framework of a collaborative program aimed at identifying antibacterial agents from microbial sources, we have identified a family of novel compounds with broad-spectrum activity against Gram-negative pathogens possessing a previously unreported chemical scaffold. These compounds were isolated from fermentation broths of a strain of the hitherto unexplored fungus *Ophiosphaerella korrae*, the causal agent of dead spot disease of *Cynodon dactylon* (Bermuda grass). Cultures of this fungus grown for 28 days in a YES medium displayed broad-spectrum antibacterial activity when tested against a panel of Gram-negative bacteria. Extraction with acetone followed by SP-207ss chromatography and reversed-phase preparative and semipreparative HPLC yielded four structurally related isocyanide containing natural products as the compounds responsible for the observed bioactivity. Structural elucidation of the family of compounds was based on 1D and 2D NMR and High Resolution Mass Spectrometry (ESI-TOF). Their relative stereochemistry was determined by *J*-based configuration analysis combined with the presence of key NOESY correlations. Complementary Mosher ester derivatization analysis allowed the establishment of their absolute configuration.

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S13: *Productos Naturales en la Señalización Química en Sistemas Biológicos*

DETERMINATION OF THE STEREOCHEMISTRY OF BISTRATAMIDE N

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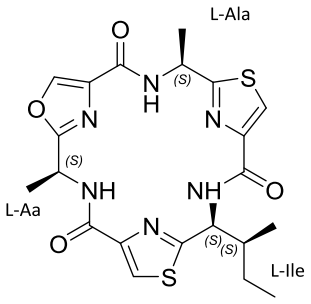
Key words: *Bistratamides, cyclic peptides, marine natural products, Marfey's method, tunicate*

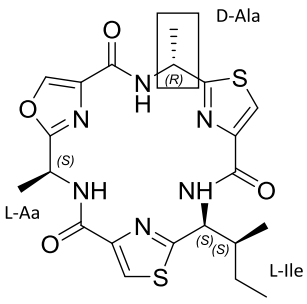
Bistratamides constitute a family of cyclic peptides, most of which incorporate amino acids linked to thiazole and oxazole rings [1]. Bistratamides N and M have been isolated from the ascidian *Lissoclinum bistratum* and show slight cytotoxicity against a panel of tumour cell lines.

Bistratamides N and M have the same planar structure but with changes in the stereochemistry of two amino acids. Whilst bistratamide M has two alanines with the L configuration, bistratamide N contains both L- and D-alanine but their positions could not be determined by NMR techniques.

For bistratamide N, the use of different hydrolysis methodologies and Marfey's method with subsequent analysis by HPLC MS [2] has allowed us to elucidate the stereochemistry of the L- and D-alanines present in the molecule as well as to determine their positions. Furthermore, the absolute stereochemistry of the L-isoleucine residue has been determined using the advanced Marfey's method [3].



Bistratamide M



Bistratamide N

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STRUCTURAL STUDIES OF CHLOROPHYLL C PIGMENTS

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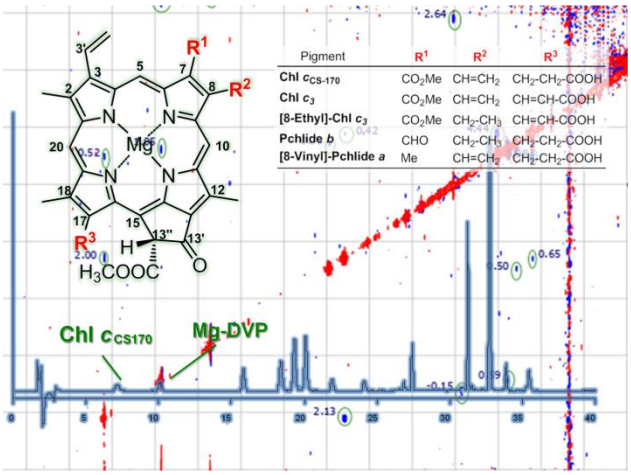
Keywords: *structural elucidation, chlorophyll c family, NMR, UV-vis, ESI-MS*

Chlorophyll (Chl) *c* pigments are found in the golden-brown eukaryotic algae (Chromophytes), where they function as light-harvesting pigments together with Chl *a* and carotenoids. Differently from other chlorophylls, they present a fully unsaturated tetrapyrrole macrocycle instead of a Mg-chlorin. In addition to this fully conjugated porphyrin system, they feature a unique acrylate moiety at C17 and different substituents patterns at C7 and C8, dividing them into Chl c_1, c_2 and c_3-type categories. [1]

Due to the improvement in separation techniques, new members of this family and Chl *c*-like pigments are being discovered, leading to the eleven types of Chl *c* identified so far.

In order to shed light on the actual structure of these pigments, we present here a structural study based on NMR spectroscopy and mass spectrometry to unequivocally establish the structure of three members of this family: Chl c_3, a closely eluting pigment ([8-ethyl]-Chl c_3), and the initially denominated Chl $c_{CS\text{-}170}$ ([7-methoxycarbonyl-8-vinyl]-Pchlide *a*). [2,3]



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NITRARAINE, AN ALKALOID WITH AN UNRESOLVED STRUCTURE

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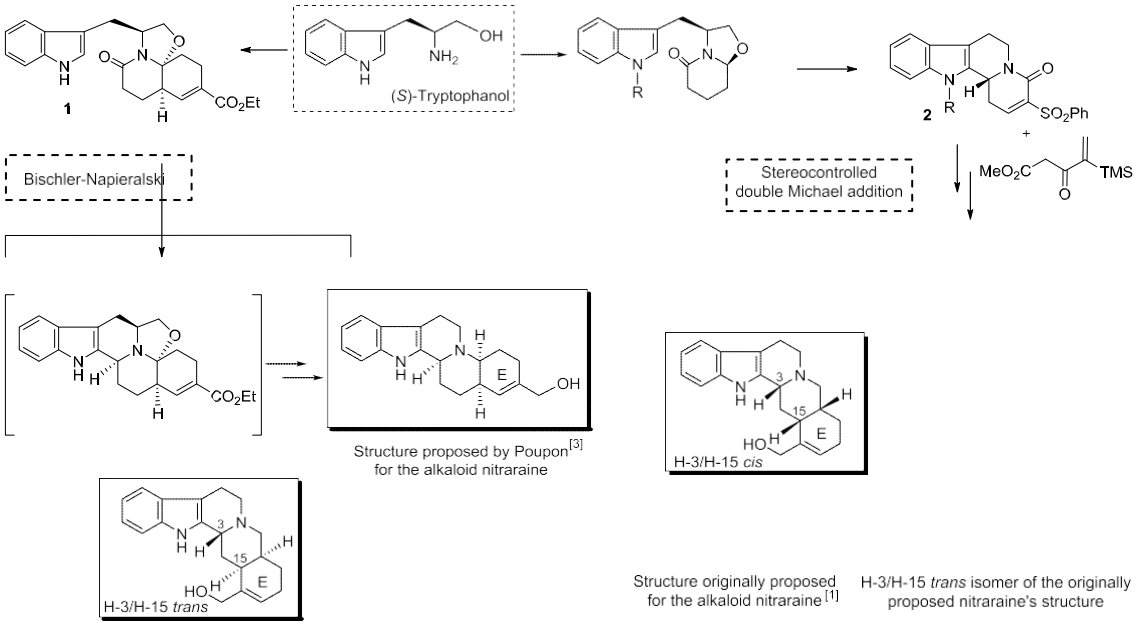
Keywords: *Indole alkaloids, Nazarov's reagent, double Michael reaction*

Nitraraine is an indole alkaloid isolated in 1985 from *Nitraria schoberi* L., collected in Kyzyl- Kum (Uzbekistan).[1] The proposed structure for nitraraine proved to be wrong by total synthesis.[2] An alternative structure was proposed by Poupon[3] in 2011.

We present here straightforward procedures for the synthesis of the different structures proposed for the alkaloid nitraraine. Our approaches involve, as key steps, the direct construction of the pentacyclic system by a Bischler-Napieralski cyclization of oxazoloquinolone lactam **1**,[4a] or the stereocontrolled generation of the E ring by a double Michael addition of a new silylated Nazarov reagent, previously developed in our laboratory,[4b] to a tetracyclic unsaturated lactam **2**.



The mp and NMR datat of our synthetic products were different from those reported for the natural product, so the real structure of this alkaloid still remains unresolved.

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SULFONYL NAZAROV REAGENTS AS *CIS*-DECALINS PRECURSORS

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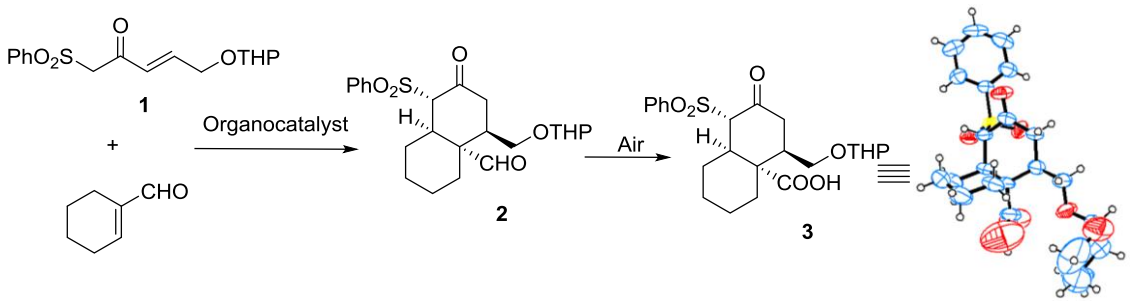
Keywords: *Nazarov reagents, sulfones, cis-decalins, terpenes*

The cis-decalin framework is present in the molecular structure of various classes of natural products such as cis-clerodanes,[1] kalihinenes,[2] thelepoganes,[3] cadinanes,[4] eremophilanes,[5] and valeranones.[6] These products have been typically obtained by isolation from natural sources. Many of these cis-decalin-based natural products exhibit wide-ranging and interesting biological activities. It is evident that many of these natural products have varying degrees of substitution patterns and four or more contiguous stereogenic centres on the decalin skeleton and, hence, pose a considerable synthetic challenge. The structural complexity of these natural products together with their interesting biological properties have led to a significant interest in the development of new and efficient methods for the synthesis of cis-decalins and the aforementioned natural products.[7]

Deslongchamps annulation have been used for the synthesis of *cis*-decalins [8] but without control of the absolute stereochemistry.[9] To the best of our knowledge there are no examples in the literature where sulfonyl Nazarov reagents have been employed for cis-decalins synthesis. Here we describe a very simple entry to these kind of skeletons using sulfonyl Nazarov reagents and commercial organocatalysts.



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S13: *Productos Naturales en la Señalización Química en Sistemas Biológicos*

NEW RESULTS IN THE SYNTHESIS OF PHORMIDOLIDES B-C

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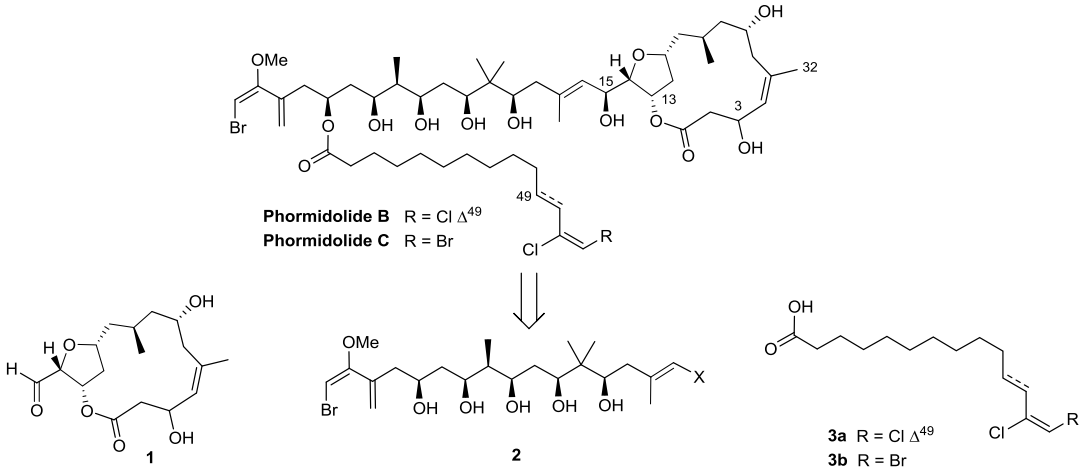
Keywords: *polyketides, macrolides, polyols, fatty acids, natural products*

Phormidolides B and C are marine polyketides structurally related to oscillariolide [1] and phormidolide A.[2] These molecules were isolated from a *Petrosiidae* sponge in the coasts of Pemba (Tanzania). Both Phormidolides B and C inhibit the growth of tumour cell lines in the micromolar range. Our objectives are the total synthesis of this family of compounds and complete their stereochemical assignment. The proposed retrosynthetic analysis is based on two main disconnections to give three molecular fragments: the macrolide **1**, the polyol chain **2** and the fatty acids **3a** and **3b**.



Recently our group developed a stereoselective synthesis of macolactone 1.[3] An improved procedure for the synthesis of **1** and the achievements in the preparation of **2** and **3** will be described.

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Presentaciones Póster (PP)

Listado de presentaciones póster

SYNTHESIS OF A-TYPE PROCYANIDIN ANALOGS FROM FLAVYLIUM SALTS AND THEIR RADICAL SCAVENGING ACTIVITY

A. Alejo

ASYMMETRIC APPROACH TOWARDS APOCAROTENOIDS BELONGING TO THE MEGASTIGMANE FAMILY

Miguel A. Romero

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SYNTHESIS OF A-TYPE PROCYANIDIN ANALOGS FROM FLAVYLIUM SALTS AND THEIR RADICAL SCAVENGING ACTIVITY

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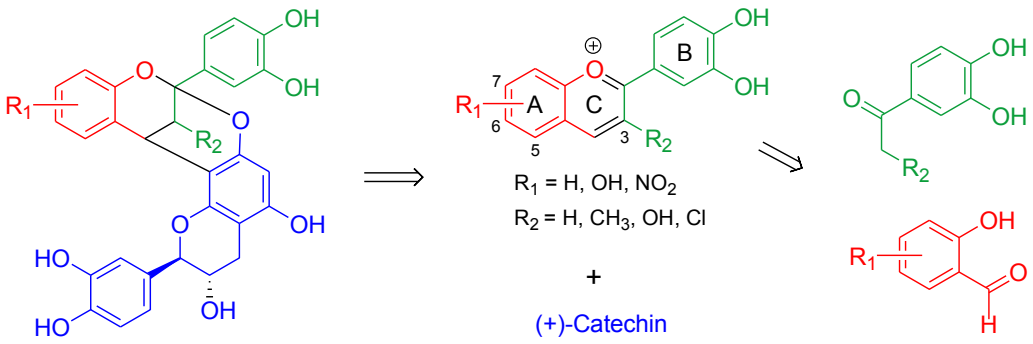
Keywords: *A-type procyanidin analogs; flavylium salts; π-nucleophiles; synthesis; microwave; antioxidant activity*.

A-Type procyanidins, such as dimers A-1 and A-2, isolated from cocoa beans, cranberry or peanut skin [1], and trimer cinnamtannin B-1, isolated from cinnamon, lychee or bay laurel [2], exhibit significant biological properties, including antioxidant activity [1] and antiaggregant and antiapoptotic effects in human platelets [2]. However, additional studies on the structure-activity relationship of such unusual bridged structure of dioxabicyclo[3.3.1]nonane have been limited by the scarcity of commercial oligomers with a double link (A-type). For this reason, the search for new natural sources of these compounds and the development of organic synthesis routes are of great interest [3]. The aim of this work was to explore the reactivity of a selection of flavylium salts with π-nucleophilic units (*i.e.*, catechin) to give the double link. Thus, flavylium salts (*i*) with no substitution at the A ring, (*ii*) with one or two hydroxyl electron-donating groups at C-5/7, and (*iii*) with a nitro electron-withdrawing group at C-6 (all of them with varying substituents at C-3) have been used. Microwave irradiation was required to obtain reasonable yields of A-type procyanidin analogs when OH groups in A ring were present, unless a Cl atom was at C-3. In addition, the radical scavenging activity of the A-type analogs synthesized was also evaluated.



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ASYMMETRIC APPROACH TOWARDS APOCAROTENOIDS BELONGING TO THE MEGASTIGMANE FAMILY

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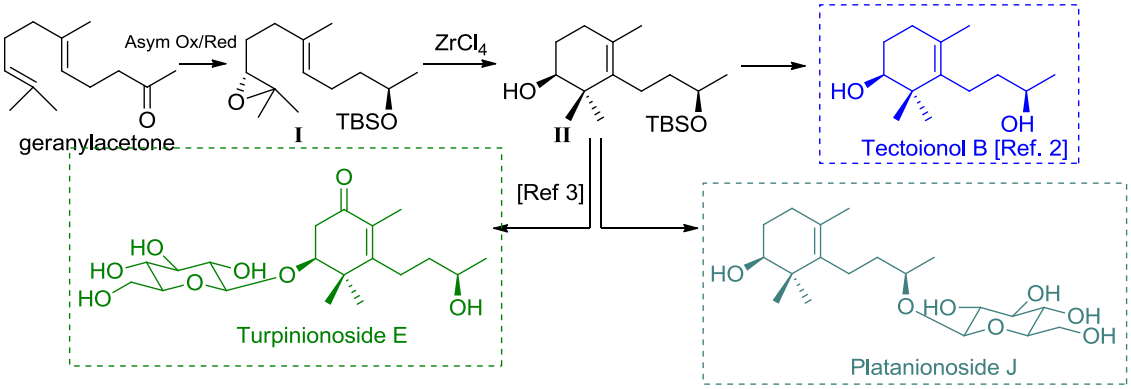
Keywords: *Apocarotenoids, megastigmane glycosides, asymmetric synthesis*

The apocarotenoids are a group of natural products possessing predominantly the cyclohexene structure, occurring widely in living organisms, and arise biosynthetically through the oxidative cleavage of carotenoids. Among them, the megastigmane family is a expanding class of compounds widely distributed in plant kingdom and having a wide range of biological properties of interest [1]. The megastigmane skeleton is characterised by possessing 13 C atoms, including a cyclohexane ring substituted either at C-1, C-5, C-6 and/or C-4, and an aliphatic chain of four C atoms attached to C-6. A number of this apocarotenoids are glicosylated at different positions of the structure.



Scheme 1. Asymmetric approach

We have carried out a few-step asymmetric approach to this kind of compounds starting from geranyl acetone (Scheme 1). The key stage is the formation of **II**, process in which $ZrCl_4$ acts as Lewis acid opening the oxirane ring to lead to **II** with selective formation of tetrasubstituted double bond. This new procedure has been implemented after testing several Lewis acids and experimental conditions, under the guidance of theoretical calculations. Regioselective deprotection/glycosylation protocol allows to obtain different members of this family of apocarotenoids.

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IODINE A SOFT REACTIVE FOR AROMATIZATION ON TERPENE SYNTHESIS

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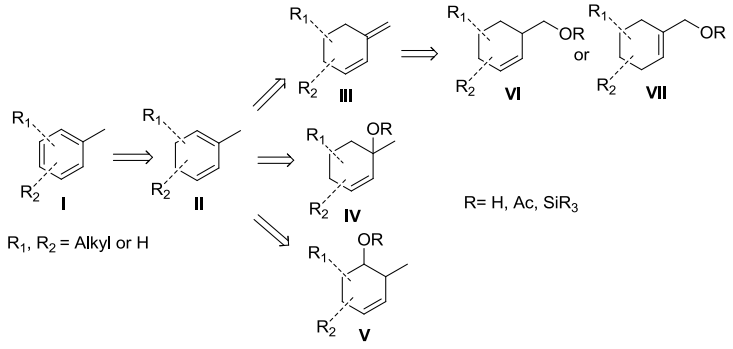
Keywords: *terpenoids, iodine, aromatization, rearrangements*

In the field of terpenoids only a few examples of iodine aromatization have been reported [1]. This process collides with the fact that most of the carbocyclic skeleton presents angular methyls and consequently, the aromatization of these structures in a lot of cases involves necessarily rearrangements. It was then reasoned that if the use of $\mathbf{I_2}$ and/or the liberation of significant quantities of HI provokes the presence of carbocationic species, the production of rearrangements and migrations permitting the aromatization would then be possible. Bering this in mind, we wondered whether a 4 π system in a cyclohexane framework such as **II** would evolve easily to the corresponding aromatics **I** in presence of $\mathbf{I_2}$. In this line of thinking, the possible precursors of **II**, such as diene **III** or the allylics alcohol I**V** and **VII**, or even the homoallylic alcohols **V** and **VI** may also well undergo this transformation.



Scheme: Working Hypothesis

Here we describe efficient procedures based on the use of iodine for the aromatization of a series of terpenes possessing dienes and homo- or allylic alcohols (and several derivatives) in their structure. Different examples are reported as a proof-of-concept study.

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THEONELLATETRAHYDROPYRIMIDINE: Unprecedented Cytotoxic Alkaloid from Theonella sp.

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Keywords: *sponge, marine natural products, NMR, DFT calculations*

Theonellatetrahidropyrimidine (**1**) was isolated and characterized from Indonesian sponge *Theonella* sp.[1] during the PharmaMar's ongoing program to study cytotoxic substances from marine sources. This new metabolite was modestly active against leukemia cells (IC_{50} = 5 μg/mL) and inactive against solid tumor cell lines. Its planar structure was deduced from mass spectrometry along with 1D and 2D RMN experiments. It possesses an unusual skeleton consisting of an uncommon 1,4,5,6-tetrahydropyrimidine ring, previously described for manzacidins [2].

The relative stereochemistry of compound **1** (figure 1) was defined by a combination of ^{1}H-^{1}H coupling constant analysis, nOe experiments, *J*-based configurational analysis and DFT computational calculations.

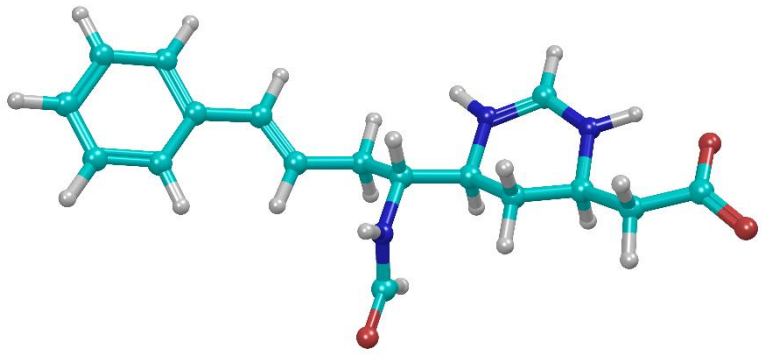

Figure 1. 3D model of theonellatetrahydropyirimidine **1**.

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PHTHALIMIDE-LACTONES STIMULATE GERMINATION OF PARASITIC WEEDS

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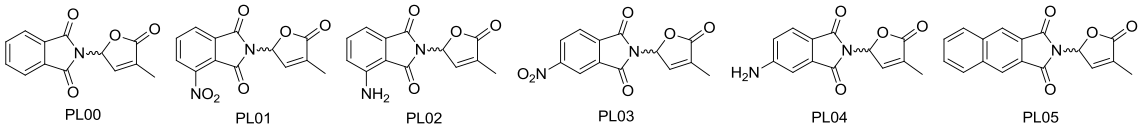
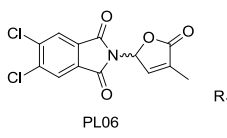
Keywords: *Parasitic weeds, Broomrape, Phthalimide, Strigolactone, Seed germination*.

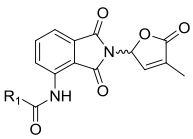
Parasitic weeds cause high damage on crops production each year and their seed bank is almost indestructible. The strategy of suicidal germination is based on the principle of applying germination stimulants in the soil to make the parasites germinate before sowing a crop to which they can attach. This process leads the parasitic seedlings to an inevitable death due to nutrient starvation.[1] Synthetic analogues of germination-inducing factors constitute a cheap and feasible strategy to control seed bank of weeds, although, the stimulant should be easily synthesized and economical to afford mass production.

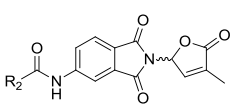
We synthesized a family of N-substituted phthalimides with a lactone ring and containing different substituents in the aromatic ring. The synthetic procedure is simple and starts with commercially available phthalimides. We called this compounds phthalimide-lactones. Recently, we have also synthetized new amide derivatives with different chain sizes in positions 3 and 4. The complete collection (PL00-18) was purified and assayed against parasitic weeds *O. minor, O. cumana* and *P. ramosa.*

In summary, our structure-activity relationship analysis demonstrated high selectivity according with the structural modification and parasitic species tested. Some of our structural modifications induced levels of germination comparable with the positive control GR-24, a synthetic analogue of strigolactones, natural and most active host-derived germination-inducing factors. The use of these compounds as new leads for weed control is discussed.









Compound	R_1
PL07	$-CH_3$
PL08	$-CH_2CH_3$
PL09	$-CH_2CH_2CH_3$
PL10	$-CH_2CH_2CH_2CH_3$
PL11	$-CH_2CH_2CH_2CH_2CH_3$
PL12	-Ph

Compound	R_2
PL13	$-CH_3$
PL14	$-CH_2CH_3$
PL15	$-CH_2CH_2CH_3$
PL16	$-CH_2CH_2CH_2CH_3$
PL17	$-CH_2CH_2CH_2CH_2CH_3$
PL18	-Ph

Acknowledgements

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SINTESIS Y EVALUACIÓN BIOLÓGICA DE DERIVADOS DE COLCHICINA Y AMINOCOMBRETASTATINA

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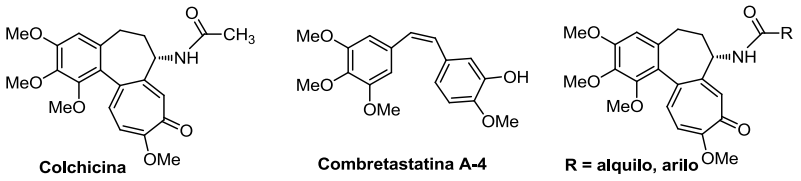
Palabras Clave: *colchicina, aminocombretastatina, VEGF, telomerasa, hTERT, c-Myc*

La colchicina, un alcaloide, y la combretastatina A-4, un *cis*-estilbeno, son productos naturales con una potente actividad antitumoral debido a su capacidad disruptora de microtúbulos.[1] Asimismo, ambos compuestos, así como algunos derivados de los mismos, han mostrado poseer propiedades antiangiogénicas.[2]

La angiogénesis es el proceso de formación de nuevos vasos sanguíneos a partir del lecho vascular ya existente. Esta proliferación de vasos sanguíneos está rigurosamente controlada. En enfermedades como el cáncer, el proceso angiogénico se encuentra activado, permitiendo el aporte de oxígeno y nutrientes al tumor, lo que facilita su crecimiento y metástasis.[3] En la angiogénesis participa un elevado número de factores, entre los que destaca el factor de crecimiento endotelial vascular VEGF.[4]

La cantidad de divisiones que puede realizar una célula viene determinada por el acortamiento de los telómeros, fragmentos de nucleótidos no codificantes ubicados en el extremo de las cadenas de ADN. Éstos pueden ser reparados por la telomerasa, estando el gen que codifica dicha enzima desactivado en las células sanas y activado en muchos tipos de tumores malignos.[5] El componente proteico de la telomerasa, denominado hTERT, está regulado por factores transcripcionales como c-Myc.[6]

En esta comunicación se presentará la síntesis de análogos de colchicina y análogos nitrogenados de combretastatina A-4 y su acción citotóxica sobre las líneas celulares tumorales HT-29 y MCF-7, así como la capacidad de estos compuestos para inhibir la secreción de la proteína VEGF y la expresión de los genes VEGF, hTERT y c-Myc.



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DISACÁRIDOS CIANOGÉNICOS Y BENZOILADOS EN HOJAS DE PSYDRAX LOCUPLES

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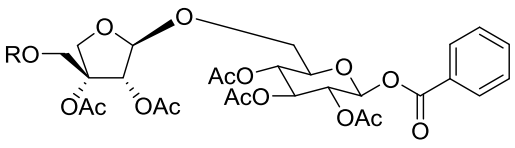
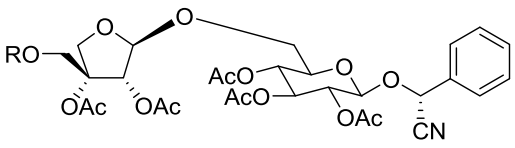
Palabras Clave: *Psydrax locuples, Disacáridos benzoilados, Glicósidos cianogénicos.*

Las plantas del género *Psydrax* y otras Rubiaceas relacionadas son usadas en la medicina popular africana frente a malaria, fiebre, dolores de cabeza, reumatismos, diarrea, conjuntivitis, micosis y otros cuadros infecciosos. Apenas existe bibliografía fitoquímica sobre este género: únicamente tres compuestos en la especie *Psydrax livida* [1]. Recientemente hemos comunicado las propiedades antioxidantes y citotóxicas de los extractos obtenidos de hojas de *Psydrax locuples*, planta arbórea utilizada particularmente en Mozambique para tratar la "doença da lua" en niños y recién nacidos, un síndrome relacionado con la epilepsia caracterizado por fiebre, vómitos, diarrea, dolor de cabeza y cólicos abdominales [2].

A partir del extracto de acetato de etilo de sus hojas se han aislado, mediante sucesivas cromatografías en columna y cromatografías en capa fina preparativas, varios disacáridos acetilados con estructura de (2*R*)-β-D-apiofuranosil-(1→6)-β-D-glucopiranosa. Estos disacáridos se pueden clasificar en dos familias en función de si el hidroxilo de la posición 1 de la β-D-glucopiranosa se encuentra benzoilado o si se encuentra unido a un residuo de mandelonitrilo formando glicósidos cianogénicos relacionados con la oxyanthina presente en *Psydrax livida* [1].





Estos disacáridos son prácticamente desconocidos en el reino vegetal, tanto los benzoilados como los cianogénicos, siendo la mayoría nuevos productos naturales.

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MDN-0101, AN ANTIPLASMODIAL TETRONIC ACID ISOLATED FROM CULTURE BROTHS OF THE FUNGUS COLEOPHOMA EMPETRI

G. Crespo[1], J. Martín[1], V. González-Menéndez[1], G. Pérez-Moreno[2], P. Sánchez-Carrasco[2], I. Pérez-Victoria[1], L. M. Ruiz-Pérez[2], D. González-Packanowska[2], F. Vicente[1], O. Genilloud[1], G. F. Bills[1], F. Reyes[1]

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Key words: *tetronic acid,* Coleophoma empetri*, antiplasmodial, structural elucidation*

Malaria is an infectious disease caused by parasites belonging to the genus *Plasmodium*. Two billion people live in areas at risk from the disease, and annually up to one million people die from malaria infection. The discovery and development of new drugs for the treatment of malaria is thus of major importance.

Tetronic and tetramic acids are structural motifs that can be found in a wide range of natural products of various classes, including alkaloids, terpenes, and macrolides. Although a wide range of biological activities has been described for natural products belonging to these structural classes, only two previous publications report on their antiplasmodial activity. Ascosalipyrrolidinone A, a tetramic acid isolated from the marine obligate endophytic fungus *Ascochyta salicorniae*, was reported to have bioactivity in the low micromolar range against the strains K1 and NF 54 of *P. falciparum* [1]. On the other hand, the tetronic acid nodulisporacid A isolated from the marine derived fungus *Nodulisporium* sp. CRIF1 and the tetramic acid vermelhotin, obtained from an unidentified fungus (CRI247-01) belonging to the Order Pleosporales displayed moderate inhibition of *P. falciparum* strain 94 [2].

As part of a collaborative program focused on the discovery of new antimalarial compounds that might overcome the emerging resistance to current treatments, we discovered that acetone extracts of the fungus *C. empetri*, isolated from leaf litter of the plant *Kalmia latifolia,* displayed activity against *P. falciparum* 3D7. Bioassay-guided fractionation of these extracts using a combination of low resolution chromatography on SP207ss resin and reversed phase HPLC yielded the new tetronic acid MDN-0101 as the compound responsible for the observed activity. Data on the isolation, structural elucidation and biological activity against *P. falciparum* of this new antiplasmodial compound will be presented.

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S13: *Productos Naturales en la Señalización Química en Sistemas Biológicos*

IN PURSUIT OF SPEED: HOW TO RUN FASTER qNMR

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Keywords: *Nuclear Magnetic Resonance, Quantitative analysis*

Nuclear Magnetic Resonance (NMR) has been successfully used for many years for quantitative proposes (qNMR). However, until recent times this technique has suffered from a lack of general acceptance, in particular within the pharmaceutical industry. In contrast to other well-established analytical methods such as chromatography NMR gives a universal detection, providing the analysed molecules include active nuclei (^{1}H, ^{13}C, etc.) in their structure. In addition qNMR provides information about the existence of analytes that are difficult to detect by other techniques such as solvents. Nowadays, qNMR has become a recognized method for metabolomics and quality control of complex natural samples such as foods, plants or herbal remedies.[1] However, generally accepted qNMR workflows change with frequency when used by different laboratories and include a number of parameters that are susceptible of further optimization. In this communication, the authors review underlying concepts and will provide a detailed framework for qNMR measurements in optimal conditions.[2]

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PHYTOTOXIC ACTIVITY OF DIFFERENT JUGLONE AND LAWSONE DERIVATIVES

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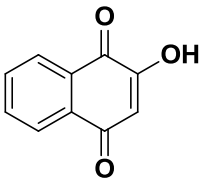
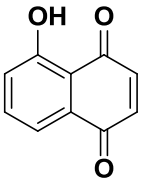
Keywords: *naphthoquinones, bioassay, phytotoxicity, weed control*.

Naphthoquinones, a class of phenolic compounds derived from naphthalene ring, are known by a broad-range of bioactivities described for them, including anti-inflammatory, antifungal and anticancer properties [1]. Owing to this wide range of biological activities, these structures could be promising candidates for weed control.
The work described herein reports on the preparation of different compounds modifying the hydroxyl group position of two natural naphthoquinones (juglone and lawsone) in order to evaluate their physicochemical properties and to improve their bioactivity. Twelve acyl and ten ether derivatives of each starting material were prepared. These derivatives with different chain length in positions 2 and 5 were evaluated in a bioassay of general activity (etiolated wheat coleoptiles bioassay). The most active compounds with better activity profiles were selected and evaluated on STS phytotoxic bioassay. Their potential structure and activity will be further described.



Lawsone



Juglone

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NUEVOS SIDERÓFOROS DE LA BACTERIA PATÓGENA DE PECES *Photobacterium damselae subsp. damselae*

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Palabras Clave: *Sideróforo, Photobacterium damselae* subsp *damselae*, *vibriosis*.

Photobacterium damselae subsp *damselae* (*Phdd*) es la bacteria responsable de una forma de vibriosis en una amplia variedad de peces y otros animales marinos [1],[2]. Teniendo en cuenta que los mecanismos de captación de hierro(III) mediante sideróforos, compuestos quelatantes que biosintetizan las bacterias para adquirir ese elemento del medio extracelular y transportarlo al citoplasma, constituyen un importante factor de virulencia bacteriano, su caracterización estructural será muy útil en el desarrollo de nuevos tratamientos contra dicha enfermedad infecciosa.

Estudios previos realizados por nuestros grupos de investigación permitieron detectar y caracterizar la vibrioferrina como uno de los sideróforos producidos por muchas cepas de *Phdd*, cuya estructura fue predicha a partir de aproximaciones genómicas y proteómicas al encontrar el clúster de genes que codifican su síntesis. Sin embargo, dicho clúster no es universal en todas las cepas y está ausente en otras cepas igualmente patógenas, por lo que debe existir un segundo sistema de captación de hierro(III) por dichas cepas. El hecho de que la búsqueda *in silico* en el genoma de estas cepas no haya permitido hasta el momento deducir cuál es el clúster genético involucrado en su producción, parece indicar que su estructura debe ser distinta a los reportados hasta la fecha. El fraccionamiento de sobrenadantes libres de células de cultivos de la cepa RM71 (no productora de vibrioferrina), crecida en condiciones de déficit de hierro, mediante resina XAD-4 y geles filtrantes del tipo Sephadex LH-20 y G-25 permitió detectar una fracción con actividad sideróforo que fue sometida a purificación por HPLC. Hasta ahora tenemos evidencias que indican que su estructura tiene al menos un fragmento de citrato.

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CARACTERIZACIÓN ESTRUCTURAL DE LAS ASPINOLIDAS PRODUCIDAS POR TRICHODERMA ARUNDINACEUM (Ta37) Y SUS MUTANTES SILENCIADOS EN LOS GENES TRI4 Y TRI5, EN DIFERENTES MEDIOS DE CULTIVO

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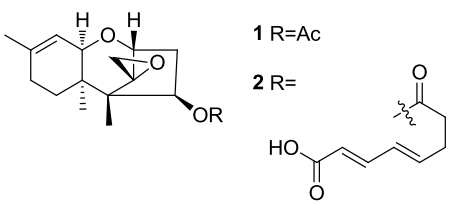
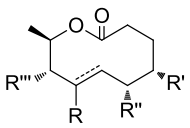
Palabras Clave: *Trichoderma arundinaceum, aspinolidas, tri4, tri5, genes*

Trichoderma es un género de hongos filamentosos conocido por su habilidad de actuar como agentes de biocontrol contra hongos fitopatógenos. Entre los metabolitos producidos por *Trichoderma*, los trichotecenos son micotoxinas que han mostrado un amplio abanico de actividad biológica. Dentro del clade Brevicompactum, *Trichoderma brevicompactum* y *Trichoderma arundinaceum*, producen respectivamente dos trichotecenos diferentes, trichodermina (**1**) y harzianum A (**2**). Los genes t*ri4* y *tri5* involucrados en la biosíntesis de trichotecenos en *T. brevicompactum* y *T. arundinaceum* se han clonado y caracterizado.

Recientemente, se ha publicado que la disrupción de estos genes suprime la producción de harzianum A (**2**) en *T. arundinaceum.* Los ensayos de enfrentamientos realizados con estos mutantes, contra *Botrytis cinerea,* han demostrado que los mutantes *tri4* y *tri5* mantienen un nivel significativo de inhibición del crecimiento de *B. cinerea,* mediante la sobreproducción de una nueva familia de metabolitos con esqueleto policétido denominadas aspinolidas. En esta comunicación se presentaran los resultados obtenidos en el estudio de la producción de estos nuevos metabolitos, en diferentes medios de cultivo, empleando la cepa silvestre Ta37 y los mutantes TaΔTri4 y TaΔTri5. Los resultados han permitido caracterizar estructural y químicamente esta nueva familia de policétidos.

Las aspinolidas parecen tener un efecto redundante con harzianum A (**2**) y estar implicadas en la inhibición del crecimiento de *B. cinerea* observado en los enfrentamientos entre ambas especies de hongos.





3 Aspinolidas

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ACTIVIDAD ANTIOXIDANTE DE Tabebuia rosea (Bertol.) A. DC.

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Palabras Clave: *antioxidante, DPPH, Tabebuia*

Tabebuia rosea, se ha empleado en medicina tradicional como agente anti-infeccioso. Existen antecedentes en la literatura indicando que los extractos y alguna de las fracciones obtenidas de *Tabebuia rosea* tienen actividad anti-antioxidante *in vitro* [1]. A partir de su raíz se han aislado metabolitos tales como algunas naftoquinonas y tabebuialdehídos A-C [2]. Debido a la poca información disponible con relación a los componentes y al efecto antioxidante de esta especie, se evaluó dicha actividad utilizando los extractos obtenidos de las hojas en un modelo *in vitro*.

Las hojas de *Tabebuia rosea* secas y molidas, se extrajeron con metanol durante seis días a temperatura ambiente. Se realizaron extracciones sucesivas líquido-líquido con diferentes solventes. Los extractos obtenidos se concentraron y se emplearon para los ensayos *in vitro*. Se evaluó la actividad antioxidante preparando los extractos a concentraciones de 500 y 1000 µg/mL. Se empleó una solución de DPPH a 20 µg/mL. Se utilizaron como controles ácido ascórbico, ácido gálico y Trolox a 5, 25, 50, 100 y 200 µg/mL. Todas las soluciones resultantes se mezclaron con DPPH y fueron incubadas en oscuridad durante 30 minutos a temperatura ambiente. Se leyó la absorbancia a 517 nm. El extracto en acetato de etilo obtenido presentó la mayor actividad en la inhibición del radical DPPH superior al 90%, con un IC_{50} de 157.5 µg/mL. El extracto en acetato de etilo se fraccionó sobre columna cromatográfica con el fin de identificar los compuestos responsables de la actividad antioxidante.

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Al programa de becas nacionales doctorales de COLCIENCIAS (Colombia), a la Vicerrectoría de Investigación, Innovación y Extensión de la Universidad Tecnológica de Pereira (Colombia), y al Grupo de Alelopatía de la Universidad de Cádiz (España).

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A NEW TETRAPEPTIDE FROM BACILLUS CEREUS STRAIN ISOLATED FROM THE SOFT CORAL ANTILLOGORGIA ELISABETHAE (SYN. PSEUDOPTEROGORGIA ELISABETHAE)

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Key Words: *Marine microorganisms, Bacillus cereus, cyclopeptide, Antimicrobial activity.*

Bacteria belonging to *Bacillus* genus are present in numerous environments and they are considered as microbial factories for the production of a large number of biologically active molecules [1]. In the case of *Bacillus subtilis*, it has been postulate that about 4 % of its genome is devoted to produce antimicrobial compounds [2, 3]. Cyclic lipopeptides like surfactines, iturines and fengicines have been isolated from several strains of *Bacillus* usually associated to plant rhizomes and some of them have shown activity in the control of pathogenic infections in the host plants [2]. Furthermore, the emetic toxins valinomycin and cerulolide isolated from *Bacillus cereus* strains, are the more remarkable compounds due to its activity [3].

As part of our search of novel and bioactive compounds from marine microorganisms, two new compounds, the tetrapeptide *cyclo*-(L-phenylalanyl-*trans*-4-hydroxy-L-prolyl-L-leucyl-*trans*-4-hydroxy-L-proline) (**1**) and 4-(*R*)-hydroxysattabacin (**2**), along with the known diketopiperazine and the methyl, isopropyl and propyl esters of the *p*-hydroxybenzoic acid (**3–5**) were isolated from the organic extracts of the culture of the *B. cereus* RKHC-09 strain in two culture media (MOLP and B1). This strain was recovered from the soft coral *Antillogorgia elisabethae* recollected in the Colombian Caribbean Sea. The structure of compound **1** was elucidated by mono and bi dimensional NMR experiments, and its absolute stereochemistry was established by Marfey´s method. Compound **1** showed mild activity against *Colletotrichum gloeosporoides* C26 (yam pathogen). The methyl and propyl ester of *p*-hydroxybenzoic acid (**4** and **5**) showed antimicrobial activity against *S. aureus* ATCC 33591 and *S. cerevisiae*, with a MIC of 2 μM.

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SÍNTESIS DE (±) STEMOAMIDA BASADA EN Ti(III)

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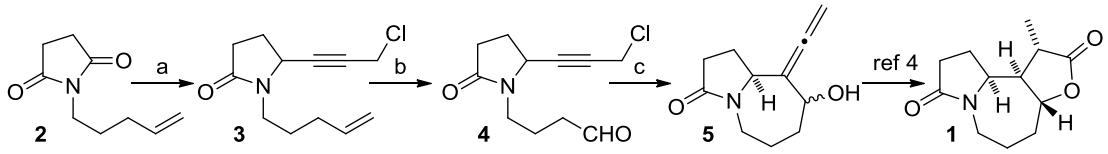
Palabras Clave: *Alcaloides de Stemona, Titanio (III), α-Alenoles.*

Los alcaloides del género *Stemona* son un grupo de productos naturales con más de 42 estructuras aisladas [1], que representan una familia de alcaloides policíclicos caracterizados por la presencia de un núcleo de pirrolo[1,2*a*]azepina con interesantes propiedades biológicas [2]. De entre los muchos alcaloides presentes en *Stemona tuberosa*, (+)-stemoamida (**1**) posee un núcleo tricíclico con un grupo funcional aleno y cuatro estereocentros consecutivos. Un estudio reciente de síntesis bio-inspirada de (+)-stemoamida se basa en un proceso de lactonización del intermedio clave **5** [3]. Nosotros hemos preparado este intermedio usando una metodología desarrollada en nuestro grupo de investigación basada en un proceso de ciclación de haluros propargílicos catalizada por Ti(III) que genera alenos exocíclicos (esquema 1). A partir del compuesto **2**, obtenido con rendimientos casi cuantitativos desde la sal sódica de la succinimida [4], se consigue la desimetrización selectiva originando **3**. Para ello, se trata cloruro de propargilo con *n*-BuLi y se adiciona a **2** para dar un hidroxi-derivado que se reduce inmediatamente con $NaBH_3CN$. Tras degradar quimioselectivamente el doble enlace terminal, se obtiene el aldehído **4**. Por último, la ciclación de **4** catalizada por $[Cp_2TiCl]$ genera el aleno **5** como una mezcla 2.7/1 de diasterómeros. Esta mezcla puede usarse directamente en la preparación de stemoamida, como ya se había descrito previamente [3]. Por tanto, se ha logrado una nueva síntesis formal de stemoamida más eficaz.



Esquema 1. a) i: cloruro de propargilo, n-BuLi, THF, 50º C; ii: $NaBH_3CN$, MeOH, AcOEt, 78º C, 50%; b) OsO_4 cat., KIO_4, THF/H_2O, 0º C a 5º C, 59%; c) $TiCl_2Cp_2$, Mn, 2,4,6-colidina, TMSCl, THF, reflujo, 76%.

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LAUROKANOLS, NEW GROUP OF OXASQUALENOIDS ISOLATED FROM LAURENCIA VIRIDIS

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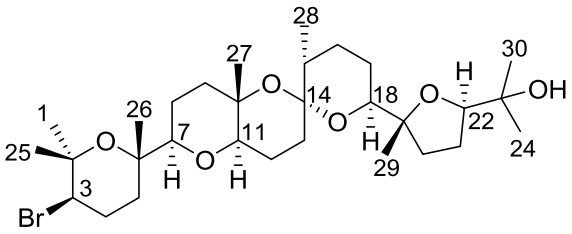
Keywords: *Oxasqualenoids, Laurencia, marine polyether*

Pharmaceutical industry has a special interest to find new bioactive molecules that may be useful in the treatment of diseases without an effective therapy. Red alga of the genera *Laurencia* and *Chondria* have been shown to produce a variety of cyclic bioactive polyethers [1]. Within this group, oxasqualenoids possess interesting pharmacological properties shuch as potent cytotoxicity, protein phosphatase PP2A inhibition and activity as integrin antagonist [2,3].

In this communication we described a new group of oxasqualenoids that, although related with the thyrsyferol series, are characterized to possess, rather the characteristic bicyclic system consisting of two transfused tetrahydropyrans, a new tricyclic system having a third ring of tetrahydropyran bonded to the transfused rings in a spiro form. Structure elucidations of these molecules have been achieved by the use of spectroscopic techniques. Biological activity studies are currently in progress [4].



Laurokanol (**1**)

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S13: *Productos Naturales en la Señalización Química en Sistemas Biológicos*

EL FITATO COMO INHIBIDOR DE LA CALCIFICACIÓN VASCULAR

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Palabras Clave: *fitato, inhibidor, calcificación, hidroxiapatita*

El fitato (myo-inositolhexafosfato) es un producto natural que se encuentra en las semillas utilizadas en nuestra alimentación (como son cereales, legumbres y frutos secos) y que está presente en fluidos fisiológicos y tejidos de mamíferos en bajas concentraciones que dependen de su aporte exógeno [1]. El fitato ha manifestado tener un potente efecto inhibidor sobre el proceso de formación y crecimiento de cristales de hidroxiapatita. Así, ha demostrado efecto inhibidor en distintos procesos de calcificación patológica, como son la litiasis renal cálcica [1-3] en la sialolitiasis [4,5] y en las calcificaciones subcutáneas [6,7].

En el presente trabajo, se ha estudiado el efecto inhibidor del fitato sobre la calcificación vascular en un modelo "in vitro" y en pacientes con enfermedad renal crónica (ERC). En el modelo in vitro, 1mg/L de fitato provocó una inhibición del (76.6%, p=0.039) sobre la formación de cristales de hidroxiapatita con respecto al experimento control.Con respecto al estudio en pacientes, aquellos con calcificación aórtica abdominal (CAA) indetectable o leve presentaron una mayor ingesta dietética de fitato (29.6%, p= 0.041) y unos mayores niveles de fitato en orina (36.3%, p = 0.037), en comparación con los que presentaban CAA moderada o severa.

El fitato posee un claro efecto inhibidor sobre la calcificación vascular mediante su adsorción sobre los cristales de hidroxiapatita dificultando su formación y posterior crecimiento. Además, una dieta con un consumo adecuado de fitato podría tener un importante papel en la prevención de las calcificaciones vasculares en pacientes con ERC.

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S13: *Productos Naturales en la Señalización Química en Sistemas Biológicos*

SYNTHESIS OF ENT-ACINETOBACTIN AND OTHER ANALOGUES AND THEIR SIDEROPHORE ACTIVITY EVALUATION IN AEROMONAS SALMONICIDA

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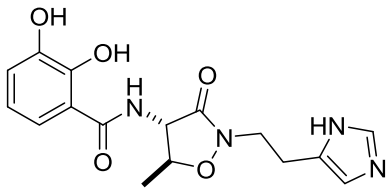
Key words: *Sideróforos, receptores de sideróforos, Aeromonas salmonicida*

Aeromonas salmonicida subsp. *salmonicida* (*Ass*) is the causative agent of furunculosis in salmonid fish which results in a chronic or acute haemorrhagic septicaemia [1]. We have found that acinetobactin (**1**) is one of the catechol-type siderophores produced by *Ass* under iron-limiting conditions. Acinetobactin (**1**) was isolated and characterized in 1994 for the first time from low-iron cultures of *Acinetobacter baumannii* ATCC1960 [2], and its structure was then corrected in 2009 [3].

In order to compare the influence of the configuration of the asymmetric centers in **1** and the presence of the methyl group in the isoxazolidinone ring on the siderophore activity, *ent*-acinetobactin and other analogues were prepared. They were evaluated by growth promotion assays *in vitro* against three *Ass* strains: the wild-type strain (WT), a Δ*fstB* mutant (acinetobactin-producing strain lacking the acinetobactin receptor) and a Δ*asbD* mutant (does not produce acinetobactin but bears the acinetobactin receptor). The results indicate that there is a lack of stereoisomeric influence on the siderophore activity, that the presence of the methyl group at isoxazolidinone ring is required for using the FstB receptor as the route of entry and that the presence of an imidazole ring or a similar ring as triazol is required for the siderophore activity.



Acinetobactin (1)

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S13: *Productos Naturales en la Señalización Química en Sistemas Biológicos*

OPTIMIZACIÓN DE LAS CONDICIONES DE EXPRESIÓN DE LA PROTEÍNA RECOMBINANTE FrpA, RECEPTOR DEL SIDERÓFORO PISCIBACTINA

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Palabras Clave: *Sideróforos, receptores de sideróforos, proteína recombinante*

Photobacterium damselae subsp *piscicida* (*Phdp*) es la bacteria causante de la pasteurelosis, una infección que afecta a una amplia variedad de peces marinos de interés acuícola, por lo que existe un creciente interés en el desarrollo de nuevos métodos de prevención y control [1]. La mayoría de las bacterias sintetizan sideróforos, compuestos quelatantes de hierro(III), para adquirir este elemento del medio extracelular y transportarlo al citoplasma. Estos mecanismos de asimilación de hierro son un importante factor de virulencia bacteriano [2]. Nuestro grupo logró aislar y caracterizar la piscibactina como el sideróforo sintetizado por *Phdp* [3]. Con el fin de profundizar en la caracterización de este sistema es necesario determinar como la piscibactina interacciona con su receptor, la proteína FrpA. Con este fin, en la actualidad estamos completando la síntesis total de piscibactina y, además, buscamos caracterizar estructural y funcionalmente tanto la proteína FrpA, como el complejo piscibactina-Fe(III)-FrpA, lo que implica el aislamiento y cristalización de ambos. Con este objetivo, buscamos las condiciones óptimas de expresión de FrpA en *E. coli*. Para ello se clonó el gen *frpA* en dos vectores de expresión, pBAD (inducible por arabinosa) y pET20-b(+) (inducible por IPTG). Los vectores obtenidos contienen una cola de His que puede estar ubicada en la posición N-terminal, C-terminal o en un *loop* de la proteína. Estas His son necesarias para la purificación mediante resinas de afinidad de Ni. Los constructos obtenidos se utilizaron para transformar diferentes cepas de *E. coli* (BL21CodonPlus, DE3 y C43) y se realizaron ensayos variando los tiempos de expresión y la temperatura de incubación. De los ensayos de expresión realizados hasta el momento, la mayor producción de FrpA se ha obtenido con las cepas BL21 CodonPlus y BL21 DE3, con los constructos que contienen las His en la posición N-terminal y usando tiempos de incubación superiores a 24 h.

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S14. Aplicaciones Científico-Tecnológicas del Análisis Térmico (AAT) / Scientific and Technological Applications of Thermal Analysis

El simposio se centra en: a) el desarrollo de nuevos sistemas de medida, b) el desarrollo de nuevas técnicas de determinación de parámetros termodinámicos, c) el análisis térmico de material orgánico o inorgánico, d) el estudio de aplicaciones en campos tan diversos como el farmacéutico, el alimentario o la nanotecnología, e) la simulación de procesos térmicos o su modelado.

The symposium will be centered in: a) last developments in new measurement systems, b) last developments in new techniques for determination of thermodynamic parameters, c) thermal analysis of organic and inorganic materials, d) the study of applications in different fields (pharmaceutical, food industry, nanotechnology, etc., e) the simulation and modelling of thermal processes.

Organizadores:

Francisco Fraga (USC)

Joan Josep Suñol (UdG)

e-mail de contacto: joanjosep.sunyol@udg.edu

Miércoles 22 de Julio 2015

18:30	***Sesión de Pósteres***

Jueves 23 de Julio 2015

08:40 – 09:40	**PL-5**	***Conferencia Plenaria*** (Común a todos los simposios) **Avelino Corma Canós** *"Intentos para Establecer Puentes entre la Catásisis Homogénea y Heterogénea"*

Chairman: J. J. Suñol

10:00 – 10:30	**S14-IL-01**	**Marta Fernández García** "*El Análisis Térmico y la Química en la Ciencia de Polímeros*"

Chairman: A. Manich

10:30 – 10:45	**S14-OC-01**	**Eva C. Vázquez-Barreiro** "*Cinética del Curado del Diglicidiléter de Bisfenol-A (BADGE, n=0) Utilizando ZnTPyP como Agente de Reticulación*"
10:45 – 11:00	**S14-OC-02**	**C. Rodríguez-Tinoco** "*Multi-calorimetric Analysis to Study the Transformation Kinetics of an Organic Glass Former over a Wide Temperature Range*"
11:00 – 11:30		Pausa Café ***Sesión de Pósteres***

Chairwoman: M. Fernández-García

11:30 – 11:45	**S14-OC-03**	**A. Manich** "*DSC y TMA en la Caracterización de Composites TiO_2/PET*"
11:45 – 12:00	**S14-OC-04**	**J. J. Suñol** "*Diagramas de Fase: Aleaciones Magnéticas con Memoria de Forma*"
12:00 – 12:15	**S14-OC-05**	**A. Deltell** "*Efecto Magnetocalórico en Aleaciones tipo Heusler: Refrigeración Magnética*"
12:15 – 12:30		**Concesión del Premio del GECAT**
12:30 – 13:30		**Junta del Grupo Especializado de Calorimetría y Análisis Térmico**

13:30	***Ceremonia de Clausura***

Comunicaciones Invitadas (IL)

S14: *Aplicaciones Científico-Tecnológicas del Análisis Térmico*

EL ANÁLISIS TÉRMICO Y LA QUÍMICA EN LA CIENCIA DE LOS POLÍMEROS

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Palabras Clave: *Polímeros, control estructural, química, análisis térmico, calorimetría diferencial de barrido, microcalorimetría.*

Los polímeros son unos materiales con características específicas dependiendo de su estructura macromolecular. El análisis térmico de estos materiales nos permite conocer no solo su estabilidad térmica sino también sus procesos de cristalización, su nano-organización dentro del material, su capacidad de interaccionar con otras moléculas, además de otras muchas propiedades. Esta presentación se centra en los distintos métodos para sintetizar polímeros con peso molecular y polidispersidad controlada, además de funcionalidad deseada, mediante polimerización radical controlada. Entre ellos, los copolímeros de bloque son un campo de creciente interés dentro de la nanotecnología y la nanociencia, puesto que son capaces de auto-organizarse tanto en estado sólido, en disolución y en superficie y generar distintas morfologías en la escala nanométrica. El estudio térmico de estos sistemas permite conocer su potencial en numerosas aplicaciones, ya sea como compatibilizantes de mezclas, máscaras, sensores, sistemas de reconocimiento, etc. Numerosos ejemplos se detallarán a lo largo de la presentación poniendo de manifiesto polímeros con distintas estructuras químicas y, por tanto, diferentes aplicaciones.

Comunicaciones Orales (OC)

S14: *Aplicaciones Científico-Tecnológicas del Análisis Térmico*

CINÉTICA DE CURADO DEL DIGLICIDILÉTER DE BISFENOL-A (BADGE, n = 0) UTILIZANDO ZnTPyP COMO AGENTE DE RETICULACIÓN

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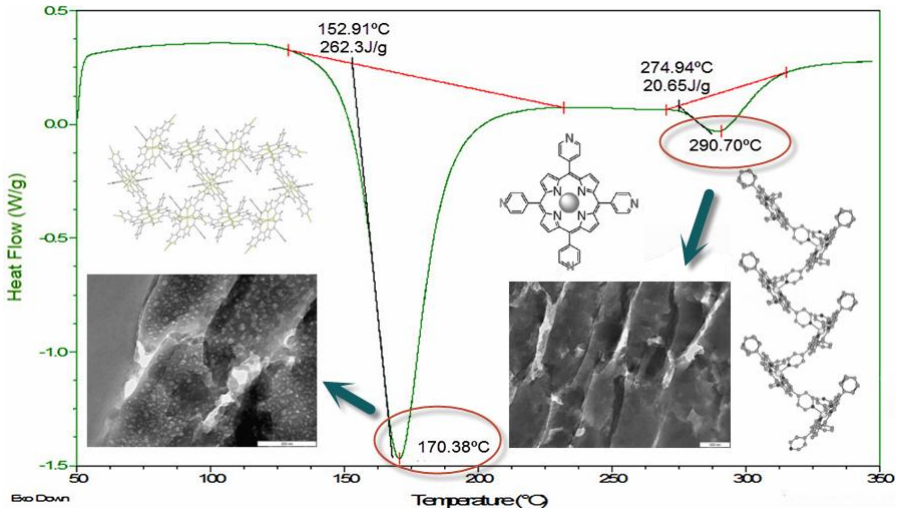
Palabras Clave: *Cinética, propiedades térmicas, resinas, macrociclos*

El curado de la resina BADGE, n = 0, (diglicidileter de bisfenol A) utilizando como agente entrecruzante el ZnTPyP (zinc 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine) fue estudiado mediante calorimetría diferencial de barrido. Este estudio forma parte de un proyecto cuyo objetivo es introducir agentes entrecruzantes derivados de macrociclos [1], con el fin de mejorar la estabilidad de la resina a altas temperaturas. Adicionalmente, estos compuestos permiten complejar iones metálicos en su estructura, lo que podría conducir a nuevas propiedades. Al determinar la entalpia de la reacción de curado a varias temperaturas, se observó la existencia de dos picos exotérmicos a 170ºC y a 290ºC con unos valores de la entalpia de 258.1±7.4 J/g y 27.7±5.8 J/g respectivamente.

La Figura muestra una curva calorimétrica del proceso de reacción de los compuestos anteriormente citados y las imágenes TEM del material a esas temperaturas:



Agradecimientos:
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S14: *Aplicaciones Científico-Tecnológicas del Análisis Térmico*

MULTI-CALORIMETRIC ANALISYS TO STUDY THE TRANSFORMATION KINETICS OF AN ORGANIC GLASS FORMER OVER A WIDE TEMPERATURE RANGE

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Keywords: *Ultrastable glasses, calorimetry, propagating front transformation.*

Glasses with an exceptional kinetic and thermodynamic stability, comparable to ordinary glasses aged for millions of years [1], can be prepared by thermal evaporation [2]. These glasses present a series of differences that makes them unique compared with conventional glasses: higher onset temperature of the glass transition and density, lower enthalpy, molecular anisotropy and optical birefringence among others [3]. Ultrastable glasses are so tightly packed that the transformation to the supercooled liquid is heterogeneous starting at surfaces/interfaces [4,5,6]. These anomalous properties persist in thin-film vapor-deposited glasses grown at other temperatures and therefore embedded with different stabilities.

Calorimetry provides a convenient tool to measure the transformation front velocity. In this context, we use different calorimetric techniques (DSC at 10^{-2} K/s and QA-FSC up to 100 K/s) to obtain the transformation front velocity for glasses in a large temperature range, up to Tg + 75K [6]. We have also developed an ad-hoc surface normalization procedure of the heat capacity curves that unambiguously permits us, on one hand, determining if the transformation into the SCL occurs via propagating fronts or through a bulk process, as typically occur in conventional glasses [6], and, on the other hand, deriving the value of the front velocity for the various stabilities in the explored temperature interval [6,7]. While previous measurements highlighted the importance of the mobility of the liquid in the propagating front, we also observe a strong dependence on the stability of the glass. Our data, combined with other techniques, suggest that additional factors such as the structure of the glass may play a significant role in the value of the growth front velocity [7].

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S14: *Aplicaciones Científico-Tecnológicas del Análisis Térmico*

DSC Y TMA EN LA CARACTERIZACIÓN DE COMPOSITES TiO_2/PET

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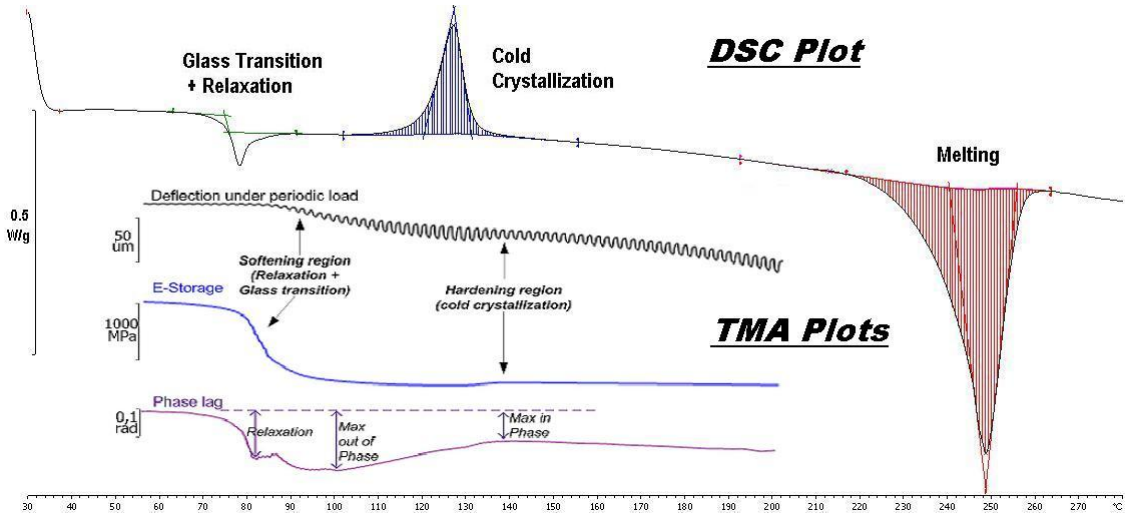
Palabras Clave: *Composites, PET, anatasa, DSC, TMA*

Las partículas de TiO_2 en la forma cristalina anatasa se utilizan como mateantes de fibras sintéticas y se incluyen antes de la extrusión. Los composites cerámica/polímero que se obtienen pueden presentar distintas propiedades según el tamaño y concentración de partículas que se incluyan, así como su distribución en el seno del polímero, lo cual afectará a la estabilidad térmica que dependerá del tamaño y perfección de los cristales que se formen como consecuencia del efecto nucleante/antinucleante de las partículas [1]. Se ha estudiado la influencia del tamaño (nano/micro), la concentración (1%, 2%, 3%) y su distribución gracias a la presencia del dispersante éster de ácidos montánicos/alcoholes multifuncionales (2%, 4%) en la estabilidad térmica de los composites obtenidos que se ha valorado mediante DSC y TMA.



El estudio de las relaciones significativas entre los parámetros obtenidos por ambos métodos pone de manifiesto que la cristalinidad (DSC) se correlaciona significativamente con los parámetros de deformación, temperatura, caída de módulo y ángulo de desfase que caracterizan la transición vítrea en el TMA, y que los parámetros de deformación, módulo ángulo de desfase están fuertemente correlacionados, siendo este último el parámetro que mejor se correlaciona con las medidas de módulo y deformación. Los fenómenos de cristalización fría aparecen en los composites nanoanatasa/PET de cristalinidad media más baja (32%) que la conseguida en los composites microanatasa/PET (39%).

Agradecimientos: El trabajo experimental se ha financiado con el Proyecto MAT2010-20324-C02 y la presentación de resultados con ayuda del proyecto IPT2012-0644-310000.

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S14: *Aplicaciones Científico-Tecnológicas del Análisis Térmico*

DIAGRAMAS DE FASE: ALEACIONES MAGNÉTICAS CON MEMORIA DE FORMA

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Palabras Clave: *Aleaciones magnéticas, Memoria de forma, Diagramas de fase*

Las aleaciones magnéticas con memoria de forma se caracterizan por la coexistencia de dos transformaciones, una estructural (de una estructura cristalográfica cúbica austenítica a una estructura martensítica ya sea tetragonal, ortorrómbica o monoclínica) y otra magnética (de una fase ferromagnética a una fase paramagnética). Todas las combinaciones son posibles: austenita ferromagnética, austenita paramagnética, martensita ferromagnética, martensita paramagnética); dependiendo de la composición y de las condiciones de producción y tratamiento térmico. Estas aleaciones se caracterizan por su respuesta frente a esfuerzos, campos magnéticos y/o cambios de temperatura [1,2].

El análisis térmico mediante calorimetría diferencial de barrido permite determinar las temperaturas de transformación características y parámetros termodinámicos como los cambios entálpicos y entrópicos. Una vez determinadas es posible construir diagramas de transformación en función del contenido en uno de los elementos o de un parámetro relacionado con la configuración electrónica de la aleación, el número promedio de electrones de valencia e/a. En el presente trabajo se muestran diversos diagramas de fase, comparando los resultados obtenidos en aleaciones en forma masiva o en forma de cinta; así como la influencia del tratamiento térmico. En concreto en aleaciones tipo Heusler Ni-Mn-(In,Sn). Se constata que las temperaturas de transformación son más elevadas en el masivo que en las cintas. Por otra parte, el tratamiento térmico favorece el aumento de las temperaturas.

Agradecimientos: El trabajo experimental se ha financiado con el Proyecto MAT2013-47231-C2-2-P.

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S14: *Aplicaciones Científico-Tecnológicas del Análisis Térmico*

EFECTO MAGNETOCALÓRICO EN ALEACIONES TIPO HEUSLER: REFRIGERACIÓN MAGNÉTICA

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Palabras Clave: *Refrigeración magnética, Efecto magnetocalórico.*

Equipos y dispositivos basados en la refrigeración magnética son una alternativa a los sistemas de refrigeración convencionales. Algunas aleaciones magnéticas tipo Heusler se caracterizan por tener una respuesta termomagnética basada en el efecto magnetocalórico: la aplicación de un campo magnético externo favorece cambios estructurales, magnéticos y de temperatura que comportan la absorción o cesión de calor entre la aleación y su entorno.

La realización de medidas termomagnéticas en el intervalo de temperaturas en que se produce el intercambio de calor permite determinar los cambios entrópicos empleando la relación termodinámica de Maxwell entre entropía y magnetización [1]. Interesan entropías altas a bajo campo magnético.

En el presente trabajo se presentan cálculos entrópicos realizados en aleaciones tipo Heusler no estequiométricas de los sistemas Ni-Mn-In y Ni-Mn-Sn a partir de medidas magnéticas isotermas. Los valores obtenidos dependen de la composición, de la microestructura y/o del tratamiento térmico. La reducción dimensional disminuye el cambio entrópico. Dependiendo del tratamiento térmico la entropía asociada puede aumentar o disminuir [2]. Los cambios composicionales no provocan tendencias claras.

Agradecimientos: El trabajo experimental se ha financiado con el Proyecto MAT2013-47231-C2-2-P.

Referencias

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Presentaciones Póster (PP)

Listado de presentaciones póster

THERMOGRAVIMETRIC ANALYSIS TO OPTIMIZE THE LOW-TEMPERATURE PYROLYSIS PROCESS OF BITUMINOUS COALS

V. Kulakova

ANÁLISIS TÉRMICO Y ENSAYO DE TRACCIÓN DE COMPOSITES TiO_2/PET

D. Cayuela

S14: *Aplicaciones Científico-Tecnológicas del Análisis Térmico*

THERMOGRAVIMETRIC ANALYSIS TO OPTIMIZE THE LOW-TEMPERATURE PYROLYSIS PROCESS OF BITUMINOUS COALS

V. Kulakova[1], M.P. Gómez-Carracedo[2], J.M. Andrade[2], L. Butuzova[1]

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Keywords: coal, pyrolysis, primary tar, thermogravimetry, optimization

Thermoanalytical methods play a significant role for investigating the kinetics and decomposition of coal reactions during pyrolysis processes, especially for optimizing the technological processes. The primary aim of this research is to improve the low-temperature pyrolysis of coals and to determine optimum conditions to produce primary tar. Thermogravimetric analyses at different heating ranges and low-temperature pyrolysis of low and medium rank bituminous coals from Donetsk basin were carried out in this research.

Results (Fig. 1) showed that low and medium rank coals had different maximum temperatures (T_{max}) of thermal decomposition, 405 °C and 460 °C, respectively. It was found that low-temperature pyrolysis of low-rank coal at T_{max} increased the quantity of the major products, as semicoke (up to 67.0 wt. %) and primary tar (up to 14.8 wt. %). A decrease on the pyrolysis temperature from 520 to 405 °C leads to more solid and liquid products. The primary tar produced at 405 °C included about 50% more neutrals than that obtained under standard conditions. The quantity of aliphatics of the liquid part at 405 °C increased by 8 times, compared to the liquid at 520 °C. Note that the yield on liquid products augments when the heating rate increases from 6.5 to 16.3 °C/min (Fig. 1). Thus, two important technological parameters such as pyrolysis temperature and heating rate were established, which lead to maximum yield of more valuable primary tar from coals.

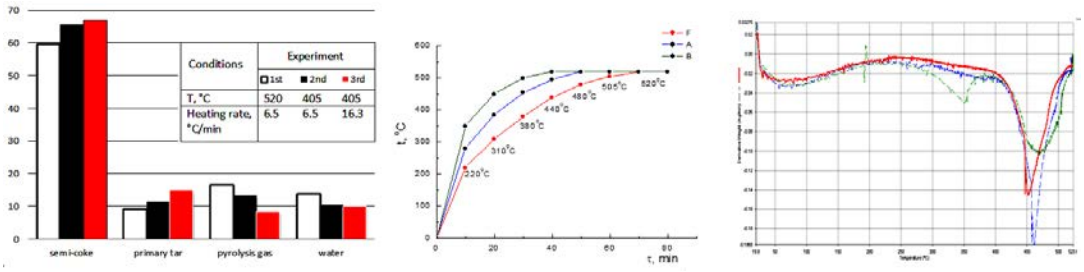

Fig. 1. Results of thermogravimetric analysis and pyrolysis experiments

Acknowledgement

V. Kulakova acknowledges the European Union for the Trans-European Mobility Project on Education for Sustainable Development supported by Erasmus Mundus Programme.

S14: *Aplicaciones Científico-Tecnológicas del Análisis Térmico*

ANÁLISIS TÉRMICO Y ENSAYO DE TRACCIÓN DE COMPOSITES TiO_2/PET

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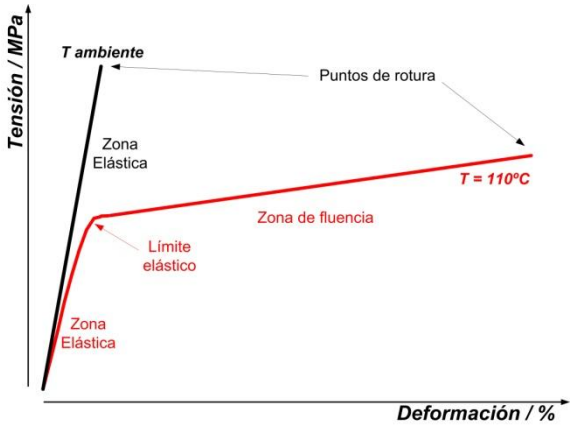
Palabras Clave: *Composites, PET, anatasa, tracción, fluencia, análisis térmico*

La anatasa es una forma cristalina del TiO_2 utilizada como mateante en la producción de fibras sintéticas. Además de su efecto de protección a la radiación UV, su inclusión en matrices poliméricas puede modificar diversas propiedades de los composites [1]. En este trabajo se presenta la influencia de la concentración y el tamaño de la anatasa (nano/micro), y la concentración de dispersante (éster ácidos montánicos/alcoholes multifuncionales MAWMA), en el comportamiento a tracción de estos composites a temperatura ambiente y a 110ºC por encima de la transición vítrea, relacionando los parámetros de tracción con los obtenidos mediante calorimetría diferencial de barrido y análisis termomecánico.



Módulo inicial: Aumenta con el tamaño de partícula y disminuye con la temperatura de ensayo (1814 a 265 MPa). Las diferencias más relevantes se observan con contenidos bajos de partícula (1%) y dispersante (2%). Las diferencias atribuibles al tamaño disminuyen con la proporción de partícula (3%) y dispersante (4%). Valores de fluencia: La tenacidad aumenta con el tamaño de partícula (12,30 a 17,75 MPa) y las diferencias disminuyen con el aumento de la concentración. La deformación también depende del tamaño y concentración de anatasa. Los valores más elevados se obtienen con contenidos medio-bajos de partícula y bajos de dispersante. El módulo de refuerzo es más elevado para la nanoanatasa y disminuye con la concentración de dispersante. Valores de rotura: La temperatura de ensayo disminuye la tenacidad y aumenta la deformación de rotura. El tamaño de partícula afecta negativamente a la tenacidad y los valores más elevados se obtienen a concentraciones bajas de nanoanatasa (50 MPa). La temperatura de ensayo enmascara los efectos que influyen en la deformación de rotura. Parámetros de análisis térmico: Los parámetros que mejor se relacionan con el comportamiento a tracción de los composites son la cristalinidad X (DSC), la temperatura de inicio de la caída del módulo de Young TEon y su valor mínimo Emin determinados por TMA.

Agradecimientos: El trabajo experimental se ha financiado con el Proyecto MAT2010-20324-C02 y la presentación de resultados con ayuda del proyecto IPT2012-0644-310000.

Referencias

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S15. Ingeniería Química y Medioambiente (IQMA) / Chemical Engineering and Environment

La Ingeniería Química es básica para el diseño de procesos químicos, tanto para la investigación de nuevas producciones o mejoras en la producción de compuestos como para el tratamiento de efluentes en los distintos procesos de fabricación. Tiene diferentes orientaciones destacando el estudio general de procesos químicos, la ingeniería de las reacciones químicas y de los procesos catalíticos, el estudio del medio ambiente y la biotecnología como aspectos más destacados, sin descuidar la economía de los procesos. Por ello los objetivos del symposium en esta área tecnológica estarían en la investigación de los recursos, el desarrollo sostenible, el tratamiento de emisiones y el cuidado del medio ambiente o la química en la sociedad como items relevantes.

Chemical Engineering is a key discipline in chemical processes design, either in developing new processes and enhancing current ones or in the treatment of effluents during production processes. It serves in different aspects of the chemical processes such as chemical engineering reaction and catalysis, separation and purification, biotechnology and studies of the environment, not forgetting process economy. For this, the symposium aims for this technologic discipline are resource investigation, sustainable developing, emission treatment and environment conservation, or the role of chemistry in Society as more relevant items.

Organizadores:

Alberto Arce (USC)

Ana Soto (USC)

e-mail de contacto: ana.soto@usc.es

Simposio patrocinado por el Grupo Especializado en Ingeniería Química

Miércoles 22 de Julio 2015

	Sesión A: "Ingeniería Química"			Sesión B: "Bioingeniería y Medio Ambiente"
	Chairmen: Javier Bilbao /Gloria Villora			**Chairmen:** Tomás Cordero / Mario Díaz
S15-IL-01a	**Eva Martín del Valle** *"Chemical Engineering Approach for Cancer Treatment and Diagnosis"*	**15:30 – 16:00**	**S15-IL-01b**	**Martine Poux** *"Intensified Technologies for the Development of the Green Process Engineering"*
S15-OC-01a	**E. Rodríguez** *"Craqueo Catalítico de una Mezcla de Ceras de Pirólisis de HDPE y Gasóleo de Vacío en Condiciones de Refinería"*	**16:00 – 16:20**	**S15-OC-01b**	**M. Díaz** *"EGG Protein Revalorization: Fractionation, Applications and Future Prospects"*
S15-FC-01a	**M. Ibáñez** *"Desactivación y Regeneración de un Catalizador de Zeolita HZSM-5 en la Transformación de DME en Olefinas"*	**16:20 – 16:25**	**S15-FC-01b**	**J. L. Urrea** *"Hydrolisis of Sludge: Role of Structural Components of the Floc"*
S15-FC-02a	**M. Sánchez-Contador** *"Efecto de la Adición deZeolita H-ZSM-5 en la deshidrtación de metanol a DME en condiciones de STD"*	**16:25 – 16:30**	**S15-FC-02b**	**L. Barreda** *"Human Blood Plasma Gels Preparation for Culture Cell Applications in Tissue Engineering"*
	Pausa Café	**16:30 – 17:00**		Pausa Café
S15-OC-02a	**M. O. Guerrero-Pérez** *"Nanofiber- Shaped Mixed Oxide Catalysts Prepared by electrospun"*	**17:00 – 17:20**	**S15-OC-02b**	**L. Carro** *"Ibuprofen Removal from Real Wastewater Combining Biological and Chemical Treatments"*
S15-OC-03a	**V. R. Ferro** *"From Molecular Modelling to the Conceptual Design of New Industrial Processes via the Cosmo-Based Thermodynamic Models"*	**17:20 – 17:40**	**S15-OC-03b**	**G. Zarca** *"Novel Ionic Liquid-Based Separation Processes to Recover Carbon Monoxide from Nitrogen-Rich Streams"*

Miércoles 22 de Julio 2015

S15-FC-03a	**M. Elviro** *"Enzimatic Activity Loses of Catalase Recovered by IMAC Chromatography"*	**17:40 – 17:45**	**S15-FC-03b**	**W. Chang** *"Ozone / Hydrogen Peroxide-Based Advanced Oxidation to Remove Ibuprofen from Aqueous Solution"*
S15-FC-04a	**J. Cuéllar** *"The Superior Performance of the 4-dodecylbenzenesulfonic Acid as Catalysts in Transesterification and Esterification Reactions"*	**17:45 – 17:50**	**S15-FC-04b**	**S. Cotillas** *"Regeneration of Urban Treated Wastewater: Integrated Electrochemical Processes"*
S15-FC-05a	**P. Marín** *"Reactores Catalíticos con Membrana Selectiva para la Producción y Separación de Hidrógeno de Elevada Pureza"*	**17:50 – 17:55**	**S15-FC-05b**	**M. J. Martín de Vidales** *"Wastewater Manegement in Batch Processes. A Pharmaceutical Manufacturing Plant Case of Study"*
S15-FC-06a	**I. Hita** *"Modelado Cinético del Hidrotratamiento de Líquido de Pirólisis de Neumáticos Usados"*	**17:55 – 18:00**	**S15-FC-06b**	**D. Arán** *"Eliminación de Cobre de Efluentes Acuosos Biochar de Origen Vegetal"*
S15-FC-07a	**F. J. Navarro** *"Aprovechamiento de Fosfoyeso en la Formulación de Betunes Asfálticos para su Uso en Pavimentación de Carreteras"*	**18:00 – 18:05**	**S15-FC-07b**	**J. M. Arsuaga** *"Eliminación de As(V) Acuoso mediante Materiales Funcionalizados con Grupos Amino"*
S15-FC-08a	**J. Muñoz** *"Procesado de Emulsiones Submicrónicas de Biodisolventes"*	**18:05 – 18:10**	**S15-FC-08b**	**E. Mena** *"Electro-Biorremediación de Suelos Contaminados con Diesel Aplicando Cambios Periódicos de Polaridad"*
18:30	***Sesión de Pósteres***			
	Reunión del Grupo Especializado de "Ingeniería Química"			

Jueves 23 de Julio 2015

08:40 – 09:40	**PL-5**	***Conferencia Plenaria*** (Común a todos los simposios) **Avelino Corma Canós** *"Intentos para Establecer Puentes entre la Catálisis Homogénea y Heterogénea"*

Sesión A: "Ingeniería Química"			**Sesión B: "Bioingeniería y Medio Ambiente"**
Chairmen: Eva Martín del Valle /Francisco Hernández			**Chairmen:** Juan Rodríguez / Aurora Santos
S15-IL-02a	**Giulio Sarti** *"Solubility and Permeability of Pure and Mixed Gases in Glassy Membranes"*	**10:00 – 10:30**	**S15-IL-02b** **Damiá Barceló** *"Fate and Risks of Pesticides, Pharmaceuticals, Illicit Drugs and Personal Care Products in the Iberian River Basins of Ebro and Llobregat: Challenges and Solutions Using Advanced Treatment Technologies in a European Context"*
S15-OC-04a	**L. Gómez-Coma** *"Acoplamiento de la Etapa de Desorción a una Planta de Absorción No Dispersiva"*	**10:30 – 10:50**	**S15-OC-04b** **A. González-Garcinuño** *"Carbon Source Optimization for Specific Fatty Acid Production in Microalgae"*
S15-FC-09a	**A. Fernández Barquín** *"Estudio de la Separación CO_2 / N_2 mediante Membranas de Matriz Mixta Permeoselectivas"*	**10:50 – 10:55**	**S15-FC-09b** **C. García** *"Simultaneous Production of Lactic and Lactobionic Acids from Whey in Competitive Cultures"*
S15-FC-10a	**J. Izquierdo** *"Caracterización de las Corrientes de un Micro-Hidrociclón"*	**10:55 – 11:00**	**S15-FC-10b** **D. Puyol** *"The Partition-Release-Recovery Concept for Domestc Wastewater Treatment: From Theoretical Approach to Practical Conceptualization"*
	Pausa Café	**11:00 – 11:30**	Pausa Café

Jueves 23 de Julio 2015

S15-OC-05a	**M. G. Montalbán** *"Synthesis and Characterization of Curcumin-Loaded Silk Fibroin Nanoparticles"*	**11:30 – 12:00**	**S15-OC-05b**	**I. Barbarias** *"Producción de Adsorbentes a partir del Char de Pirólisis Rápida de Lodos de Depuradora"*
S15-FC-11a	**Mª José Salar-García** *"Síntesis y Caracterización de Nuevas Caracterizaciones Cátodo-Membrana para su Uso en Pilas de Combustible Microbianas"*	**12:00 – 12:05**	**S15-FC-11b**	**I. García-Herrero** *"Evaluación de Sostenibilidad Ambiental de un Proceso Innovador de Electrólisis de Dimetil carbonato a partir de CO_2"*
S15-FC-12a	**A. Atxutegui** *"Modelo de Dispersión de Gases en un Reactor Spouted Bed Cónico"*	**12:05 – 12:10**	**S15-FC-12b**	**A. del Castillo** *"Valorización de CO_2: Electroreducción hacia Formiato con Electrodos Nanoparticulados de Sn"*
S15-FC-13a	**T. Cordero-Lanzac** *"Preparación de Electrodos de Fibras de Carbono con Nanopartículas de Pt a Partir de Lignina"*	**12:10 – 12:15**	**S15-FC-13b**	**F. Fernández-Rodríguez** *"Ingeniería Química e Infusión Intravenosa"*
S15-FC-14a	**A. L. García-Costa** *"Densidad de Corriente de Intercambio como Parámetro Característico de Catalizadores Utilizados en Procesos CWPO"*	**12:15 – 12:20**		

12:30 – 13:30	**MESA REDONDA** **Modera: Alberto Arce Arce**	*"Tendencias y Retos de la Ingeniería Química"*

13:30	***Ceremonia de Clausura***

Comunicaciones Invitadas (ILa)

Sesión A: "Ingeniería Química"

S15: *Ingeniería Química y Medioambiente*

CHEMICAL ENGINEERING APPROACH FOR CANCER TREATMENT AND DIAGNOSIS

Eva M. Martin del Valle[1]

[1] Departamento Ingeniería Química, Universidad de Salamanca. Plaza Los Caídos s/n, Salamanca. emvalle@usal.es

Palabras Clave: *Nanobiotechnology, cancer therapy, design*

Nanotechnology has made tremendous strides in the last decade, emerging first as a basic science and then rapidly as an engineering discipline. In particular, nanotechnology as applied to biology and medicine has attracted significant interest because of the unique properties of nanomaterials and their size similarity to biological components.

The term nanobiotechnology refers to the application of nanomaterials produced via chemical processes to the field of biology. Concepts ranging from colloid and surface science to particle catalysis are applied to the field of biology.

In this way Chemical Engineers are at the forefront of this rapidly developing field, with the potential to propel discoveries from the bench to bedside.

In this talk, new trends in nanoparticle design and applications to biological field will be highlight. Specifically applications in cancer therapy will be presented.

S5: *Ingeniería Química y Medioambiente*

SOLUBILITY AND PERMEABILITY OF PURE AND MIXED GASES IN GLASSY POLYMERS

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Keywords: *permeability, solubility, diffusivity, glassy polymers*

Glassy polymers are often used in different applications including membrane separations of gases, vapours or liquids and controlled environment packaging fabrications. To such aims the solubility and solubility-selectivity in the glassy matrix of fluid phases is of crucial importance, together with the mobility or diffusivity coefficient inside the glass. The possibility to calculate in a predictive way the relevant transport properties in glassy polymers is here inspected in detail with particular attention to the methods recently developed for the non-equilibrium thermodynamics of glassy phases (NET-GP), based on solid thermodynamic foundations.

The solubility of pure and mixed gases, as well as of liquids, are examined in general terms by reviewing the thermodynamic approach developed in recent years, applicable to the different equations-of-state models suitable for polymeric phases. The different procedures considered to obtain the pure component parameters as a separate information are discussed. Direct predictive applications are shown considering both more traditional glassy polymers as well as high free volume matrices of great interest as PTMSP, PIM1 and modified PIM matrices; solubility isotherms of pure components as well as of gaseous mixtures are calculated at different operating conditions.

The transport properties of gaseous or vapour penetrants in glassy polymer systems are analysed following a fundamental and simple approach which utilizes the diffusive flux as the product of a purely kinetic factor, the mobility, and a thermodynamic factor, which in turn is related to the dependence of the penetrant chemical potential on its concentration in the glassy polymer. The thermodynamic factor is provided by the NET-GP approach used for solubility (the non-equilibrium lattice fluid - NELF - in particular), while a simple exponential function of penetrant concentration is used for the mobility coefficient, thus introducing the only two adjustable parameters entering the transport model, i.e. the penetrant mobility at infinite dilution and the plasticization factor, namely the coefficient that characterizes the dependence of mobility on the concentration.

The transport model provides a simple and effective expression for the representation of penetrant permeability in glassy polymeric membranes, using only two adjustable parameters. The model describes accurately all the types of permeability dependence on penetrant pressure, which may be either constant, decreasing or increasing with pressure itself. Furthermore, the model is able also to represents accurately the non-monotonous behaviours observed in the presence of plasticization effects. Remarkably, the same transport model can also provide the diffusion time-lag in transient permeation experiments, either with or without the occurrence of plasticization.

The procedures considered clearly indicate what are the relevant physical properties of the polymer matrix and of the penetrants which are required, and how they can be obtained experimentally through independent measurements. Finally, the permeability parameters follow clear general correlations versus polymer and penetrant properties, which offer a solid bases for predictive estimations.

Comunicaciones Invitadas (ILb)

Sesión B: "Bioingeniería y Medio Ambiente"

S15: *Ingeniería Química y Medioambiente*

INTENSIFIED TECHNOLOGIES FOR THE DEVELOPMENT OF THE GREEN PROCESS ENGINEERING

Martine POUX

Laboratoire de Génie Chimique --- University of Toulouse – France

Key words: *Microreactor, microwave, pulsed reactor, esterification, waste cooking oil*

The recent development of new chemical routes bearing in mind the green chemistry concept is an useful and necessary means to move towards a greener, safer and more environmentally friendly industry. It will be a great success if adequate processes for the implementation at the industrial scale are available. Green Process Engineering tools propose different approaches to achieve this last step [1]. These approaches consist in, with increasing order of process complexity, starting from the improvement of the existing methods, considering a change of technology, or to the implementation of new synthesis routes. New technologies are now usually referred to intensified systems and according Stankiewicz's definition, they make possible using much less to produce much more [2].

One of the well known technologies is the microreactors or microsystems. Due to the small dimensions and the high surface to volume ratio, heat and mass transfer are increased and the temperature can be perfectly controlled. They are specially adapted for highly exo/endothermal reactions and mass transfer limited reactions.

Oscillatory baffles reactors enhance also mass transfer and heat transfer by operating with an oscillatory or pulsed flow rate with creates recirculation flow patterns in the vicinity of the baffles. Oscillatory baffles reactors can provide long residence time and they are suitable for industrial scale production.

The use of some specific methods such as microwaves could intensify the chemical reactions and many examples are available in the literature. But the development of microwave reactors for the process industry is still relatively slow because of the lack of control and reproducibility of the results and the poor understanding of the electromagnetic phenomena.

This presentation will give a comparison of these technologies with a bach reactor taking the example of the biodiesel synthesis from waste cooking oil [3, 4].

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S15: *Ingeniería Química y Medioambiente*

FATE AND RISK OF PESTICIDES, PHARMACEUTICALS, ILLICIT DRUGS AND PERSONAL CARE PRODUCTS IN THE IBERIAN RIVER BASINS OF EBRO AND LLOBREGAT: CHALLENGES AND SOLUTIONS USING ADVANCED TREATMENT TECHNOLOGIES IN A EUROPEAN CONTEXT

Damià Barceló[1,2], Paola Verlicchi[3,4], Mira Petrovic[2,5], Pablo Gago-Ferrero[1], Daniel Molins-Delgado[1], Silvia Diaz-Cruz[1], Nicola Mastroianni[1], Marianne Köck-Schulmeyer[1], Cristina Postigo[1], Miren Lopez de Alda[1], Sandra Perez[1], Antoni Ginebreda[1]

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Occurrence of emerging organic contaminants (EOCs) in environmental waters is directly related to their incomplete removal in wastewater treatment plants (WWTPs). Therefore, there is a need to develop and evaluate advanced treatment technologies, e.g., membrane bioreactors (MBR) and photocatalytic processes to remove EOCs and thereby diminish their presence in surface waters. On the other hand, occurrence of EOCs in the aquatic environment is also linked to the flow rate of the receiving waters. In this respect, Mediterranean rivers are characterized by important fluctuations in the flow rates and heavy contamination pressures from extensive urban, industrial, and agricultural activities, which translates into contamination levels of EOCs most often higher than in other European basins.

This presentation summarizes the findings of several studies and monitoring programmes conducted in two Spanish river basins (Ebro and Llobregat) with the aim of getting a better insight about the sources and fate of pesticides, and the EOCs pharmaceuticals, personal care products, and illicit drugs. The occurrence of these contaminants is discussed in relation to their removal in WWTPs, and influence of hydrological conditions in the receiving river waters. The removal of some of them (e.g., acetaminophen, diclofenac, ibuprofen, carbamazepine, atenolol, cocaine and methadone) with advanced water treatments and the study of the formed transformation products and their toxicity is also presented. In addition, the risk posed by these EOCs in both surface and effluent wastewaters was assessed towards different aquatic organisms by determining hazard indexes. These indexes are further correlated with some biological descriptors characterizing both the structure and functioning of the receiving aquatic ecosystems. Finally, an analysis of the strategies under discussion within the European countries in order to reduce the environmental risk posed by the occurrence of the most critical EOCs in surface waters will also be presented.

Acknowledgements. This study has been financially supported by the EU through the FP7 project SOLUTIONS (603437), and by the Generalitat de Catalunya (Consolidated Research Groups “2014 SGR 418—Water and Soil Quality Unit” and 2014 SGR 291—ICRA). It reflects only the author's views. The EU is not liable for any use that may be made of the information contained therein. Merck is acknowledged for the gift of LC columns.

Comunicaciones Orales (OCa)

Sesión A: "Ingeniería Química"

S15: *Ingeniería Química y Medioambiente*

CRAQUEO CATALÍTICO DE UNA MEZCLA DE CERAS DE PIRÓLISIS DE HDPE Y GASÓLEO DE VACÍO EN CONDICIONES DE REFINERÍA

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Palabras Clave: *Craqueo catalítico; FCC; Ceras*; HDPE;

El objeto de este trabajo es evaluar las sinergias derivadas de la co-alimentación de ceras de pirólisis de polietileno de alta densidad (HDPE) y gasóleo de vacío (VGO) a las unidades de craqueo catalítico (FCC) de las refinerías.

Se efectuaron 3 baterías de ensayos, usando como alimentación: ceras de pirólisis flash de HDPE, VGO y una mezcla 20% ceras y 80% VGO. Las reacciones de craqueo catalítico se realizaron en un reactor simulador de Riser en el intervalo de condiciones de operación de la unidad FCC: temperaturas entre 500 y 560°C, relaciones catalizador/alimentación (C/O) entre 3 y 7 y un tiempo de contacto de 6 segundos, usando en todos los casos un catalizador comercial de FCC.

Los productos de reacción se identificaron mediante GC-MS y se analizaron mediante GC en línea y TGA (coque), agrupándolos en los siguientes "lumps": gases secos (C_1-C_2), gases licuados (LPG, C_3-C_4), gasolina (C_5-C_{12}), aceite de ciclo ligero (LCO, C_{13}-C_{18}) y pesado (HCO, C_{18+}) y coque. En base a los resultados con las alimentaciones puras y suponiendo un comportamiento individual lineal, se estimaron de forma ponderada los resultados de la co-alimentación.

Al comparar los resultados experimentales y los estimados (Fig. 1) se observa un aumento de las fracciones gaseosas y coque en detrimento de la gasolina a altas temperaturas por encima de los valores esperados. Esto se debe a la naturaleza olefínica de las ceras, cuyas reacciones de craqueo y ciclación aumentan con la temperatura, desfavoreciendo las de transferencia de hidrógeno. Como consecuencia la gasolina obtenida presenta una fracción olefínica superior a la esperada y a la obtenida con la alimentación convencional de las unidades FCC.

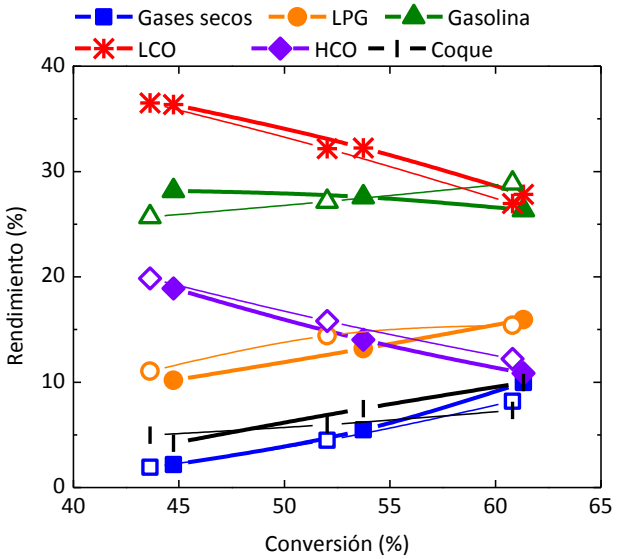

Fig. 1. Rendimientos vs. Conversión 20% Ceras +80% VGO. C/O=5 (experimental, línea gruesa; ponderado, fina).

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S15: *Ingeniería Química y Medioambiente*

NANOFIBER-SHAPED MIXED OXIDE CATALYSTS PREPARED BY ELECTROSPUN

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Keywords: *electrospun, vanadium oxide, mixed oxide catalysts*

Vanadium is a key component for selective and environmental catalysts; supported vanadium oxide catalysts find many industrial applications for selective oxidation, ammoxidation and reduction reactions for bulk and environmental processes. Thus, Vanadium oxides are important in the development of alkane transformation processes as well as for removal of pollutants (catalytic oxidation). Moreover, the properties of these materials can be modulated and improved by the incorporation of other metals (Sb, Mo, Nb, Te, etc.) into their crystal structure. In this respect, a substantial amount of information is now available on the crystallography, structural chemistry, thermal reactivity, and surface chemical properties of these materials prepared at the macroscale. However, and although the particle shape and dimensions are key factors determining the extent, accessibility and reactivity of materials' surface area, much less attention has been paid to the synthesis and properties of morphological- and size-controlled vanadium based mixed oxide nanomaterials. Although it has been previously documented that new or different properties could be reached by reducing their particle dimensions to 1–100 nm (nanoscale).

Electrospinning is a simple and versatile technique that has emerged in the last decade as powerful tool to prepare a wide range of nanostructured metal oxide materials, from zero-dimensional nanoparticles (electrospraying) to one-dimensional nanofiber or nanotubes. Then, the objective of this work has been the preparation and characterization of different vanadium oxide-based nanofibers and the study of their catalytic possibilities. The oxide fibers (of nominal composition: V2O5, V3O7, SbVO4, Mo6V3Nb1Te1, Mo5V4Nb1Te1) were prepared by electrospinning of suitable metallic salt/PVP solutions in ethanol, followed by their calcination up to different temperatures. On the other hand, carbon fiber-supported VPO catalysts were prepared by electrospinning, stabilization and carbonization of P-containing fibers followed by vanadium salt precursor deposition and decomposition. For comparison purposes, powdery catalysts of similar composition were prepared and studied. After washing and drying, the fibers were characterized by TEM, XRD, Raman, XPS and N2 gas adsorption at -196 ºC.

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FROM MOLECULAR MODELLING TO THE CONCEPTUAL DESIGN OF NEW INDUSTRIAL PROCESSES *via* THE COSMO-BASED THERMODYNAMIC MODELS

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Keywords: *Molecular modelling, Process simulation, COSMO-RS*

We have successfully integrated COSMO-RS results to process simulations using Aspen Tech´s software [1] in order to develop potential new industrial processes with mixtures of components not available in the simulators´ databases. We have applied this procedure to bioprocesses and especially to processes involving ionic liquids (ILs), being our main goal to provide technical and economic information about the potential industrial applications of ILs. All this, with the aim of enriching the design/selection of ILs with optimized properties for specific applications. In this regard, it has to be considered the nature of the ILs as *designer solvents*, consensually accepted in the scientific and technological forum related to this theme. We have been able to accomplish complex process simulations using COSMO-based property packages. The concept of complex simulations includes not only robust flow diagrams (different process operations involving multiple stream recycles) but also multi-component mixtures of hydrocarbons and other organic (polar) components. The simulations carried out include: the IL regeneration by vacuum distillation [2] and stripping with air; the aromatic compounds separation from aliphatics in naphtha [3]; the volatile organic compounds (acetone, ammonia and toluene) retention from air by absorption [4]; the ammonia absorption refrigeration cycles using ILs as absorbers [5]; the desulfurization of naphtha; the transport operations of ILs and their mixtures with organic compounds through conductions, etc.

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ACOPLAMIENTO DE LA ETAPA DE DESORCIÓN A UNA PLANTA DE ABSORCIÓN NO DISPERSIVA

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Palabras Clave: *absorción, desorción, líquidos iónicos, contactores de membranas*

Al igual que la absorción la desorción es una etapa sumamente importante en la captura de dióxido de carbono debido a la necesidad de recuperar los disolventes encargados de combatir el calentamiento global[1]. Tradicionalmente se han usado aminas para minimizar el contenido de CO_2 en las corrientes gaseosas. Sin embargo los líquidos iónicos están en continuo crecimiento debido a sus numerosas ventajas como son su despreciable presión de vapor, su estabilidad térmica, química y electroquímica y su capacidad para ser regenerados.

Al mismo tiempo que los líquidos iónicos han aumentado su presencia en este tipo de procesos, los contactores de membrana[2] también han sufrido un incremento en sustitución de las típicas torres de absorción debido a sus numerosas ventajas en comparación con éstos equipos como son su pequeño tamaño, ya que tienen una alta relación área volumen, su alta eficiencia energética, su flexibilidad operacional, la capacidad de controlar los flujos de gas y líquido de forma independiente y la ausencia de pérdidas de disolventes entre otras muchas.

En este tipo de procesos se usa, por lo general, una corriente de gas típica de los procesos de post-combustión, es decir, con una concentración del 15% de CO_2 y el resto de Nitrógeno. En este trabajo se busca realizar un diseño utilizando tanto los contactores de membranas como los líquidos iónicos para acoplar una etapa de desorción a una planta ya existente de absorción. En la etapa de absorción el gas circula a través de las fibras y el líquido iónico (LI) en contracorriente a través de la carcasa[3]. Para acoplar la etapa de desorción, (i) se han analizado las opciones de operación: vacío, ó corriente de arrastre a alta temperatura; y (ii) se ha optado por tomar la corriente líquida de salida del primer contactor y a ella se ha acoplado un segundo contactor de tal forma que en esta segunda etapa esta corriente líquida se introduzca del mismo modo, a través de la carcasa, empleando una corriente caliente de nitrógeno que circula a través de las fibras para eliminar el CO_2 presente en el líquido iónico.

Agradecimientos

Los autores desean agradecer tanto al Ministerio de Economía y Competitividad (Proyecto CTQ2013-48280-C3-1-R) como a la Real Sociedad Española de Química ST-Cantabria la financiación de esta investigación.

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SYNTHESIS AND CHARACTERIZATION OF CURCUMIN-LOADED SILK FIBROIN NANOPARTICLES

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Keywords: *silk fibroin, nanoparticles, curcumin, ionic liquids, ultrasounds.*

The biocompatibility and controlled degradation of silk fibroin makes it an ideal candidate for a nanoscale drug-delivery vehicle. Nanoparticles are small enough to penetrate through small capillaries, allowing enhanced cellular uptake of an encapsulated drug or therapeutic molecule [1]. Some previous studies have shown that curcumin, which is a yellow polyphenol extracted from the rhizome of turmeric, has excellent activity as an anticancer agent as it inhibits proliferation of various tumor cells in *in vivo* animal models and in humans [2]. In this work, silk fibroin nanoparticles have been obtained by dissolution of silk fibroin in ionic liquids (ILs) using high-power ultrasound energy. This is a considerably greener option compared with the traditional ways of dissolution of silk based on ionic aqueous solutions, such as 9.3M LiBr or 50% (w/v) $CaCl_2$ solution and ionic hydro-alcoholic solutions such as a $CaCl_2$/Ethanol/Water mixture [3]. Figure 1 summarizes the overall process of silk fibroin nanoparticles preparation from silk-ILs solutions.

Figure 1. Scheme of silk nanoparticles preparation using ILs

The aim of this work has been to load silk fibroin nanoparticles with curcumin and to characterize them. Size and Z potential distribution have been measured using DLS (Dynamic Light Scattering).

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Acknowledgments

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Comunicaciones Orales (OCb)

Sesión B: "Bioingeniería y Medio Ambiente"

S15: *Ingeniería Química y Medioambiente*

EGG PROTEIN REVALORIZATION: FRACTIONATION, APPLICATIONS AND FUTURE PROSPECTS

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Keywords: *revalorization, egg, food, fractionation, applications.*

The egg industry is rather recent and it has made enormous progress since the 1960s. At industrial scale, egg is transformed in egg products of first (whole egg, yolk, albumen), second (ready-cooked meal) or even third transformation (e.g. bioactive egg compounds such as active peptides).Along with changes in egg-processing technology, there has been a continuing growth of further processed egg products [1].Currently, as an increase in the added value of egg products is pursued, it is important to explore new technological applications. One of the main approaches is the fractionation of egg components accompanied by a move forward towards new innovative applications [2].

On account of its multifunctional properties, hen egg yolk is a key ingredient in a wide variety of products. However, individual constituents of yolk are difficult to separate due to different practical and economic reasons, so, nowadays only plasma and granules can be easily fractionated at an industrial scale [3]. Different works [1,2] have reported interesting composition and properties of granules and plasma. Plasma is composed of LDLs and livetins, whereas granules are mainly constituted by HDLs, phosvitin and LDLs [1]. Granules show many interesting characteristics to be employed as ingredient in food industry, providing some advantages in relation with the use of egg yolk. In fact, some applications of granules at a pilot scale have lately been developed [1]. Plasma is also an abundant source of many bioactives, such as egg yolk immunoglobulin Y (IgY) and phospholipids [2].

In addition, the effect of different treatments (temperature, high pressures, hydrolysis…) on egg compounds is another way to obtain interesting products with novel properties and applications [4].

Moreover, new materials and procedures have been developed in recent years from by-products or from raw materials of little value. In this way, natural base materials have gained more attention for the development of different biomaterials with a wide variety of applications ranging from substrates for cell culture to biosorbents.

To sum up, nowadays egg industry is knowing a continuous growth, so the next years should provide even more breakthroughs in this field.

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IBUPROFEN REMOVAL FROM REAL WASTEWATER COMBINING BIOLOGICAL AND CHEMICAL TREATMENTS

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Keywords: *advanced oxidation, ibuprofen, recalcitrant pollutants, wastewater*

The increase of water consumption, its shortage and the strictly control of water quality parameters is leading to the study and application of new treatments to reuse and recycle it. At the same time, the presence of some recalcitrant pollutants in wastewater is a major issue because of the toxic effects to human health and environment. Most of the technological processes commonly used incur in high costs or low treatment efficiency to accomplish current legislation limits. The combination of different treatments has been proposed as new alternative to remove these compounds from wastewaters. In this work, ibuprofen, an organic compound commonly used as an analgesic, has been selected as a model of recalcitrant pollutant of actual concern due to its growing occurrence in effluents from treatment plants and surface waters [1]. Besides, it is being evaluated to be included as priority substance in the European policy of water [2], and hence, there is a need to efficiently remove it. We present here results of biological treatment combined with advanced oxidation process (AOP) to remove it in water coming from a wastewater treatment plant.

First, real wastewater containing ibuprofen was treated through the biological process in aerobic conditions. This treatment decreased the chemical oxygen demand (COD), improved water quality to be treated in chemical reactors and decreased about 30% of ibuprofen initial concentration. The wastewater from the biological process was then treated through AOP with O_3 and H_2O_2. Ibuprofen concentration was reduced at ppb levels. The final effluent was not toxic, with much less color than the initial one and the COD was significantly reduced. These results confirm the effectiveness of the combination treatment studied.

This work was partially financed by the BIOQUIM-RESCUE project, from ACC1Ó (Catalan Government) with support of FEDER. Additional support from the Catalan Government was also provided (2014SGR-1582).

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NOVEL IONIC LIQUID-BASED SEPARATION PROCESSES TO RECOVER CARBON MONOXIDE FROM NITROGEN-RICH STREAMS

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Keywords: *carbon monoxide, absorption, membranes, ionic liquids, facilitated-transport*

Huge amounts of carbon monoxide are nowadays produced in some chemical industrial processes after performing a partial combustion of hydrocarbons. Moreover, hydrogen may also be generated along with CO in reducing environments as in carbon-black manufacturing. Therefore, the selective recovery of both compounds from nitrogen-rich waste gas streams employing an efficient technology and their subsequent conversion into valuable products such as methanol or dimethylether, among others, may be an alternative approach to reduce the environmental footprint and obtain economic benefits. Among the currently available gas separation technologies, only reactive absorption can be applied in CO/N_2 separations given the analogous properties of both gases. This technology employs a proprietary solvent containing a copper(I) salt dissolved in an aromatic hydrocarbon, which can selectively bind CO molecules. Although high product purity and yield can be achieved with this technology, several issues discourage its implementation at large scale, namely the partial solubility of the copper(I) salt, its long-term activity and stability, toxicity and flammability of the solvent and the susceptibility to corrosion.

In order to overcome these shortcomings, we have performed the reactive absorption of carbon monoxide into an ionic liquid which also contains copper(I). This class of solvents has attracted considerable attention due to their outstanding properties: negligible vapour pressure, excellent salvation properties and chemical stability. Particularly, we have selected the Lewis acid-based ionic liquid 1-hexyl-3-methylimidazolium chlorocuprate(I) to study the thermodynamic equilibriums of CO and N_2 absorption. Results showed that this ionic liquid provides high CO/N2 selectivities, up to 100, at relatively low pressures (< 20 bar) while having a low CO binding energy that allows regenerating the solvent by simple means. In addition, the reaction kinetics between CO and an ionic liquid have been assessed for the first time. On the other hand, a membrane process is also proposed to simultaneously recover both CO and H_2 from the gas mixture employing supported ionic liquid membranes containing the reactive ionic liquid selected in this work. In this process, copper(I) acts as a carrier that enhances the flux of CO across the membrane. In this way, final concentrations of H_2 and CO are closed to the 2:1 ratio employed in the synthesis of hydrocarbons from syngas feed.

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CARBON SOURCE OPTIMIZATION FOR SPECIFIC FATTY ACID PRODUCTION IN MICROALGAE

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Key words: *fatty acid, microalgae, carbon source*

Microalgae have been identified as an excellent feedstock to produce a wide variety of bioproducts due to their versatility for growth and nutrients incorporation. In recent years, nutraceutical market has evolved rapidly and microalgae are playing an essential role in this field [1]. Microalgae could accumulate high quantity of vitamins, carotenes or fatty acids with extraordinary commercial value. However, an optimization in production technology must be done in order to decrease cost and improve yield.

This work is focused on manufacture of high value fatty acids with microalgae. It looked for select the ideal carbon source (and the optimal concentration) which allows reducing cost and rising the percentage of desirable fatty acid. For reaching this objective, it was well studied lipid synthesis pathway in microalgae and laboratory experiments were carried out in order to prove the hypothesis. *Scenedesmus abundans* was selected as microalga strain for these studies due to its growth and nitrogen metabolism has been described previously [2].

On one hand, sodium acetate has been found as a promising carbon source if we look for fatty acids with an even number of carbons like palmitic, stearic or myristic acid. On the other hand, sodium propionate has been selected as the best option if we tried to raise the relative proportion of fatty acids with an odd number of carbons. Other substances have been identified as potential elicitors for reaching fatty acids with high number of carbons (more than twenty).

Summing up, different carbon sources are assimilable by microalgae and modify, in different ways, the relative fraction of desirable fatty acids. These advances could be transferred to industrial process, causing a yield improvement with an irrelevant extra-cost.

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PRODUCCIÓN DE ADSORBENTES A PARTIR DEL CHAR DE LA PIRÓLISIS RÁPIDA DE LODOS DE DEPURADORA

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Palabras Clave: *Lodos de depuradora, char, adsorbentes, pirólisis*

El char obtenido en el proceso de pirólisis rápida de lodos de EDAR es una materia prima potencial para la producción de adsorbentes de bajo coste dada su naturaleza orgánica. Las especiales características de los lodos de EDAR y del char obtenido en la pirólisis rápida (especialmente el alto contenido de cenizas y su baja superficie específica BET) hacen que de forma general el material obtenido no se considere como carbón activo, sino con la denominación genérica de adsorbente.

El proceso de activación se ha llevado en todos los casos en un reactor de lecho fijo a 800 ºC con CO_2 como agente activante y variando el tiempo de reacción (entre 15 y 90 min). Además en este trabajo se ha querido analizar el efecto de la extracción de la fracción inorgánica de la matriz carbonosa mediante diferentes procedimientos y estudiar su influencia sobre las propiedades de los adsorbentes. Para ello, primero se ha procedido directamente a la activación del char sin ningún tipo de tratamiento. A continuación, se ha estudiado la activación del char pretratado con una disolución de HCl (3M) donde se consigue reducir la fracción inorgánica de la muestra en más de un 35 %. Por último, se ha llevado a cabo la activación del char pretratado con HCl (3M) y una disolución del 15 % en peso de Na_2CO_3 con el objetivo de rebajar el contenido de sílice presente en el char, consiguiendo una reducción del 60 % del total de cenizas.

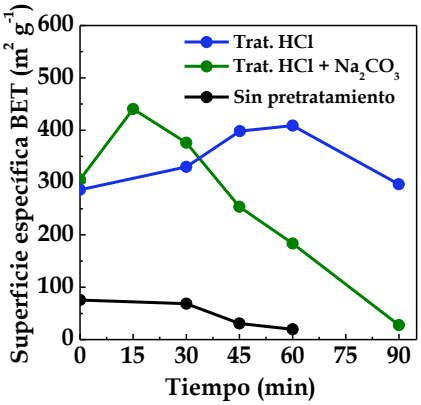

Figura 1. Evolución de la superficie específica BET durante la activación del char.

Como se observa en la Figura 1, las superficies específicas BET de los adsorbentes obtenidos sin ningún tipo de pretratamiento son muy bajas (20-75 $m^2\ g^{-1}$) por su elevado contenido inorgánico, lo que inhibe el desarrollo de la porosidad en el interior del material. En cambio, cuando se emplea algún tiempo de pretratamiento para eliminar las cenizas, se observa una mejora significante en la porosidad del material, alcanzando valores máximos de superficie específica BET de 408 $m^2\ g^{-1}$ (tras 60 min) para el char pretratado con HCl y de 440 $m^2\ g^{-1}$ (tras 15 min) para el char tratado con HCl y Na_2CO_3. Estas mejoras atribuidas a la extracción de parte de las cenizas se atribuyen a una mejora de la accesibilidad de CO_2 a la matriz carbonosa. Es más, se observa que la cinética de activación del precursor tratado con HCl y Na_2CO_3 es más rápida que la del precursor sometido solo al tratamiento de HCl por su menor contenido de cenizas.

Comunicaciones Flash (FCa)

Sesión A: "Ingeniería Química"

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DESACTIVACIÓN Y REGENERACIÓN DE UN CATALIZADOR DE ZEOLITA HZSM-5 EN LA TRANSFORMACIÓN DE DME EN OLEFINAS

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Palabras Clave: *DME, HZSM-5, propileno, desactivación, coque*

Introducción El Dimetil Éter (DME) es una alternativa al metanol para la producción de olefinas [1]. El catalizador de zeolita HZSM-5 es adecuado para obtener una alta selectividad de propileno, con una reducida desactivación por coque [2]. A pesar de todo, la desactivación por coque es un factor limitante en cuanto a la aplicación industrial. En este trabajo se ha estudiado el origen de la desactivación y regeneración de un catalizador de zeolita HZSM-5 utilizando diferentes condiciones de operación.

Experimental El catalizador está preparado con una zeolita HZSM-5 (SiO_2/Al_2O_3 = 280, Zeolyst Int.), aglomerada con boehmita (30 wt%) y Al_2O_3 (20 wt%), para conferir la estructura meso y macroporosa, a la vez de mayor resistencia mecánica. Los experimentos se han llevado a cabo en un reactor de lecho fijo, a presión atmosférica, 325, 350 y 375 °C, tiempo espacial de 3 y 4 $g_{catalizador}$ h $(mol_C)^{-1}$ y operando en ciclos de reacción-regeneración de 18 h. Los catalizadores desactivados se han caracterizado utilizando técnicas analíticas como TPD, TPO, FTIR, FTIR-TPO/MS, entre otros. La regeneración se ha realizado *in-situ,* con aire (25 mL min^{-1}), subiendo la temperatura a 10 °C min^{-1} hasta 550 °C y manteniendo en estas condiciones durante 2 h.

Resultados La Figura 1a muestra los resultados de TPD (desorción) del coque de los catalizadores desactivados y la Figura 1b los relativos a la TPO (combustión). Relacionando estos resultados con los de disminución de la conversión (no mostrados aquí) se puede indicar que existen dos fracciones de coque: aromáticos alquilados que se desorben y que no desactivan el catalizador pero son precursores de otra fracción, de especies más condensadas y desactivantes (observadas en la TPO).

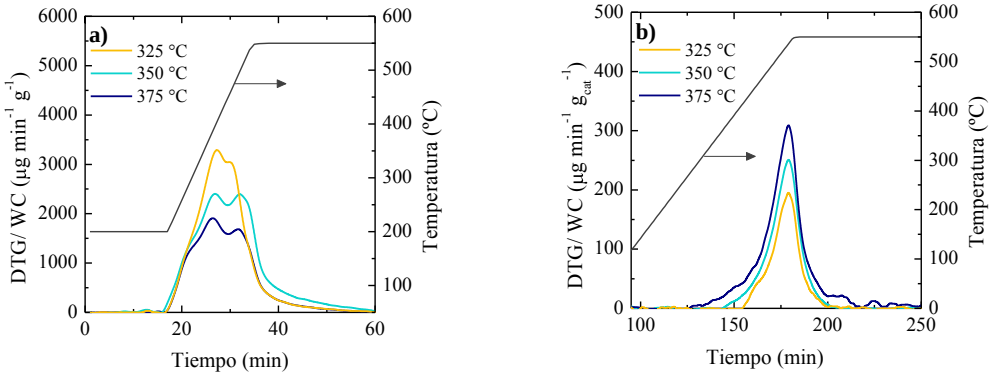

Figura 1. Perfiles de desorción (a) y combustión (b) de los catalizadores desactivados a diferentes temperaturas y tiempo espacial de 3 $g_{catalizador}$ h $(mol_C)^{-1}$

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S15: *Ingeniería Química y Medio Ambiente*

EFECTO DE LA ADICIÓN DE LA ZEOLITA H-ZSM-5 EN LA DESHIDRATACIÓN DE METANOL A DME EN CONDICIONES DE STD

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Palabras Clave: *Metanol, zeolita, acidez, steaming*

Introducción. La síntesis de dimetil éter (DME) en una etapa o proceso STD (*Syngas To DME*) se presenta como una alternativa para obtener combustibles a partir de fuentes sostenibles. Éste proceso se lleva a cabo en el intervalo 250 – 400 °C (con límite a 300 °C en el caso de catalizadores de cobre) y presiones superiores a 18 bar, sobre un catalizador bifuncional compuesto por una función metálica, donde se sintetiza el metanol, que se deshidrata a DME en la función ácida [1]. En este trabajo se ha estudiado el efecto de la acidez de la función ácida (con diferente relación SiO_2/Al_2O_3 y tratamientos de desaluminización), con el objetivo de obtener un mayor rendimiento de DME, con una baja producción de hidrocarburos.

Experimental. Se ha partido de zeolitas H-ZSM-5 comerciales (Zeolyst Int.), con relaciones SiO_2/Al_2O_3 de 80 y 280. A su vez la H-ZSM-5 de SiO_2/Al_2O_3 = 280 sin tratar se ha comparado con la tratada mediante desaluminización térmica (HZ-280_T) y por *steaming* "seco" (HZ-280_ST), empleando el agua adsorbida en la propia zeolita para desaluminizarla [2]. Las reacciones se han llevado a cabo en un reactor de lecho fijo en el intervalo 150 – 350 °C, 20 bar, con un tiempo espacial de 6 g_{cat} h $(mol_C)^{-1}$ y con una alimentación de metanol diluido en N_2 (9 % en vol.).

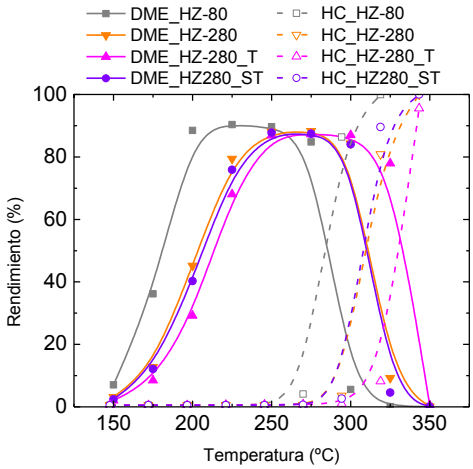

Figura 1. Efecto de la temperatura de reacción en el rendimiento de DME e hidrocarburos (HC).

Resultados y conclusiones. En la Figura 1 se puede observar que la zeolita con relación SiO_2/Al_2O_3 = 80 solo es apropiada por debajo de los 250 °C ya que la producción de HC se dispara para temperaturas superiores, mientras que la de relación 280 sin tratar y tratada por steaming seco permiten operar hasta 275 °C. El tratamiento térmico permite alcanzar los 300 °C, con un rendimiento de hidrocarburos del 1 %.

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ENZIMATIC ACTIVITY LOSES OF CATALASE RECOVERED BY IMAC CHOMATOGRAPHY.

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Key Words: *catalase activity, IMAC, inhibition.*

Chromatography is widely used for large protein purification at both the analytical and process scales. IMAC (Immobilized Metal Affinity Chromatography) is based in the reversible interaction between some transition metals and the appropriate accessible aminoacids, allowing an easy protein recovery. This type of chromatography takes advantage of its ability for obtain concentrated protein in one only step with fast adsorption and elution kinetics [1].
Catalase is used as model enzyme, as its adsorption and elution by IMAC is well known. However, the activity of the eluted catalase is not usually measured.

In this work the adsorption of catalase by IMAC, and then the elution was performanced. In order to obtain the adsorbed catalase the most usual methods of elution were employed: competitive agents as imidazole, NaSCN and pH gradients.

In one hand, Michaelis-Menten parameters and the activity of the catalase in different concentrations of the elution agent, solution and pH were obtained. Consequently it was possible to obtain the optimum solvent in which the activity of the enzyme is maximum.
In other hand, the effect of the column in the activity of catalase recovered was also measured.

To sum up, it was concluded that:

- The imidazol produces a mixed inhibition.
- The column acts as an acompetitive inhibitor.
- The elution with imidazol shows an acompetitive inhibition, where solvent produced more activity lose compared with the column effect.
- The NaSCN solvent poison the active center of the catalase, as is shown in literature [2].
- The most concentrate eluting agent causes the highest inhibition effect.

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THE SUPERIOR PERFORMANCE OF THE 4-DODECYLBENZENESULFONIC ACID AS CATALYST IN TRANSESTERIFICATION AND ESTERIFICATION REACTIONS

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Keywords: *4-dodecylbenzenesulfonic acid, catalyst, biodiesel, transesterification, esterification.*

Biodiesel is usually obtained by the transesterification of triglycerides with a basic catalyst. However, this type of catalyst require the use of high quality raw materials (without water because it causes hydrolysis of biodiesel, and without free fatty acids (FFAs) because they react with the catalyst to produce soaps, which reduces the reaction yield and hinders separation of glycerol from methyl ester). Consequently, this process is expensive and biodiesel thus obtained is not economically competitive with petrodiesel. Acid catalysts catalyze the esterification and transesterification reactions simultaneously, allowing the use of low-cost raw materials with high acidity and thus decreasing the global cost of the biodiesel production. The usual inorganic catalysts, such as sulfuric acid, are not suitable because the rate of transesterification is very slow. Nevertheless, the use of acid organocatalysts can prevent this drawback, as they can achieve very high conversions in a reasonably short reaction time. This is because a hydrophobic moiety in its molecular structure endows the acid catalyst with an amphiphilic nature and thus provides higher solubility in the oil phase (phase in which transesterification reaction takes place) than that of inorganic acids.

In this work, the superior performance of the 4-dodecylbenzenesulfonic (DBSA) acid as catalyst in transesterification and esterification reactions (fig. 1) is disclosed.

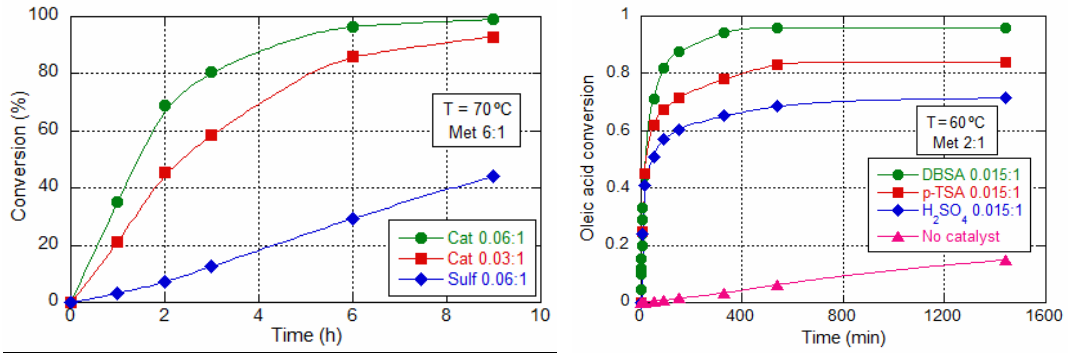

Fig. 1. Superior catalytic activity of DBSA, vs. other acid catalysts, in the transesterification of triglycerides [1] and in the esterification of oleic acid.

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REACTORES CATALÍTICOS CON MEMBRANA SELECTIVA PARA LA PRODUCCIÓN Y SEPARACIÓN DE HIDRÓGENO DE ELEVADA PUREZA

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Palabras Clave: *membranas compuestas, producción de hidrógeno, simulación de reactores químicos, integración de procesos.*

El hidrógeno se puede producir a partir de muy diversas materias primas, ya sean fósiles (carbón, gas natural) o renovables (biomasa, biogás). Una de las etapas clave en los procesos de producción de hidrógeno es la reacción de desplazamiento del gas de agua. A escala industrial esta reacción se lleva a cabo en varios reactores catalíticos de lecho fijo adiabáticos con enfriamientos intermedios [1]. El uso de reactores de membrana selectiva de paladio permite separar el hidrógeno con una elevada pureza. De esta manera, reacción y separación tendrían lugar de forma integrada en un mismo equipo y como la reacción es reversible exotérmica se desplazaría el equilibrio reduciendo el tamaño del reactor [1, 2].

El reactor de membrana se ha estudiado empleando un modelo fenomenológico, que describe su comportamiento planteando los balances de conservación de materia, energía y cantidad de movimiento. Este modelo se ha completado con la cinética de la reacción en el catalizador sólido poroso, la transferencia de materia y energía en el lecho catalítico, y un modelo de resistencias en serie que describe la permeación de hidrógeno a través de una membrana compuesta de paladio. La resolución del modelo en 2D empleando el software COMSOL Multiphysics ha permitido determinar los gradientes de velocidad, concentración y temperatura en el interior del reactor. La adecuación del modelo se ha comprobado por validación con datos experimentales.

Las simulaciones realizadas con este modelo han permitido analizar el funcionamiento del reactor de membrana para las reacciones de desplazamiento del gas de agua y reformado húmedo de metano. Se ha determinado la influencia de los principales parámetros de operación y diseño del reactor (temperatura de entrada, presión, velocidad espacial, etc.) con el objetivo de optimizar su funcionamiento. Se puede concluir que mediante una adecuada selección de las condiciones de operación y diseño del reactor es posible alcanzar conversión prácticamente completa y a la vez separar con elevada pureza el hidrógeno que se produce en la reacción.

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MODELADO CINÉTICO DEL HIDROTRATAMIENTO DE LÍQUIDO DE PIRÓLISIS DE NEUMÁTICOS USADOS

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Palabras Clave: *modelado cinético, hidrotratamiento, diesel, nafta*

La refinería de residuos persigue una gestión eficiente de los residuos con el objetivo de producir combustibles alternativos de calidad. Los neumáticos usados representan un reto, debido a su creciente generación [1]. La pirólisis se presenta como una alternativa prometedora para su gestión, permitiendo maximizar la obtención de producto líquido, el cual presenta buenas características como potencial combustible de automoción [2]. Con objeto de mejorar sus propiedades, se ha llevado a cabo el hidrotratamiento de este líquido de pirolisis usando un catalizador $NiMo/Al_2O_3$ [3], y estudiando su cinética desde el punto de vista de (i) hidrodesulfuración (HDS), (ii) hidrocraqueo (MHC) e (iii) hidrodesaromatización (HDA).

Los datos cinéticos se han obtenido en un reactor de lecho fijo en las condiciones: 300-375 °C, 0-0.5 g_{cat} h g_{alim}^{-1}, 65 bar. Las especies de azufre presentes son benzotiazol (BTZ) y dibenzotiofenos (DBT) con grupos metilo (M) como sustituyentes: M_1DBT, M_2DBT, M_3DBT y M_4DBT, con contenidos iniciales en el STPO de 3,794 ppm de BTZ y 182, 752, 3,460 y 3,412 ppm, para los DBT. Los lumps de productos (para evaluar el HC) son: nafta (35-216 °C, 27.9 %), diesel (216-350 °C, 50.3 %) y gasoil (350 °C, 21.8 %), y las fracciones de composición (para evaluar la HDA) son: parafinas e isoparafinas (P+iP, 35.4 %), nafténicos (N, 22.0 %), aromáticos de 1 anillo (A_1, 31.9 %) y aromáticos de 2 anillos (A_2, 10.7 %).

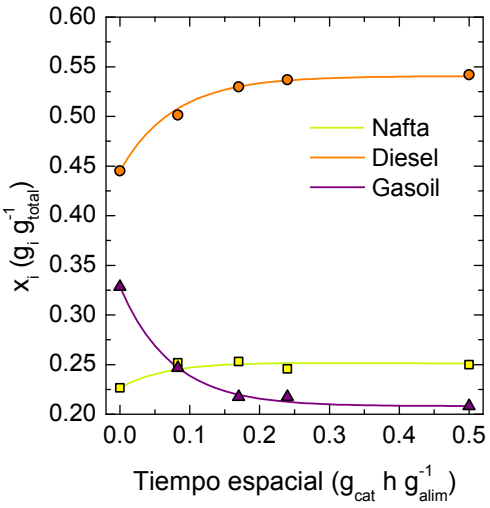

Figura 1. Evolución con el tiempo espacial de los lumps de productos a 375 °C (65 bar; TOS, 8 h).

En el caso del hidrocraqueo (Figura 1) la consideración de un esquema cinético secuencial gasoil↔diesel↔nafta con una etapa adicional de transformación de gasoil en nafta ha permitido obtener un ajuste muy preciso de la evolución de los rendimientos en función del tiempo espacial y para distintas temperaturas (datos no mostrados). Un esquema similar para la HDA (A_2↔A_1↔N↔P+iP) y una cinética del tipo Langmuir-Hinshelwood para la HDS han demostrado tener similar precisión para predecir la evolución de las otras rutas de reacción de hidroprocesado.

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APROVECHAMIENTO DE FOSFOYESO EN LA FORMULACIÓN DE BETUNES ASFÁLTICOS PARA SU USO EN PAVIMENTACIÓN DE CARRETERAS

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Palabras Clave: *Fosfoyeso, betunes, carreteras, espumas.*

El fosfoyeso es un residuo que se produce durante el proceso de obtención del ácido fosfórico a partir de la roca fosfática y del ácido sulfúrico, el cual se almacena en grandes balsas causando considerables problemas medioambientales, debido a la movilidad de contaminantes de los efluentes lixiviados [1].

En este trabajo, se ha analizado el potencial uso del fosfoyeso en un proceso conjunto de espumación y modificación de betún asfáltico empleando ácido sulfúrico como activador, para aplicaciones de pavimentación de carreteras. Los resultados obtenidos indican que el ligante resultante presenta una mejora significativa de propiedades reológicas y tecnológicas tanto a alta como a baja temperatura. De esta forma, el pavimento fabricado mostraría un comportamiento aventajado durante la puesta en servicio, aliviándose defectos habituales en las carreteras como la deformación permanente (roderas) y las fracturas de origen térmico.

La modificación observada se atribuye a la capacidad del ácido sulfúrico de liberar el fósforo que se encuentra en la estructura cristalina del fosfoyeso, quedando dicho elemento disponible para reaccionar con ciertos compuestos del betún [2].

Por otra parte, la espuma de betún producida durante el procesado se debe al desprendimiento del agua de hidratación, catalizado por el ácido sulfúrico. Este proceso permitiría la aplicación en tecnologías de "betún espumado" en las que se reduce la temperatura de fabricación de las mezclas asfálticas, con el consiguiente ahorro energético. En este sentido, la estabilidad de la espuma producida es superior a la obtenida por procesos físicos tradicionales y, además, permite mejorar el proceso de envuelta de los áridos durante la fabricación de la carretera.

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PROCESADO DE EMULSIONES SUBMICRÓNICAS DE BIODISOLVENTES

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Palabras Clave: emulsificación, microcanales, reología, disolventes verdes, *aceite esencial.*

Se presentan dos casos de estudio sobre el proceso de emulsificación de biodisolventes. El primer caso aborda la influencia de la temperatura de procesado en la emulsificación de una mezcla de disolventes verdes susceptibles de ser aplicados en productos agroquímicos, como alternativa a disolventes aromáticos que presentan diferentes problemas de seguridad y medioambientales. El objetivo ha sido emulsionar una mezcla 75/25 de una dimetilamida de ácido graso, obtenida a partir de biomasa, y α-pineno, terpeno que se puede obtener a partir de oleo-resinas de coníferas. La mezcla de disolventes adecuados constituye una solución para desfavorecer la desestabilización física de las emulsiones por maduración de Ostwald. Se ha usado un emulsionante de origen vegetal, un ester etoxilado de glicerina derivado de aceite de coco, fácilmente biodegradable y que no presenta problemas para etiquetado tipo “eco-label”. El procesado se ha realizado en dos etapas, una primera semicontinua y la segunda discontinua, usando un homogeneizador rotor-estátor con malla emulsionadora. La influencia de la temperatura de procesado entre 5ºC y 45ºC sobre la estabilidad física de las emulsiones se ha estudiado mediante ensayos viscoelásticos, curvas de flujo, difracción láser y barridos de retrodispersión de luz (MLS). La temperatura de procesado ha ejercido una influencia muy significativa en la respuesta viscoelástica de las emulsiones, cuyos espectros mecánicos sufren cambios cualitativos y cuantitativos entre 5ºC y 15ºC y en el intervalo 25ºC-45ºC, que afectan a los tiempos de relajación terminales. La evolución con el tiempo de los espectros mecánicos ha permitido detectar procesos de floculación y coalescencia, junto con la información aportda por la difracción láser y la retrodispersión de luz, de una forma más eficaz que las curvas de flujo. Estas se han caracterizado por un comportamiento no newtoniano pseudoplástico, con tendencia a alcanzar una viscosidad límite newtoniana a muy baja velocidad de cizalla.

El segundo caso presenta resultados de emulsificación, combinando la técnica antes de descrita con una homogeneización secundaria a altas presiones (5000-15000 psi) mediante la técnica de microcanales. El objetivo ha sido emulsionar aceite esencial de tomillo, usando un surfactante verde comercial no iónico, tipo alquilpolipentósido (APP). El objetivo ha sido maximizar la fracción de tamaños de gota submicrónicos, usando una cámara microfluídica de alta cizalla tipo Y. Se demuestra que el control de la energía aplicada permite obtener emulsiones prácticamente monomodales con diámetros medios de gota de Sauter y volumétrico de 370 nm y 520 nm, respectivamente.

AGRADECIMIENTOS. Parte de los resultados presentados corresponden al proyecto CTQ2011-27371 financiado por el Ministerio de Economía y Competitividad (MINECO) y fondos FEDER (Comisión Europea). Los autores expresan su agradecimiento por la financiación recibida.

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ESTUDIO DE LA SEPARACIÓN CO_2/N_2 MEDIANTE MEMBRANAS DE MATRIZ MIXTA PERMSELECTIVAS

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Palabras Clave: *separación de gases, membranas mixtas, zeolitas, permselectividad*

La separación con membranas se ha convertido en una tecnología prometedora, para la separación de CO_2 de otros gases ligeros y así reducir la concentración de los gases de efecto invernadero en la atmósfera y reducir el cambio climático [1]. La tecnología de membranas presenta una serie de ventajas respecto a las técnicas convencionales de captura de CO_2, como la simplicidad mecánica, la facilidad de escalado, el diseño modular, el bajo consumo de energía o la simplicidad de operación. Los polímeros son los materiales de membrana más avanzados en procesos de separación de CO_2. Aunque hay varias membranas poliméricas comerciales, hasta ahora no han sido una alternativa para la captura de CO_2 en la producción de energía a gran escala debido al compromiso entre permeabilidad y selectividad para una separación de gases específica, que limita la obtención de membranas altamente permeables con selectividad aceptable [2].

Una estrategia para superar estas limitaciones son las membranas de matriz mixta (MMM), materiales alternativos que combinan las propiedades de las cargas inorgánicas con la procesabilidad de los polímeros. En nuestro laboratorio, se han preparado membranas de matriz mixta (MMM) a partir de PTMSP, el polímero con mayor permeabilidad conocido, y zeolitas de tamaño de poro pequeño y ratios Si/Al de 1 a ∞, con permeabilidades elevadas y selectividades que superan el límite de Robeson así como buena resistencia térmica [3]. Se ha obervado que a mayor relación Si/Al, la adhesión entre la zeolita y la matriz polimérica empeora.

En este trabajo, se presentan los resultados obtenidos con MMM preparadas a partir de PTMSP y y zeolitas de Si/Al=5 (CHA, Rho, LTA) [4]. Se ha estudiado la permeación de N_2, O_2 y CO_2 en el rango de temperatura 25 – 60 ºC, bajo diferentes cargas de zeolita 5 – 20 % en peso. Las MMM también se han caracterizado por medio de SEM, análisis termogravimétricos (TGA) y difracción de rayos X (XRD), para estudiar la relación estructura-comportamiento.

Agradecimientos: Ministerio De Economía y Competitividad, MINECO (proyecto CTQ2012-31229, Contrato Ramón y Cajal RYC2011-08550 (C.C.C.) y contrato predoctoral FPI BES2013-064266 (A.F.B.)), y la Real Sociedad Española de Química en Cantabria (RSEQ ST-Cant.)

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CARACTERIZACIÓN DE LAS CORRIENTES DE UN MICRO-HDROCICLÓN

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Palabras Clave: *Micro-hidrociclón, caracterización*

La separación mediante hidrociclones es una técnica ampliamente utilizada para separación, clasificación y espesamiento de partículas en muchos procesos sólido-líquido [1]. Mientras que los hidrociclones habituales usados para el desarenado (diámetro interior mayor de 200 mm) permiten cortes de 40-100 µm, los micro-hidrociclones (diámetro interior menor de 150 mm) posibilitan la obtención de cortes inferiores a los 20 µm. Estos cortes más finos repercuten de una manera positiva en la calidad del producto obtenido aumentando su valor añadido.

El estudio aquí presentado forma parte de una de las primeras etapas de un proyecto de I+D+i llevado a cabo entre la empresa NOVATTIA DESARROLLOS S.L. y el grupo PROCAT-VARES del Departamento de Ingeniería Química de la UPV-EHU con el objetivo de lograr una tecnología de clasificación por hidrociclonado mucho más flexible, compacta y eficiente que la existente en el mercado actual.

El objetivo de este estudio ha sido determinar el procedimiento a seguir para lograr caracterizar correctamente las corrientes de salida (determinar la concentración y la distribución de partículas), rebose (overflow) y descarga (underflow), de un micro-hidrociclón. Para ello se ha contado con una planta piloto que permite la operación con un micro-hidrociclón de 100 mm de diámetro y posibilita la toma de muestras tanto de la corriente de alimentación como de las salidas del mismo. La alimentación utilizada en este estudio ha sido una pulpa con una concentración de 75 g/L formada por una arena feldespática y agua.

Para la caracterización de las corrientes se ha estudiado tanto el procedimiento de muestreo como la mejor forma de tratar las muestras. Tras varias pruebas se ha concluido que es necesario mantener una relación entre la muestra recogida en el overflow y el underflow para que la concentración de la alimentación no se vea afectada. De cara al tratamiento de la muestras se ha visto que la mejor solución es la filtración y posterior granulometría mediante difracción láser. Esta técnica se ha realizado en el analizador de tamaño de partículas Mastersizer 2000.

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SÍNTESIS Y CARACTERIZACIÓN DE NUEVAS CONFIGURACIONES CÁTODO-MEMBRANA PARA SU USO EN PILAS DE COMBUSTIBLE MICROBIANAS

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Palabras Clave: *Membranas poliméricas de inclusión, líquidos iónicos, cátodo, pilas de combustible microbianas.*

El uso del metabolismo bacteriano como proceso de producción de energía es objeto de numerosos estudios científicos. Más concretamente, las pilas de combustible microbianas (MFCs) se muestran como una alternativa sostenible a los combustibles fósiles. Estos sistemas aprovechan los electrones generados por los microorganismos al degradar la materia orgánica presente en un sustrato [1].

A la hora de diseñar una MFC, la elección de los materiales y su disposición en el sistema son claves, ya que afecta directamente al rendimiento [2, 3]. En este trabajo se han diseñado, sintetizado y caracterizado distintas configuraciones de membranas poliméricas de inclusión (PIMs) basadas en líquidos iónicos (cloruro de metiltrioctilamonio, $[MTOA^+][Cl^-]$) y cátodos ensamblados, para su uso en MFCs.

El rendimiento de MFCs de una sola cámara y cátodo al aire usando las nuevas configuraciones se comparó con el ofrecido por un sistema tradicional de membrana y cátodo superpuestos. Los resultados obtenidos muestran un incremento de la potencia generada del 1200% ($600 mW.m^{-3}$) respecto al sistema convencional ($50 mW.m^{-3}$) cuando se usa una PIM vertida directamente sobre la cara con platino de un cátodo hecho de tela de carbono, siendo esta cara la que está en contacto con el aire (Figura 1A) y la opuesta con el sustrato (Figura 1B).

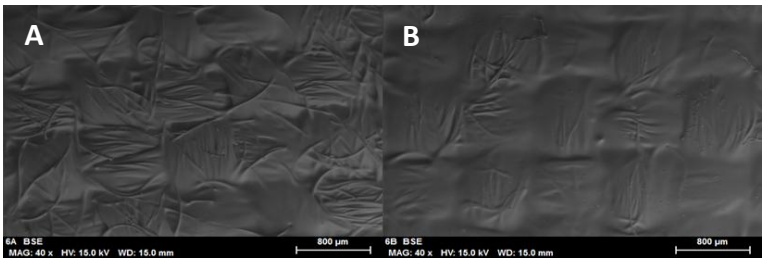

Figura 1. SEM de membrana polimérica de inclusión ensamblada en cátodo de tela de carbono. A) Cara en contacto con el aire; B) Cara en contacto con el sustrato.

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MODELO DE DISPERSIÓN DE GASES EN UN REACTOR SPOUTED BED CÓNICO

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Palabras Clave: *spouted bed, combustión, dispersión*

La combustión, gasificación y pirólisis son procesos que pueden ser llevados a cabo en contactores spouted bed cónicos, con diferentes tipos de materiales, para facilitar la fluidización de la biomasa es necesario la utilización de un material inerte. Debido a la complejidad del comportamiento del fluido en este tipo de reactores, la dispersión de los gases debe ser caracterizada mediante un modelo aproximado que prediga dicho comportamiento de manera simple, con el fin de calcular la diferencia de los gases producidos en el reactor y los de la salida. En este estudio se ha efectuado un análisis de trazadores utilizando el monóxido de carbono (CO) como compuesto a rastrear y para el modelo aproximado del sistema real se han tomado dos tanques de mezcla perfecta en serie con una corriente que conecta el primer tanque con la salida. La suma de los volúmenes de los tanques es el total de todos los equipos y líneas implicadas en el sistema real. Durante la experimentación se han utilizado diferentes caudales de entrada tanto de CO (0.5 y 1 l/min durante 9 s) como de aire (9, 14 y 19 l/min) a diferentes temperatura del reactor (400, 450, 500 y 550 ºC). Para la obtención de los parámetros característicos del modelo, se ha empleado un algoritmo de cálculo en Scilab que mediante una optimización nelder-mead ajusta el mejor resultado por medio de mínimos cuadrados de las ecuaciones diferenciales del modelo. En la Figura 1, se muestran los resultados para una de las temperaturas, evidenciándose el buen ajuste del modelo seleccionado.

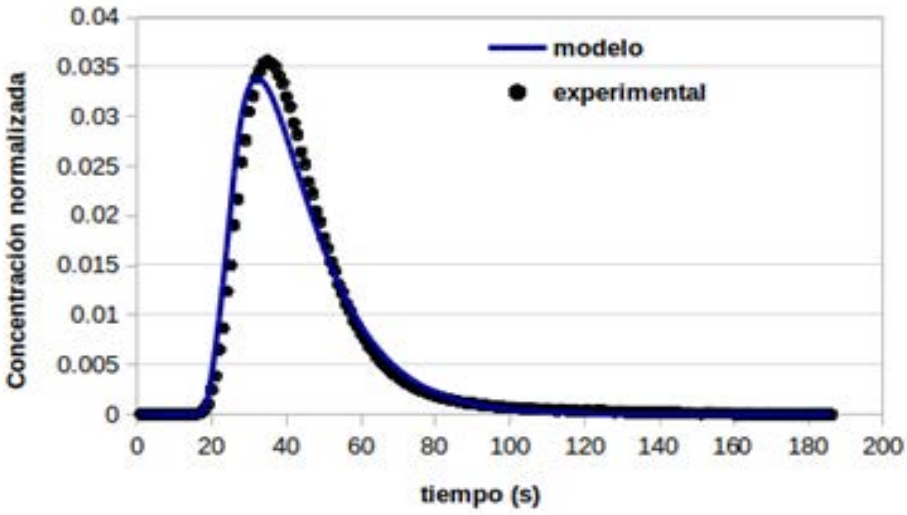

Figura1. Ajuste del modelo de dispersión a 500°C, 19 l/min de aire y 1 l/min de CO.

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PREPARACIÓN DE ELECTRODOS DE FIBRAS DE CARBONO CON NANOPARTÍCULAS DE Pt A PARTIR DE LIGNINA

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Palabras Clave: *Electrohilado, H_3PO_4, Platino, Fibras de carbón activado, Lignina*

Las fibras de carbón activado se han convertido en uno de los materiales más estudiados debido a sus buenas propiedades físicas y químicas. El uso de una nueva técnica de preparación, como el electrohilado, y de la lignina como materia prima, segundo polímero natural más abundante después de la celulosa, presentan una alternativa interesante al ser una fuente renovable con un reducido mercado [1]. Las fibras de carbono muestran buenas propiedades eléctricas, por lo que una de sus múltiples aplicaciones es su uso como electrodo en celdas electroquímicas. En este trabajo se resumen los resultados de la preparación de materiales fibrilares de carbón activado mediante electrohilado de lignina.

Las fibras de carbono se han preparado a partir de una disolución precursora de lignina Alcell® con o sin H_3PO_4. Mediante la técnica de electrohilado es posible obtener materiales fibrilares con muy buena distribución de partículas metálicas en una sola etapa [2]. Para la preparación de materiales con Pt, se ha usado acetilacetonato de Pt que se añadió a la disolución precursora. Los distintos materiales carbonosos obtenidos se han caracterizado mediante la adsorción-desorción de N_2 y CO_2, la química superficial se ha analizado con la técnica XPS, la morfología superficial se observó por SEM y TEM y, finalmente, su resistencia a la oxidación se estudió a partir de análisis termogravimétricos en atmósfera oxidante (TGA) y mediante voltametría cíclica en medio básico. Su actividad electrocatalítica se estudió en reacciones de electro-oxidación de distintos productos.

Los resultados muestran que la presencia de fósforo mejora el proceso de estabilización y las propiedades finales de las fibras de carbono, mostrando un mayor desarrollo de la estructura porosa (≈1000 m^2/g) y evitando la gasificación parcial en el proceso de carbonización de los materiales que contienen Pt. Además, el fósforo tiene una gran influencia en la distribución de tamaño de las partículas metálicas, consiguiéndose una distribución homogénea y tamaños de partículas en torno a los 2 nm. Finalmente, la resistencia a la electro-oxidación es mayor para las fibras que contienen grupos de fósforo, aumentando el rango de potencial de trabajo y la capacidad de los electrodos.

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DENSIDAD DE CORRIENTE DE INTERCAMBIO COMO PARÁMETRO CARACTERÍSTICO DE CATALIZADORES UTILIZADOS EN PROCESOS CWPO

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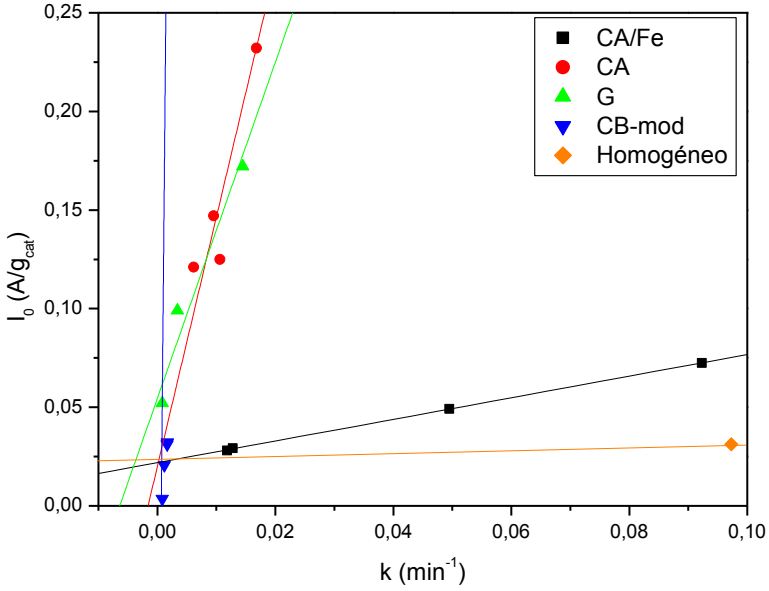
Palabras Clave: *Voltametría cíclica, CWPO, H_2O_2, Negro de humo, Carbón Activo*

Los procesos de oxidación catalítica utilizando peróxido de hidrógeno (CWPO) han demostrado su eficacia en el tratamiento de corrientes residuales contaminadas con compuestos no biodegradables. En los últimos años se han desarrollado múltiples catalizadores para este tipo de procesos. La actividad catalítica de cada uno de estos catalizadores debía ser comprobada in situ.

Este trabajo presenta una técnica de caracterización basada en la determinación de la densidad de corriente de intercambio mediante voltametría cíclica como un proceso de caracterización efectivo en la evaluación de catalizadores aplicados a procesos de CWPO.

Se ha medido este parámetro en diferentes familias de catalizadores: Grafitos (G), Negros de humo dopados con B, N, P (CB-mod), Carbones Activos (CA), catalizadores Fe/CA (CA/Fe) y sales disueltas de hierro (homogéneo), obteniendo una relación lineal entre el parámetro de densidad de corriente (I_0) y la constante cinética aparente de descomposición de agua oxigenada utilizando una cantidad constante del catalizador. En la Figura se puede apreciar las diferentes relaciones obtenidas.



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Comunicaciones Flash (FCb)

Sesión B: "Bioingeniería y Medio Ambiente"

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HYDROLYSIS OF SLUDGE: ROLE OF STRUCTURAL COMPONENTS OF THE FLOC

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Keywords: *EPS, floc, SMP, sludge, hydrolysis*

Sludge management is one of the main problems in municipal wastewater treatment plants (WWTPs), due to the large amount of sludge generated and the difficulty of dehydrating it. In order to achieve sludge with lower moisture contents, it is usually to conduct different hydrolysis pre-treatments (alkali, thermal, ultrasound, microwave…) for modifying the structure of the flocs, causing the breakdown of the bacterial cells and the release of their content. Among them, wet oxidation is frequently used as a pre-treatment step in which the sludge is solubilized and the soluble fraction is partially oxidized, yielding biodegradable products and the COD being reduced [1].

In this regard, the dewatering properties of sludge as well as its structure, surface charge, flocculation, settling properties and adsorption ability, are very related to the presence of extracellular polymeric substances (EPS). EPS bind with cells through complex interactions to form a vast net-like structure with plenty of water that protects cells against dewatering [2].

Over the past few years, considerable investigations have been performed in order to provide more detailed information about sludge minimization techniques. These studies are mainly focused on the evaluation of the efficiency of the technique on the basis of the disintegration or solubilization rates of a raw sludge [3]. Nevertheless, the information about the obtained profiles of the solubilized products or the effects of hydrolysis or oxidation reactions on the different structural components of the sludge involved during the thermal treatment is very scarce.

In order to understand the patterns of the solubilization and oxidation reactions involved in the thermal treatment of sludge, wet oxidations of a raw sludge and its structural components (SMP, LB-EPS, TB-EPS and “naked” bacteria) have been carried out and compared between them, paying special attention both the composition and characterization of the obtained products. The in-depth study of the structural components is a matter of great interest not only in terms of improving our comprehension of sludge minimization pre-treatments, but also improving the efficiency of such treatment through the optimization of operational parameters.

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HUMAN BLOOD PLASMA GELS PREPARATION FOR CULTURE CELL APPLICATIONS IN TISSUE ENGINEERING

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Keywords: *tissue engineering, human plasma, biomaterials, transglutaminase, fibroblasts.*

Blood and its derivates are very interesting human products to be used in therapeutics nowadays. Disposing of biomaterials that could be used as scaffolds for the growth and regeneration of tissue and organs, being these materials recognized as part of the body, is one of the top challenges of the tissue engineering. In this work it is proposed the preparation and characterization of different components of human blood plasma for the manufacture of biomaterials to be used in tissue engineering.

In order to synthesize the gels, the first thing to do is separating cellular fraction from plasma, by blood centrifugation; the four plasma protein fractions are separated by plasma fractionation, by modification of Cohn method. This study is made using non-fractioned plasma.

Human blood plasma gels are being synthesized by adding transglutaminase enzyme to increase their resistance and elasticity. Fibroblasts have been cultured using these gels as scaffolds in order to obtain epithelial tissue that would be very valuable for skin grafts. These gels could be prepared with the own patient blood to be used as a scaffold and in this way to avoid the rejection problems. Rapid, ideal and effecting ways of sterilization of transglutaminase enzyme are being investigated; also, new ways of cultivate skin cells in protein gels cross-linked with transglutaminase are being looked for, in order to improve the biomaterial prepared.

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OZONE/ HYDROGEN PEROXIDE-BASED ADVANCED OXIDATION TO REMOVE IBUPROFEN FROM AQUEOUS SOLUTION

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Keywords: *pharmaceutical drug*, *wastewater, ibuprofen, ozone, advanced oxidation*

Ibuprofen is a non-steroidal anti-inflammatory drug used as analgesic, for inflammatory diseases, fever or arthritis. High amounts of this pharmaceutical drug are consumed worldwide; hence, its presence in surface water is growing significantly. In addition to the risk for human health and the environment, ibuprofen is not easily degraded with conventional techniques applied in a wastewater treatment plant [1,2]. Therefore, it is required to find an alternative technology to effectively remove it from water. Advanced oxidation process (AOP) increases the oxidation potential and shows high capacity to degrade some recalcitrant pollutants from solution [3].

The present study was focused on the ibuprofen elimination through AOP. Aqueous solutions of this compound were treated by the injection of diverse ozone concentrations combined with hydrogen peroxide. Different scenarios were analyzed considering the properties of ibuprofen. Experimental conditions were optimized to reach high removal values and minimizing reagents concentration. Thus, almost 100% of ibuprofen was eliminated from solution with O_3 or O_3/H_2O_2 treatments. In most of the studied cases, intermediate compounds were not found, drastically reducing the environmental hazard of the final samples. AOP was also tested to remove ibuprofen from real wastewaters and promising results were obtained in terms of elimination, even in heterogeneous samples containing different types of organic substances. These results confirm the efficiency of the ozone/peroxide treatment to remove a recalcitrant pollutant, such as ibuprofen, from water. High elimination percentages were achieved, reporting final concentration values in the range of ppb.

The work was partially financed by the BIOQUIM_RESCUE project, from ACC1Ó (Catalan Government) with support of FEDER. Additional support from the Catalan Government was also provided (2014SGR-1582).

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REGENERATION OF URBAN TREATED WASTEWATER: INTEGRATED ELECTROCHEMICAL PROCESSES

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Keywords: *electrodisinfection, electrocoagulation, UV, electro-Fenton*

In recent years, economic development has implied the need for additional water resources to carry out further industrial or agricultural activities and also to meet the demand for domestic activities, tourism and leisure. On the other hand, the Mediterranean countries like Spain suffer cyclical periods of drought, which may eventually lead to problems of supply. In this context, the reuse of previously purified water is an alternative source cheap and secure. As a consequence, these processes have attracted increasing scientific and technical interest nowadays.

In the case of effluents from municipal wastewater treatment facilities, its turbidity and microbiological concentration are above the limits set by the Spanish legislation (RD 1620/2007). These effluents should be treated with an efficient technology that allows decreasing these parameters and economically viable. In this context, the group of Enviromental and Electrochemical Engineering of the Department of Chemical Engineering of the University of Castilla-La Mancha has accumulated a wide experience in the treatment of municipal and industrial wastewaters, both in the elimination of persistent organic pollutants as in their disinfection.

With this background, the main aim of the present work is presenting a recent research line which deals with the regeneration of municipal treated wastewaters by combined electrochemical processes. All technologies presented have as common thread the design of an electrochemical cell in which several electrochemical processes are carried out simultaneously. The performance of combined electrocoagulation-electrodisinfection [1], electrocoagulation-UV disinfection [2] and electrocoagulation-electrofenton [3] processes has been evaluated in the treatment of actual treated wastewaters from the WWTF of Ciudad Real (Spain). All these technologies exhibit a promising performance, allowing the disinfection of the effluents together with the removal of turbidity, dissolved solids and/or organic matter.

Acknowledgements

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WASTEWATER MANAGEMENT IN BATCH PROCESSES. A PHARMACEUTICAL MANUFACTURING PLANT CASE OF STUDY

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Keywords: *wastewater management, batch processes, pharmaceutical industry*

Batch processes are widely applied in different branches of chemical process industries, namely in manufacturing configured-consumer products, such as speciality chemicals, pharmaceuticals, paints, polymers, food products and cosmetics [1]. The wastewater generated is generally complex and highly toxic, containing a wide range of organic and inorganic pollutants, resulting in both high COD and salinity values. To make things worse, the batch-type production and campaign manufacturing cause a dissimilar production of wastewater depending upon the time and the production schedule. A representative example of these industries is the case of chemical-synthesis pharmaceutical manufacturing plants (csPMP). In those facilities, numerous types of chemical reactions, recovery processes and chemicals are employed in order to produce a wide variety of drug products [2] .

In this work, an extensive characterization study of the aqueous phases generated in a particular batch-type csPMP is carried out. Firstly, up to 100 aqueous samples from different processes were collected and characterized. Psychochemical characteristics hugely varied from one another: COD ranged from 0 to 560,000 mgO_2 dm^{-3}, conductivity from 0.15 to 212.16 mS cm^{-1} and pH from 0.15 to 13.13. Also, the analysis of the production during a year showed that batch and seasonal production heavily influenced on the characteristics of the wastewater generated. Despite this variability, the streams were classified under four different groups according to their characteristics and, therefore, the management strategy each one would receive. Consequently, a selection of end-of-pipe technologies (coagulation, Fenton oxidation, electrooxidation, electrodyalisis, reserve osmosis and vacuum evaporation, among others) were tested to assess their adequateness when it comes to treat the aforementioned wastewater.

This information would lay the foundations for the development of an adequate wastewater management system not only in the case of the study, but also potentially applicable to any chemical-synthesis batch-production plant.

Acknowledgements

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S15: *Ingeniería Química y Medioambiente*

ELIMINACIÓN DE COBRE DE EFLUENTES ACUOSOS MEDIANTE BIOCHAR DE ORIGEN VEGETAL

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Palabras Clave: *biochar, materia orgánica, adsorción, cobre.*

El cobre es un elemento potencialmente tóxico que puede generar problemas ambientales si se encuentra presente en concentraciones elevadas. Su presencia en los sistemas naturales se debe principalmente a su utilización en diversos procesos industriales (industrias metalúrgica y papelera, galvanizados,…) o agrícolas (pesticidas y fungicidas). En disolución el cobre se encuentra principalmente en forma de Cu^{2+}, siendo esta la forma química de mayor movilidad. Generalmente los métodos empleados para su atenuación se basan en la estabilización y/o inmovilización mediante procesos de precipitación química o métodos de adsorción. Entre los materiales adsorbentes utilizados para la retención de cobre y otros metales pesados se pueden destacar los óxidos de Fe, Mn o Al, así como el carbón activo. Una alternativa biosostenible es la obtención de biochars adsorbentes generados a partir de residuos agrícolas y forestales.

En el presente estudio se determinó la capacidad de retención de Cu que presentan cuatro tipos de biochar de origen vegetal (cáscara de arroz, acacia, eucalipto y carozo de maíz). Para ello se obtuvieron isotermas de adsorción de Cu a pH 5 y fuerza iónica de 0.1 M, determinándose la cantidad de cobre libre y de cobre en disolución mediante potenciometría con electrodo selectivo y por espectrofotometría de absorción atómica de llama, respectivamente. Se ajustaron las ecuaciones de adsorción de Freundlich y Langmuir-Freundlich a los datos experimentales obtenidos.

Se observó que estos biochars presentan una buena capacidad de inmovilización de Cu, siendo el biochar de cáscara de arroz el que presentó una mayor retención (44.5 mg/g), seguido de los biochars de acacia, maíz y eucalipto. Sin embargo, existen diferencias importantes en cómo se distribuye el cobre entre las distintas fracciones, Cu-Biochar, Cu-M.O y Cu^{2+} libre, que dependen tanto de la naturaleza de la biomasa como de las condiciones de formación de los biochars. Por otro lado, se observó una correlación positiva entre la capacidad máxima de adsorción y el ratio molar O/C debido, principalmente, al contenido de grupos funcionales polares, carboxilos e hidroxilos presentes en el biochar, que favorecen los mecanismos de adsorción superficial de Cu.

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ELIMINACIÓN DE As(V) ACUOSO MEDIANTE MATERIALES FUNCIONALIZADOS CON GRUPOS AMINO

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Palabras Clave: *Eliminación de arsénico, adsorción, funcionalización con grupos amino.*

El arsénico es un elemento altamente tóxico y carcinogénico que se presenta en los medios acuosos como As(III) y especialmente As(V). Para la eliminación de As(V) existen diversos métodos entre los que destacan los procesos de adsorción por su sencillez y economía. Para este fin se han propuesto muy variados adsorbentes naturales (bioadsorbentes y óxidos minerales) y sintéticos. Así, los óxidos de hierro muestran una notable eficacia como adsorbentes de As(V) [1]; sin embargo, recientes estudios muestran que nuevos materiales funcionalizados con grupos amino también constituyen una prometedora alternativa [2].

El objetivo de esta investigación es determinar la capacidad de adsorción de sólidos porosos mesoestructurados funcionalizados con grupos amino y comparar los resultados obtenidos con los de óxidos de hierro comerciales (goetita y magnetita). Los materiales testados fueron dos tipos de sílice mesoporosa: SBA15 funcionalizada con etilendiamina (tratada posteriormente con cobre) [3] y compuestos de tipo HMS funcionalizados con dietilentriamina. En todos los casos, la funcionalización con grupos amino se llevó a cabo por anclaje (grafting).

Las isotermas de adsorción se construyeron agregando múltiples experimentos individuales usando disoluciones acuosas de arseniato (AsO_4^{3-}). El arsénico residual se determinó colorimétricamente. En el caso del material SBA15 también se investigó el efecto del pH sobre el proceso de adsorción. En general, las isotermas de adsorción mostraron una afinidad variable por el ion arseniato, alcanzándose la capacidad máxima de adsorción de As(V) entorno a 1 mmol/g para los materiales tipo HMS.

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ELECTRO-BIORREMEDIACIÓN DE SUELOS CONTAMINADOS CON DIESEL APLICANDO CAMBIOS PERIÓDICOS DE POLARIDAD

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Palabras Clave: *Remediación de suelos, Electro-biorremediación, Cambio de polaridad*

Los procesos in-situ de biorremediación de suelos suelen tener como principal limitación la biodisponibilidad del contaminante, es decir, el contacto inmediato entre los microorganismos y los demás elementos necesarios para la biodegradación del contaminante. La tecnología de electro-biorremediación está basada en la combinación de la biorremediación con la remediación electrocinética. Los procesos de transporte electrocinético de materia (electromigración, electroforesis y electroósmosis) son utilizados para el suministro de microorganismos, aceptores de electrones o nutrientes hasta el punto donde se encuentra la contaminación [1, 2]. En estos sistemas, uno de los parámetros más importantes a controlar es la fuerte variación en el pH ocasionada por la reacciones de electrolisis del agua que tienen lugar sobre la superficie de los electrodos. En bibliografía se han propuesto diferentes estrategias para el control del pH en estos procesos [2-5]. En este trabajo se llevó a cabo la optimización del valor del campo eléctrico aplicado al utilizar la estrategia basada en el cambio periódico de la polaridad del mismo. Se llevó a cabo una serie de experimentos utilizando una instalación a escala de laboratorio en los que se estudió el tratamiento de electro-biorremediación de un suelo sintético, contaminado en laboratorio con diesel comercial. Así mismo, el suelo fue bioaumentado con una población de microorganismos específicamente aclimatados para la degradación del diesel. Se estudio el efecto del valor de campo eléctrico aplicado, realizando experimentos de dos semanas de duración, a 0.5, 1.0 y 1.5 V cm^{-1}, con una frecuencia de cambio de polaridad manual de 1 d^{-1} en todos los casos. Las conclusiones más importantes derivadas de los resultados obtenidos en los mismos fueron las siguientes: mediante el cambio periódico de la polaridad del campo eléctrico se consiguió mantener los valores de pH en torno a la neutralidad, que es el punto óptimo para los microorganismos utilizados en estos procesos; no se registraron intensidades de corriente muy elevados, por lo que la cantidad de agua movilizada por el proceso de electroósmosis y el calentamiento del suelo no produjeron modificaciones en el sistema perjudiciales para el proceso de biodegradación del diesel; finalmente, los mejores resultados, en cuanto a eficacia en la eliminación del diesel, se obtuvieron en el experimento realizado a 1.5 V cm^{-1} (22.35%, 19.18% y 35.40% a 0.5, 1.0 y 1.5 V cm^{-1}, respectivamente), aunque en este caso también se registró el mayor consumo eléctrico (42, 145 y 289 Wh kg_{Suelo}^{-1} a 0.5, 1.0 y 1.5 V cm^{-1}, respectivamente).

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SIMULTANEOUS PRODUCTION OF LACTIC AND LACTOBIONIC ACIDS FROM WHEY IN COMPETITIVE CULTURES

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Keywords: *competitive cultures, lactic acid, lactobionic acid*

The biotechnological production of lactobionic acid has received in recent years growing attention due to its numerous industrial applications, many of them in the food field as additive. Currently, bioprocesses producing lactobionic acid by microbial fermentation using *Pseudomonas taetrolens* as producer microorganism have already been implemented [1]. On the other side, dairy industry byproducts have been explored as substrate to obtain value-added products such as lactic acid [2], becoming a sustainable alternative to valorize this type of residues with high environmental impact. It is now intended to develop methods for obtaining fermented dairy products containing lactobionic acid in which this acid is produced *in situ* during the production process itself. In such processes, *P. taetrolens* has to compete with the usual fermentation processes in dairy products, in which lactic acid bacteria like *Lactobacillus casei* degrade lactose to generate the lactic acid.

The study of the interactions between *Lactobacillus casei* and *Pseudomonas taetrolens* in competitive fermentations is presented in this work. Co-cultures under the most favorable operational conditions for each microorganism, in terms of incubation temperature and aeration, were performed using residual cheese whey as substrate.

In both cases, lactobionic and lactic acid productions were lower than those obtained in pure cultures. Results suggest that the interaction between bacteria produces antagonistic effects and it is particularly harmful to *P.taetrolens*. In co-culture, *P.taetrolens* gets a very low production of lactobionic acid in spite of growing at its most favorable conditions, whereas *L.casei* is able to produce lactic acid even at the *P.taetrolens* optimal conditions. This observation was reinforced with studies of bacterial growth carried out by plating. Throughout the evolution of the co-cultures, a presence of *P.taetrolens* colonies with lower size and untypical morphology, as well as a decrease in the CFU count, was observed at earlier states than in the case of *L.casei*.

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THE PARTITION-RELEASE-RECOVERY CONCEPT FOR DOMESTIC WASTEWATER TREATMENT: FROM THEORETICAL APPROACH TO PRACTICAL CONCEPTUALIZATION

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Keywords: *resource recovery, domestic wastewater treatment, photobacteria*

The wastewater treatment field is about to enter in the fourth technological iteration where the resource recovery and energy (E) neutrality (even positive) are major drivers for technology improvement. Some novel concepts for the wastewater treatment plant of the future have been proposed [1-3]. Among them, the partition-release-recovery concept [4] is the only that allows both N and P recovery, and potentially value added organics or microbial products, respecting the E neutrality. This concept relies on the use of biological agents to selectively remove nutrients and carbon from the liquid phase (partition). The solid is separated from the regenerated water and then the E is recovered through Anaerobic Digestion (AD) of the solid phase. The release of nutrients upon AD allows to recover those using current technologies (recovery).

The technology has been tested in laboratory scale and a proof-of-concept has been described. The key point relies in the use of extremely versatile purple phototrophic bacteria (PPB) that use low-E infrared light as the E source and are able to high-concentrate C (almost 100% COD recover), N and P.

The partition step has been demonstrated in continuous mode by using a phototrophic anaerobic membrane bioreactor that was able to recover around 95% COD. However, it is necessary to supplement extra COD for complete N and P assimilation. A mechanistic model of the partition step has been proposed and validated. Some possibilities for internally deriving the extra COD from the produced PPB sludge have been explored, including fermentation, different kinds of hydrolysis, and chemical methods.

Finally, the release step has been studied by meso- thermo- and temperature-phased-AD. Although the methanization of the PPB sludge was relatively high (around 0.3 m3/KgVS), the low nutrient release, especially N, indicated that a pre-treatment would be necessary to improve protein decomposition, which is going to be addressed as the next step for optimizing nutrient recovery.

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EVALUACIÓN DE SOSTENIBILIDAD AMBIENTAL DE UN PROCESO INNOVADOR DE ELECTROSÍNTESIS DE DIMETIL CARBONATO A PARTIR DE CO_2

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Palabras Clave: *Dimetil carbonato, valorización de CO_2, análisis de ciclo de vida*

El dimetil carbonato (DMC) es un producto químico de gran interés que se utiliza como materia prima para la fabricación de policarbonatos y cuyo alto contenido en oxígeno le convierte en un potential aditivo para combustibles, en sustitución del metil tert-butil éter. La ruta más utilizada en la actualidad para la producción de DMC es la carbonilación oxidativa de metanol, aunque se están investigando nuevas rutas que puedan sustituirla, evitando así el uso de mónoxido de carbono. Entre ellas, es de particular interés su electrosíntesis a partir de metanol y CO_2. Esta vía permite el uso del CO_2 como materia prima para la fabricación de productos de valor añadido, p.ej. DMC, en lo que se conocen como procesos de captura y utilización de CO_2 (Carbon Capture and Utilisation, CCU) [1]. Además, el uso de técnicas electroquímicas permite aprovechar los picos de energía renovable, p.ej. la solar fotovoltaica, para aportar la energía requerida en el proceso. En este sentido, se ha estudiado la electrosíntesis de DMC a partir de metanol y CO_2 en una celda tipo filtro prensa en presencia del líquido iónico bmimBr y CH_3OK [1,2].

El objetivo de este trabajo es comparar la sostenibilidad ambiental de la ruta electroquímica innovadora de síntesis de DMC a partir de CO_2 y metanol con el proceso comercial de carbonilación oxidativa mediante herramientas de análisis de ciclo de vida. El proceso electroquímico ha sido simulado utilizando HYSYS. Entre los resultados obtenidos cabe destacar que el consumo energético es el principal contribuyente a la mayoría de los impactos ambientales. Se ha establecido un análisis de sensibilidad para estudiar la influencia del rendimiento de la reacción en la ruta electroquímica, concluyendo que un rendimiento del 20% sería suficiente desde el punto de vista del indicador de calentamiento global (Global Warming Potential, GWP) para que el proceso electroquímico sea ambientalmente más sostenible que el comercial, evitando al mismo tiempo la emisión de 0,5 kg de CO_2 por kg de DMC producido, debido al uso de CO_2 capturado. Posteriormente, el número de indicadores ambientales considerados se ha ampliado y sus resultados se han normalizado y ponderado para obtener un indicador global, obteniendo similares conclusiones que para el GWP.

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VALORIZACIÓN DE CO_2: ELECTROREDUCCIÓN HACIA FORMIATO CON ELECTRODOS NANOPARTICULADOS DE Sn

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Palabras Clave: *CO_2, partículas de estaño, formiato, electroreducción*

La valorización de CO_2 es una estrategia interesante para reducir las emisiones de CO_2 a la atmósfera y que permite convertir el CO_2 en productos con valor añadido. Entre las opciones de valorización, la electroreducción se presenta como una opción muy atractiva, particularmente acoplada con energías renovables, dado que puede ser una excelente vía para almacenar los excesos de producción de energía renovable intermitente (como por ejemplo solar o eólica) y al mismo tiempo permite la conversión del CO_2 capturado en productos químicos o combustibles. Mediante electroreducción se pueden obtener diversos productos, entre los que destaca el ácido fórmico/formiato, dado que se usa como materia prima en diversos procesos industriales y ha sido propuesto como "carrier" de hidrógeno y como un combustible prometedor para pilas de combustible. Actualmente, estudios recientes se centran en el uso de Sn (generalmente en forma de partículas) depositado sobre soportes porosos para ser usados como electrodos en celdas electroquímicas para la electroreducción de CO_2.

En este trabajo se sintetizaron partículas de Sn (soportadas y no soportadas sobre carbono, y con tamaños de partícula menores a 50 nm) mediante la reducción de $SnCl_2$ con $NaBH_4$ en etilenglicol y en presencia de polivinilpirrolidona (PVP). Estas partículas fueron caracterizadas mediante voltametría cíclica y TEM. Tras su caracterización, se fabricaron electrodos mediante esprayado y se caracterizaron mediante SEM y voltametría cíclica. De acuerdo con los resultados de la caracterización, el comportamiento de los electrodos fabricados se estudió en un sistema para la obtención de formiato en continuo en filtro prensa. Se probaron estos electrodos en distintas configuraciones: en configuración "gas diffusion electrode" (GDE), en el que se añadió una capa microporosa entre la capa catalítica y el soporte; y como electrodo 3-D en el que el gas atraviesa el electrodo. Los resultados de estos electrodos mejoraron los obtenidos en trabajos previos [1,2] en los que se utilizaron partículas comerciales de Sn (d=150 nm), con las que se alcanzaron velocidades de formación de producto de $1.5 \cdot 10^{-3}$ mol m^{-2} s^{-1}, con una eficiencia faradaica alrededor del 70% y una concentración de formiato de aproximadamente 1.5 g L^{-1} con un solo paso por celda.

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INGENIERÍA QUÍMICA E INFUSIÓN INTRAVENOSA

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Palabras claves: *BET, TCI, CST, PF, infusión intravenosa, ingeniería química.*

Objetivo: Exponer la oportunidad que representa el empleo de la ingeniería química en la mejora de la *infusión intravenosa* por perfil de aporte Bolo Eliminación trasferencia (*BET*).

Introducción: Desde 1968[1] en que se plantea los aspectos teóricos del BET se ha intentado este perfil por dos medios: Sistemas electrónicos con bombas informatizadas que ha conseguido un gran éxito.[2] Medios físicos con un número limitado de publicaciones y patentes[3] sin haberse realizado una aplicación rigurosa de los criterios de la ingeniería química que hubiera conducido a un mayor éxito que el desuso actual. A día de hoy por parte de la comunidad científica se está pidiendo una apertura del tema.

Material y Métodos: El aporte de soluciones líquidas se puede estudiar fácilmente por gravimetría, espectrofotometría con colección de fracciones o cámaras de flujo y picnometría.

Resultados y Discusión: El Bolo, que exige no mezcla, puede realizarse basado en el modelo flujo pistón (*PF*) o en escalón con jeringa. La Eliminación requiere un flujo másico continuo estable que se obtiene con un frasco de Mariotte. La trasferencia necesita una infusión exponencial decreciente de uno o más sumandos que se consiguen con el modelo de tanque de agitación completa (*CST*). Se discute los balances de materia que se consideraron, el no planteamiento de balance energético, el no planteamiento de las unidades básicas operativas (PF y CST) en *Ingeniería Química* y sus combinaciones posibles para una optimización del BET.

Conclusión: Unos resultados satisfactorios de BET con las combinaciones testadas en laboratorio abren oportunidades de fabricación y mercado que deseamos resaltar.

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Presentaciones Póster (PP)

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S15: *Ingeniería Química y Medioambiente*

PHOTOCATALYTIC REDUCTION OF CO_2 TO METHANOL ON A CU-DOPED TIO_2 MEMBRANE REACTOR: A VIABILITY STUDY

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Keywords: *CO_2 reduction, photocatalysis, titanium dioxide, copper, membrane reactor*

The photocatalytic reduction of CO_2 (also known as artificial photosynthesis) is an exciting option with the ability to convert CO_2 into fuels using sunlight, solving the problem of global warming and fossil fuel depletion all together. Among semiconductor materials, TiO_2 has been widely used as a photocatalyst for CO_2 transformation under illumination in order to obtain valuable products such as CO, CH_4, CH_3OH or HCOOH [1]. Besides, previous studies have shown that copper (Cu) supported on TiO_2 may play a crucial role in the CO_2 photocatalytic reduction to produce CH_4 and CH_3OH, since Cu is able to trap electrons without affecting their mobility [2]. In any case, the concentration of the reduced products is still too low (i.e. from 10 to 1000 ppm) to be practically used [1]. The breakthrough to speed up the CO_2 photocatalytic reduction reaction seems to be in the promotion of mass transfer and the avoidance of the re-oxidation of the products in the catalytic surface, maintaining the non-equilibrium reaction state [3]. In other words, by removing the products away, the reaction is forced to head to one direction. Since the molecular diameters of the reactants, that is CO_2 (0.33 nm) and water vapour (0.28 nm) are smaller than that of expected CO_2 reduced products (i.e. CO: 0.38 nm, CH_4: 0.38 nm or CH_3OH: 0.44 nm), the promotion of the reaction by gas separation is thought to be possible. Therefore, the aim of this work is the development of a Cu-TiO_2 photocatalytic membrane reactor to investigate the effect of mass transfer promotion, maintaining a non-equilibrium reaction state, as represented in Figure 1.

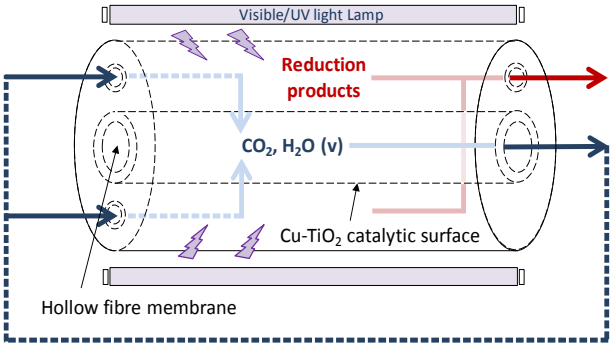

Fig. 1. Schematic representation of the CO_2 photocatalytic membrane reactor system

The specific objectives of this study are as follows: (1) to prepare and characterize Cu-TiO_2 films coated on ceramic supports with controlled pore sizes, (2) to evaluate the optimal experimental conditions to promote the photocatalytic transformation of CO_2 into methanol in the reactor and finally, (3) to verify the viability of the Cu-TiO_2 photocatalyst membrane reactor in continuous operation.

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S15: *Ingeniería Química y Medio Ambiente*

EFECTO DE LA RELACIÓN O/C EN EL REFORMADO DE BIO-OIL CON CATALIZADOR Ni/La_2O_3-αAl_2O_3

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Palabras Clave: *Bio-oil, Hidrógeno, Reformado oxidativo, Reformado autotérmico.*

Introducción. Los procesos de obtención de H_2 mediante reformado de bio-oil (líquido obtenido por pirólisis flash de biomasa lignocelulósica) son una interesante vía en progreso científico y tecnológico en la búsqueda de nuevos combustibles respetuosos con el medio ambiente. El reformado oxidativo de bio-oil (OSRB) aúna la exotermicidad de la oxidación parcial con O_2 y la endotermicidad del reformado con vapor de H_2O (SRB). El ajuste de la relación O/C permite alcanzar el estado termoneutro produciendo H_2 con nulos requerimientos energéticos [1] (reformado autotérmico de bio-oil, ATRB). En este trabajo se ha estudiado el comportamiento cinético del catalizador Ni/La_2O_3-αAl_2O_3 en el SRB, ATRB y OSRB.

Experimental. Las reacciones se han realizado con catalizador Ni/La_2O_3-αAl_2O_3 (10 % Ni, 9 % La, preparado por el método de impregnación a humedad incipiente [2]), en un reactor de lecho fluidizado a 700 ºC, S/C = 6, W/F_0 = 0.3 $g_{cat}h/g_{bio\text{-}oil}$ y O/C = 0-1.34.

Resultados. A tiempo cero, el catalizador Ni/La_2O_3-αAl_2O_3 alcanza conversión completa para todas las relaciones O/C estudiadas. En el SRB se obtiene un rendimiento inicial de H_2 del 88 %, valor que disminuye notablemente al aumentar la relación O/C (74 % para ATRB y 66 % para OSRB), debido principalmente al consumo de H_2 por oxidación a H_2O. En condiciones de alta desactivación (elevado tiempo de reacción), la conversión de bio-oil es mayor para mayor la relación O/C, al fomentarse reacciones de combustión de compuestos oxigenados (con un mayor rendimiento a CO y CO_2). Además, una mayor cantidad de O_2 en el medio favorece la combustión de los depósitos carbonosos y atenúa la desactivación por deposición de coque, de modo que el rendimiento de H_2 obtenido tras 4 h de reacción es mayor para mayor relación O/C.

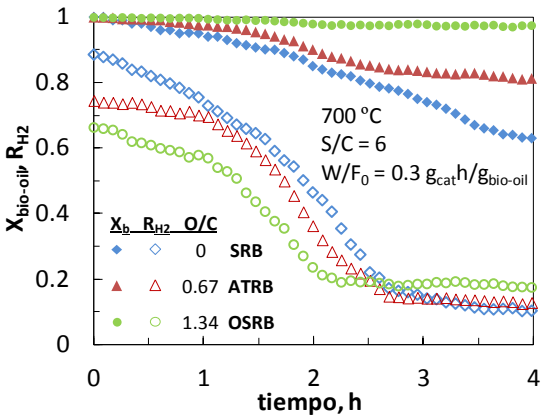

Figura 1. Evolución con el tiempo de reacción de la conversión de bio-oil y rendimiento de H_2.

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PHOTODEGRADATION OF INDUSTRIAL DYES WITH AGCL NANOCATALYST SYNTHESISED FROM THE BULK MATERIAL IN IONIC LIQUID

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Keywords: *photodegradation, nanocatalyst, silver chloride, ionic liquid, industrial dyes*

Effluents containing industrial dyes can strongly damage the aquatic systems, being responsible for very serious pollution problems. Modern dyes are chemically stable and resistant to classical degradation methods [1]. Among them, azo dyes represent the 50 % of the industrial dyes used, with a major presence in the textile sector. The degradation of these molecules is attracting much attention and effort, and different techniques are being studied to this purpose. Photocatalytic degradation methods are demonstrating to be one of the most innovative, green and efficient alternatives, depending on the activity of the catalyst used. Among them, the use of nanoparticles as photocatalytic agents is showing an increasing interest [2].

In this work, silver chloride nanoparticles have been successfully prepared by an easy and quick method using solely the corresponding powder material and an ionic liquid trihexyl(tetradecyl)phosphonium chloride, $[P_{6\,6\,6\,14}]Cl$, without adding other solvents. The obtained nanoparticles were characterised by X-ray powder diffraction, UV–vis spectroscopy, transmission electron microscopy and scanning electron microscopy. The photocatalytic activity of the nanoparticles was tested for the degradation of industrial dyes under UV radiation. The selected dyes were azo group-containing dyes (Orange II and Methyl Orange), thiazine-based dyes (Methylene Blue) and xanthenes (Rhodamine B). The decolouration of the samples was studied by UV-vis absorbance at the corresponding wavelength. The obtained results showed degradations efficiencies over 90% in one hour, pointing out the good catalytic activity of this nanomaterial.

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ENSAYOS DE VIDA ACELERADA PARA MATERIALES FOTOVOLTAICOS: CARACTERIZACIÓN DE MATERIALES

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Palabras Clave: *Solar, caracterización, fotovoltaica, materiales.*

Actualmente se está observando defectos en módulos solares expuestos durante años en el exterior, muchos de estos defectos son burbujas en los bordes, grietas en el cristal, color amarillento cerca de éstas, disminución de su eficiencia..... Es por ello el objetivo principal de este trabajo determinar la vida media de los componentes de una célula solar con la finalidad de conseguir, evitar y comprobar la resistencia de los materiales a los agentes atmosféricos y su influencia sobre la generación de electricidad de las células Por este motivo se ha sometido a la oblea de silicio monocristalino que conforma posteriormente la célula solar fotovoltaica a distintos ensayos según la norma UNE 61215.

Se han caracterizado obleas de silicio monocristalino antes y después de los tratamientos mediante estudios de rayos X, de transmitancia y reflectancia para observar la degradación sufrida. Mediante reflectancia se han observado pequeñas variaciones, causadas por la oxidación de la oblea lo que altera su composición y propiedades, por lo que se puede afirmar, que, aunque aparentemente la inspección visual de la muestra no cambia, si ha sufrido cambios estructurales. Lo que se corrobora con los resultados obtenidos por difracción de Rayos X.

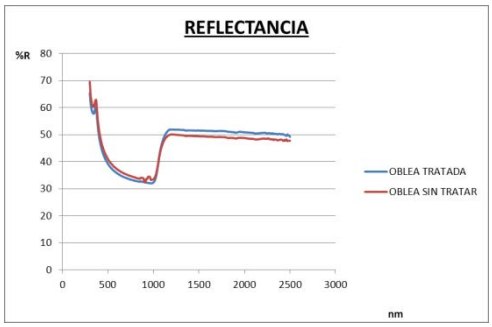

Fig. 1: Comparación de la reflectancia antes y después del ensayo de ciclos térmicos

De igual modo se ha sometido el material encapsulante a ensayos de degradación y se ha observado variaciones en las medidas de reflectancia y evidencia de adhesión, lo que puede provocar problemas, como oxidación y la corrosión de los otros componentes que forman la estructura de la célula y posteriormente del módulo fotovoltaico.

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INFLUENCE OF CARBONACEOUS ELECTRODE MATERIAL ON MICROBIAL FUEL CELL TREATING A SYNTHETIC WASTEWATER

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Keywords: *Microbial fuel cell, electric power, carbonaceous electrode, wastewater*

The use of non-renewable sources of energy, such as fossil fuels has led to a global energy crisis. Renewable bioenergy is considered as one of the ways to ensure an energy supply in the long term. Microbial fuel cell (MCF) is one of the emerging technologies that have gained increasing attention because they can treat wastewater and recovery energy at the same time. A MCF converts the energy stored in the chemical bonds of organic compounds into electrical energy through the metabolic activity of living microorganisms. However, the applicability of this technology for general purposes remains low and more information is needed on their long-term stability. Therefore, the aim of this work is to compare and assess the performance of different types of carbon-based electrodes in a dual-chamber MFC. In total, three different materials were tested under the same operational conditions: Carbon felt, carbon foam and carbon cloth were used as electrodes.

The results demonstrate that electricity can be efficiently generated using carbon felt as anode with 180 mV of average voltage and a promising electrical power generation (1062mW m^{-2}), because its surface area (higher than carbon cloth and carbon foam) which, in turn, favour the bacterial growth and, thus, electricity generation. At the same time, biological treatment was more efficient in terms of COD removal using carbon felt electrodes with a COD wastewater daily removals around 1600 mg L^{-1} day^{-1} (63%). On the other hand, the carbon cloth exhibits the lowest the values of average voltage (7.6 mV) and COD removal rate because this material is thin and has less surface area for microbial adhesion and growth.

These results indicate that carbon felt is the most promising carbon-based to be used as electrode material in MFCs, as better power generation and COD abatement rate were obtained in comparison with carbon foam and carbon cloth.

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S15: *Ingeniería Química y Medioambiente*

EFECTO DE LA RELACIÓN H_2/CO_X EN LA SÍNTESIS DE DME EN UNA ETAPA ALIMENTANDO H_2, CO Y CO_2

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Palabras Clave: *DME, CO_2, síntesis en una etapa*

El dimetil éter (DME) despierta un gran interés como combustible (bien para motores Diesel o como alternativa al LPG de uso doméstico) y como vector de hidrógeno para celdas de combustible. Este interés está potenciado por el desarrollo tecnológico de su obtención a partir de materias primas alternativas al petróleo (carbón, gas natural y biomasa), vía gas de síntesis. El proceso STD (syngas to DME) se lleva a cabo sobre catalizadores bifuncionales que contienen una función metálica para la síntesis de metanol a partir de H_2, CO y CO_2, y una función ácida para la deshidratación de metanol a DME.

El objetivo de este trabajo es estudiar el efecto de la relación H_2/CO_x en la alimentación (H_2+CO+CO_2) en el proceso STD utilizando el catalizador CuO-ZnO-MnO/SAPO-18 que ofrece un buen comportamiento, por su elevada actividad, rendimiento y selectividad de DME, estabilidad y reducida formación de parafinas [1]. Los resultados ponen de manifiesto que la mejora de los índices de reacción es insignificante para relaciones de H_2/CO_x mayores a 3 y esta relación H_2/CO_x tampoco tiene un efecto significativo sobre la desactivación del catalizador. Así mismo, se aprecia en los resultados obtenidos, la tendencia de que dicha desactivación se atenúa con la presencia de CO_2 en la alimentación.

Las reacciones se han llevado a cabo en un equipo *PID Eng. Tech Microactivity-Reference* con reactor de lecho fijo en las siguientes condiciones de operación: 275 ºC; 30 bar; tiempo espacial, 10.18 $g_{cat}h(mol_{C\ aliment.})^{-1}$; relación CO_2/CO en la alimentación entre 0-1 con relación H_2/CO_x entre 3-4; mientras que los productos de reacción se han analizado en continuo en un micro-cromatógrafo de gases *Varian CP4900*. Los índices de reacción estudiados han sido: conversión de moles de COx alimentados (X); rendimiento de DME (R), definido como la relación molar de DME en la corriente de productos; y selectividad (S).

Los resultados (Figura 1) ponen de manifiesto el buen comportamiento del catalizador, con lo que el aumento de la relación H_2/CO_x=3 (aconsejable por la estequiometría) no tiene un efecto significativo de mejora, ni sobre los índices de reacción a tiempo cero (Figura 1a), ni sobre la estabilidad (Figura 1b). Este limitado requerimiento de H_2 es interesante para la viabilidad del proceso utilizando fuentes renovables para la producción de H_2.

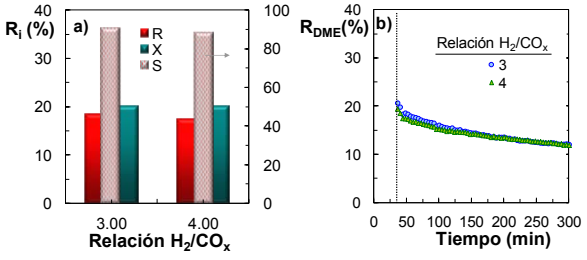

Figura 1. Efecto de la relación H_2/CO_x sobre los índices de reacción (a) y estabilidad (b). Condiciones de reacción: 275 ºC; 30 bar; 10.18 $g_{cat}h(mol_C)^{-1}$; CO_2/CO=1/3.

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EFECTO DEL TIEMPO ESPACIAL EN EL REFORMADO CATALÍTICO DE LOS PRODUCTOS VOLÁTILES DE LA PIRÓLISIS DE HDPE

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Palabras Clave: *HDPE, pirólisis, spouted bed cónico, reformado*

En los últimos años, el mundo se ha enfrentado a una crisis energética debido al agotamiento de los recursos y el aumento de los problemas medioambientales como el calentamiento global y el cambio climático. Esto se debe en mayor parte al uso de los combustibles fósiles que emiten grandes cantidades de dióxido de carbono. Por lo tanto, es necesario encontrar otros combustibles alternativos que sean económicamente competitivos y medioambientalmente sostenibles. El hidrógeno es un vector energético prometedor como sustituto de los combustibles fósiles y juega un papel muy importante en los sistemas energéticos del futuro. Además, se puede generar a partir de biomasa o residuos plásticos mediante reformado.

En este trabajo se ha estudiado la producción de hidrógeno a partir de la pirólisis de HDPE y reformado con vapor en línea de los volátiles utilizando un sistema de reacción en dos etapas. La pirólisis de HDPE se ha llevado a cabo a 500 ºC en un reactor de spouted bed cónico, mientras que el reformado catalítico de los volátiles se ha realizado en un lecho fluidizado a 700 ºC sobre un catalizador comercial de Ni. Se ha estudiado el efecto que tiene el tiempo espacial sobre la distribución de los productos y la desactivación del catalizador.

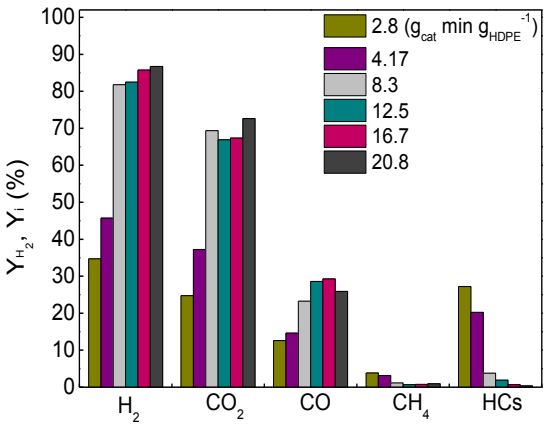

Figura 1. Efecto del tiempo espacial en los rendimientos.

En la Figura 1 se muestra el efecto del tiempo espacial sobre los rendimientos de los productos de la etapa de reformado. Al aumentar el tiempo espacial de 2.8 a 20.8 $g_{catalizador}$ min g_{HDPE}^{-1}, se obtienen mayores rendimientos de H_2, CO y CO_2. En cambio, los rendimientos de CH_4 y HCs (etileno, etano, propileno y propano) son bajos, aunque a bajos tiempos espaciales la reacción de reformado no está favorecida y se producen las reacciones de craqueo, aumentando los rendimientos iniciales de éstos. Por otra parte, a mayor tiempo espacial se obtiene mayor conversión de las ceras, además de mantener su actividad durante más tiempo.

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INMOVILIZACIÓN DE GEOMATERIALES PARA LA ELIMINACIÓN DE ARSÉNICO EN PROCESOS EN CONTINUO

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Palabras Clave: adsorción, arsénico, beads, quitosano, estudios en columna

La presencia de arsénico en aguas naturales constituye una gran amenaza para la salud y el medio ambiente y prevenir su aparición se ha convertido en uno de los grandes desafíos científicos a nivel mundial. La US-EPA ha revisado a la baja el valor máximo recomendado para el arsénico en agua potable, bajándolo de un valor de 0.05 mg/L a 0.01 mg/L [1]. La mayor parte de los métodos de tratamiento para eliminar arsénico del agua permiten reducir su contenido en disoluciones con una concentración alta de partida, pero la concentración de arsénico remanente sobrepasa incluso el valor de 0.05 mg/L, valor límite que aún es empleado en algunos países [2]. La búsqueda de una metodología que permita eliminar arsénico en aguas hasta valores seguros constituye un gran desafío y resulta de gran interés, no sólo en el ámbito científico, sino también en el medioambiental y el de salud.

En estudios previos se ha comprobado la eficacia del uso de la tecnología de la adsorción en la eliminación de contaminantes presentes en disolución acuosa [3, 4]. La utilización de materiales adsorbentes sintetizados de elevado coste resulta ser muy efectiva, especialmente en disoluciones con concentraciones de contaminante muy bajas de partida. Sin embargo, también es posible utilizar materiales más baratos, procedentes de subproductos de deshecho obteniéndose resultados comparables a los materiales sintéticos [5].

Tras realizar un barrido inicial de distintos biomateriales y geomateriales para estudiar su eficacia en la eliminación de arsénico, se ha procedido a la selección de dos de ellos, lodo rojo (subproducto industrial) y magnetita (material preparado en el laboratorio) para proceder a la inmovilización de los mismos con el objeto de utilizar el material inmovilizado en estudios en columna que permitan el tratamiento de grandes volúmenes de agua. Se han estudiado distintas matrices de inmovilización, obteniéndose buenos resultados mediante la inmovilización en beads (esferificaciones) de quitosano. Aun cuando la inmovilización en la matriz de quitosano produce una inhibición significativa en la capacidad de adsorción de los materiales estudiados, la mejora en el comportamiento mecánico e hidrodinámico de los materiales inmovilizados permite su empleo en procesos en continuo, extremadamente difíciles de realizar con los materiales nativos.

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EFECTO DE LA PROPORCIÓN Pt-Pd EN LA HIDRODECLARACIÓN DE DICLOROMETANO CON CATALIZADORES BIMETÁLICOS SOPORTADOS SOBRE ZIRCONIA SULFATADA

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Palabras Clave: *hidrodecloración, diclorometano, paladio, platino, zirconia*

La hidrodecloración catalítica (HDC) se presenta como una tecnología emergente para el tratamiento de diclorometano (DCM), contaminante que aparece en la atmósfera debido a su amplio uso en la industria química y farmacéutica. En este trabajo se estudia el efecto de la proporción de Pt-Pd en la HDC de DCM con catalizadores soportados sobre zirconia sulfatada.

Se prepararon catalizadores soportados sobre zirconia sulfatada (SZ: SO_4^{2-} - ZrO_2), con proporciones atómicas Pt:Pd de 0:1, 1:3, 1:1, 3:1 y 1:0, mediante impregnación a humedad incipiente, utilizando cloruro de paladio y ácido hexacloroplatínico como precursores de la fase activa. Estos fueron calcinados y reducidos *in situ,* previamente a la reacción, a 450 ºC en corriente de aire y a 300 ºC con H_2, durante 1 h y con una caudal de 50 cm^3/min (c.n.) en ambos casos. Los catalizadores se caracterizaron mediante diferentes técnicas.

Los experimentos de HDC de DCM se llevaron a cabo en un micro-reactor de lecho fijo, en las siguientes condiciones de operación: C_0 = 1000 ppm; P = 1 atm; T = 150-250 ºC; tiempo espacial = 0,8 kg·h·mol^{-1}; Q_t = 100 cm^3/min; H_2/DCM = 100.

En las Fig. 1 y 2 se puede observar una mayor estabilidad en los catalizadores bimetálicos, en particular el SZ Pt-Pd (1:3) que además es más activo, lo que se puede asociar a su mayor dispersión.

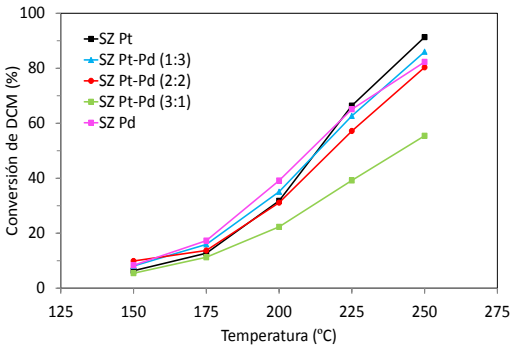

Fig 1. Efecto de la temperatura en la conversión de DCM con los distintos catalizadores

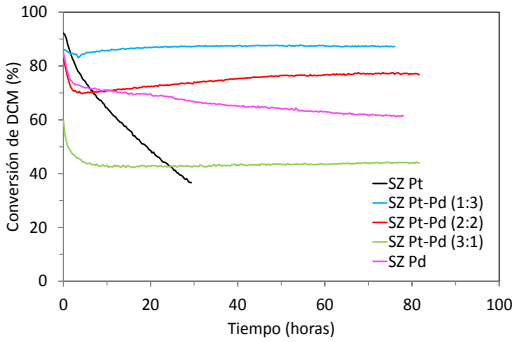

Fig 2. Evolución de la conversión de DCM a 250 ºC con los distintos catalizadores

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POLYHYDROXYALKANOATE PRODUCTION BY MIXED CULTURES USING CHEESE WHEY

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Keywords: *polyhydroxyalkanoate, mixed cultures, volatile fatty acid, cheese whey*

Whey is the by-product of cheese production and it is produced in large volumes. Approximately 50% of worldwide production is not properly treated, representing a serious problem from an environmental point of view. Due to its high lactose content, cheese whey (CW) could be considered a valuable by-product which could be used for the production of biopolymers such as polyhydroxylkanoanes (PHA´s). PHA´s are biopolyesters synthesized by different bacteria as intracellular storage of carbon and energy. The production of PHA´s is considered a sustainable alternative to conventional plastics and can be obtained from different wastes/by-products using mixed microbial cultures. The process for PHA production consist on three stages: (1) Acidogenic fermentation; (2) PHA producing culture with a feast and famine regime and (3) PHA production stage using a fed-batch reactor under growth limited condition. In this work was studied the feasibility of producing PHA using CW as substrate. The effect of the Sludge Retention Time (SRT) at pH 6 on the productivity of volatile fatty acids (VFA) and on the profile of VFA was determined. The results showed that at short SRT (4 days) the degree of acidification reached a yield of nearly 98 %, being butyric acid the main product, while longer SRT (10 days) acidification was lower around 70 %, being acetic and propionic acid, the major products. In a second series of experiments the effect of the organic acids composition on biopolymer composition and yield was evaluated in a fed batch reactor. A direct relationship was observed between the type of VFA used and the composition of the biopolymers. The maximum storage yield observed was 0.37 Cmmol HA/Cmmol VFA.

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CARACTERIZACIÓN DE LAS PROPIEDADES ANTIOXIDANTES DE EXTRACTOS NATURALES PARA LA OBTENCIÓN DE NANOPARTÍCULAS

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Palabras Clave: *capacidad antioxidante, extractos vegetales, nanopartículas, hierro, química sostenible, adsorción*.

La nanotecnología es un campo que ha ido creciendo en los últimos años debido a que las nanopartículas de algunos materiales ven incrementadas sus propiedades o aplicaciones en esa escala de tamaño. Al mismo tiempo, la problemática ambiental mundial actual hace cada vez más necesario el desarrollo de procesos de química sostenible alternativos que reduzcan el impacto en el medio ambiente.

En este trabajo se han sintetizado nanopartículas metálicas de hierro mediante un método de química sostenible alternativo a los procesos convencionales[1], los cuales emplean reactivos agresivos para el medio ambiente o requieren el uso de equipos costosos. Este método alternativo se basa en la capacidad antioxidante de extractos vegetales inocuos para el medio que reducen cationes metálicos en disolución, gracias a su alto contenido en polifenoles[2]. Para la elaboración de los extractos se emplea biomasa procedente de especies autóctonas gallegas como el roble, el castaño, el pino y el tojo.

Se evalúa la capacidad antioxidante de los extractos mediante diversos métodos (decoloración de $DPPH^{\cdot}$ y TEAC), el contenido de polifenoles (Folin-Ciocalteu) y se determinan otros parámetros, como el pH, el potencial redox y la DQO. La estimación del tamaño de las nanopartículas sintetizadas se lleva a cabo mediante fotografías de TEM.

En vista de los resultados obtenidos, se selecciona el extracto considerado apropiado, y se realiza un estudio de la remediación de cromo hexavalente con las correspondientes nanopartículas de hierro sintetizadas. Se estudia la capacidad de eliminación de Cr(VI) de estas nanopartículas en función del pH, realizando su inmovilización en diversos soportes. Se comprueba que la eliminación del Cr(VI) ocurre mediante dos mecanismos, adsorción y reducción.

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EFFECT OF ENGINEERED NANOMATERIALS ON WASTEWATER BIOTREATMENT

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Keywords: biodegradation, flow cytometry, graphene oxide, nanoparticles, TiO_2

Recent decades have seen the emergence of engineered nanomaterials (ENM), and the substantial advantages of these are now widely recognized. The use of ENM in commercial products and materials is following an increasing rate and it is difficult to find any industrial sector in which their implementation as additives has not been evaluated yet. ENM are added to cosmetics, textiles, pharmaceuticals, paints and foods, among others, providing many advantages such as large surface-to-volume ratio, high surface activity, and strong adsorption ability for immobilization of biomolecules [1].

Consequently, the occurrence of these materials in either urban or industrial wastewaters is becoming increasingly common. Even more, the unique characteristics of the nanomaterials, make them particularly attractive for water/wastewater physicochemical treatment applications such as disinfection, adsorption and membrane separation [2]. As wastewater treatment plants are usually the last barrier before the water is discharged into the environment, it is important to understand the effects of these ENM in the biotreatment process. Although the literature provides an increasing number of studies about the toxicities, environmental behaviors and ecotoxicities of these materials, not much research has been conducted on their effect on biological wastewater treatment in the long term [3].

Taking into account these considerations, the aim of the present work was to study the *Pseudomonas putida* response, in terms of activity and viability, to different concentrations of two ENM, which can be present at significant concentrations in WWTP due to their ample use: TiO_2 and graphene oxide. A pure culture of *P. putida* instead of a sludge was selected for this work principally for the following reasons: i) the use of a pure culture accelerates and amplifies the response of the system to perturbations and ii) *P. putida* is the predominant species in activated sludge and the results obtained can be employed as a reference during the comparison with those from other work using mixed cultures,

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EGG PROTEIN REVALORIZATION: FRACTIONATION, APPLICATIONS AND FUTURE PROSPECTS

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Keywords: *revalorization, egg, food, fractionation, applications.*

The egg industry is rather recent and it has made enormous progress since the 1960s. At industrial scale, egg is transformed in egg products of first (whole egg, yolk, albumen), second (ready-cooked meal) or even third transformation (e.g. bioactive egg compounds such as active peptides).Along with changes in egg-processing technology, there has been a continuing growth of further processed egg products [1].Currently, as an increase in the added value of egg products is pursued, it is important to explore new technological applications. One of the main approaches is the fractionation of egg components accompanied by a move forward towards new innovative applications [2].

On account of its multifunctional properties, hen egg yolk is a key ingredient in a wide variety of products. However, individual constituents of yolk are difficult to separate due to different practical and economic reasons, so, nowadays only plasma and granules can be easily fractionated at an industrial scale [3]. Different works [1,2] have reported interesting composition and properties of granules and plasma. Plasma is composed of LDLs and livetins, whereas granules are mainly constituted by HDLs, phosvitin and LDLs [1]. Granules show many interesting characteristics to be employed as ingredient in food industry, providing some advantages in relation with the use of egg yolk. In fact, some applications of granules at a pilot scale have lately been developed [1]. Plasma is also an abundant source of many bioactives, such as egg yolk immunoglobulin Y (IgY) and phospholipids [2].

In addition, the effect of different treatments (temperature, high pressures, hydrolysis…) on egg compounds is another way to obtain interesting products with novel properties and applications [4].

Moreover, new materials and procedures have been developed in recent years from by-products or from raw materials of little value. In this way, natural base materials have gained more attention for the development of different biomaterials with a wide variety of applications ranging from substrates for cell culture to biosorbents.

To sum up, nowadays egg industry is knowing a continuous growth, so the next years should provide even more breakthroughs in this field.

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REACTION LAG-PHASE IN THE CWPO OF 4-NITROPHENOL SOLUTIONS WITH P-DOPED CARBON BLACK CATALYSTS

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Keywords: *Carbon Black, Doped carbon, Catalytic wet peroxide oxidation, 4-Nitrophenol.*

Previous works have demonstrated that Chemviron Carbon Black (CB) is a catalyst capable to combine a good activity with an adequate stability for long term use and high efficiency of H_2O_2 consumption in the catalytic wet peroxide oxidation (CWPO) process [1]. Phosphorous doping was now used as a mean to increase the catalyst performance. To assess catalytic activity the CWPO of 4-nitrophenol (4-NP) was carried out under the referred conditions. 4-NP was monitored by HPLC, as described previously [2]. Experiments at 50 °C evidenced that the oxidation of 4-NP starts only after 2 h with 4-nitrocatechol (4-NC) identified as intermediate. Several hypotheses have been proposed including the need for a redox starter such as 4-nitrocatechol (4-NC). However, adding 4-NC to the initial solution did not affect the initial reaction lag-phase (Fig. 1-A). Thus, the presence of 4-NC is not the trigger to start 4-NP oxidation. On the other hand, a temperature increment or a decrease of the initial pH, led to elimination of the lag-phase, while complete conversion of 4-NP was achieved after 8 h (Fig. 1-B).

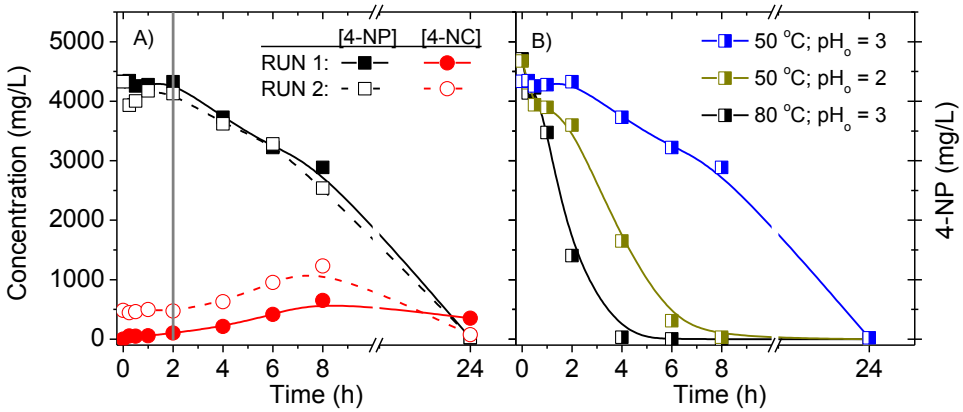

Figure 1. (A) 4-NP and 4-NC concentration evolution in CWPO runs with P-doped CB (2.5 g/L), the stoichiometric amount of H_2O_2, pH$_o$ = 3, T = 50 ºC and without (RUN 1) or with (RUN 2) 4-NC at the beginning of reaction; (B) 4-NP concentration evolution at the conditions in (A), except temperature and pH$_o$.

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USO DE LODOS ROJOS COMO ADSORBENTES

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Palabras Clave: *lodos rojos, adsorción, beads quitosano, colorantes.*

El destino de los residuos constituye actualmente uno de los problemas más visibles y complejos de la sociedad. Entre los medios naturales, el agua es uno de los que necesitan una mayor y estrecha vigilancia en cuanto a su contenido en sustancias tóxicas, por lo que la eliminación de éstas es objeto de un interés científico creciente. La utilización de los óxidos de hierro en la depuración de aguas es un proceso bien conocido, ya que estos elementos poseen altas capacidades de adsorción de contaminantes como pueden ser los colorantes. En las últimas décadas han recibido especial atención los materiales residuales de la industria metalúrgica, entre los que destacan los lodos rojos de bauxita generados en la producción de aluminio, los cuales tienen un alto contenido en óxidos de hierro y, debido a ello, excelentes propiedades adsorbentes [1].

En el presente estudio se utilizan los lodos rojos para la adsorción de dos colorantes, azul de bromotimol y el azul ácido 25, comúnmente empleados en la fabricación de tintes. Se evalúa la adsorción en función del pH del medio y se ajusta el proceso según los modelos teóricos propuestos por Langmuir y Freundlich [2]. Debido a la dificultad en la utilización del lodo rojo como adsorbente ya que es un polvo muy fino, se desarrolla un material híbrido (beads de quitosano con lodo rojo), con lo que se consigue inmovilizar al lodo rojo facilitando su manejo. Se estudia el proceso de adsorción en este material ajustándolo a los modelos teóricos y se estudia la cinética de adsorción.

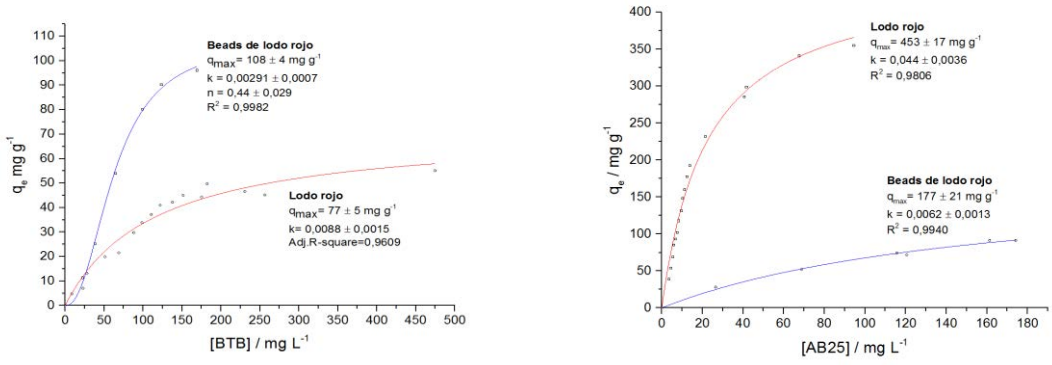

Figura 1. Isotermas de adsorción de azul de bromotimol (BTB) y azul ácido 25 (AB25) con lodo rojo y con beads de lodo rojo.

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ANALOGÍAS ENTRE LA TRANSFORMACIÓN EN OLEFINAS DE CLOROMETANO Y METANOL SOBRE CATALIZADOR DE ZEOLITA HZSM-5

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Palabras Clave: *Clorometane, Metanol, Olefinas ligeras, zeolita HZSM-5*

La creciente demanda de olefinas ligeras (C_2-C_4) como materias primas y el aumento de la disponibilidad de gas natural, sirven de estímulo para que la industria del petróleo considere la producción por valorización directa del gas natural, evitando los costes asociados a la valorización vía gas de síntesis. Una ruta interesante de valorización del gas natural a gran escala es su transformación catalítica en hidrocarburos, vía clorometano (MeCl).

El objetivo de este trabajo ha sido comparar la transformación de MeCl y de MeOH atendiendo al conocimiento actualizado de las etapas comunes y sus mecanismos. Se han comparado los resultados de transformación de MeCl y MeOH sobre un catalizador de zeolita HZSM-5 con relación SiO_2/Al_2O_3=30 (CZ-30), utilizando un reactor de lecho fijo en las siguientes condiciones de operación: 400-450 ºC; 1.5 atm; tiempo espacial 2.4 g_{cat} h $(mol_{CH2})^{-1}$. En la Figura 1 se comparan conversiones y selectividades.

En base a las analogías entre ambos procesos se ha establecido un esquema de reacción básico para la transformación de MeCl, identificando la formación de iones metoxi como el primer intermedio de reacción y la formación del "pool de hidrocarburos" como la etapa clave para la obtención de las olefinas [1]. A partir de ellas, por mecanismos de iones carbenio, tienen lugar las reacciones derivadas, de craqueo, aromatización y transferencia de H_2, para formar los subproductos. En base a las características particulares de las etapas donde se reflejan los resultados de la Figura 1, la menor reactividad del MeCl respecto al MeOH, se explica por la dificultad de formación de los iones metoxi.

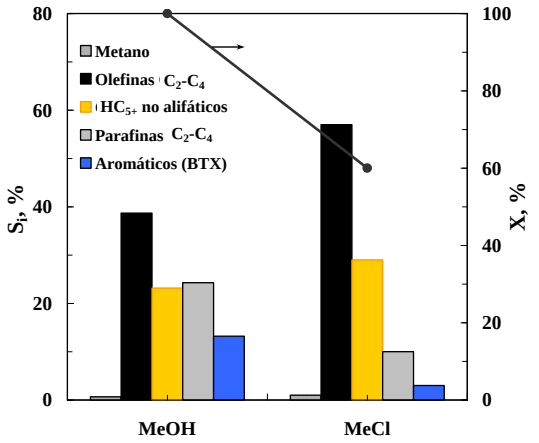

Figura 1. Comparación de la conversión y selectividad de productos a tiempo cero en las transformaciones de MeOH y MeCl sobre catalizador CZ-30 a 450 ºC y tiempo espacial, 2.4 g_{cat} h $(mol_{CH2})^{-1}$.

Por otro lado, la mayor desactivación en la transformación de MeCl es consecuencia de la ausencia de H_2O en el medio. La mayor selectividad de olefinas ligeras así como la de hidrocarburos C_{5+} no aromáticos (recirculables al reactor para potenciar el rendimiento de olefinas), son resultados esperanzadores para la viabilidad del proceso.

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S15: *Ingeniería Química y Medioambiente*

NANOFIBER-SHAPED MIXED OXIDE CATALYSTS PREPARED BY ELECTROSPUN

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Vanadium is a key component for selective and environmental catalysts; supported vanadium oxide catalysts find many industrial applications for selective oxidation, ammoxidation and reduction reactions for bulk and environmental processes. Thus, Vanadium oxides are important in the development of alkane transformation processes as well as for removal of pollutants (catalytic oxidation). Moreover, the properties of these materials can be modulated and improved by the incorporation of other metals (Sb, Mo, Nb, Te, etc.) into their crystal structure. In this respect, a substantial amount of information is now available on the crystallography, structural chemistry, thermal reactivity, and surface chemical properties of these materials prepared at the macroscale. However, and although the particle shape and dimensions are key factors determining the extent, accessibility and reactivity of materials' surface area, much less attention has been paid to the synthesis and properties of morphological- and size-controlled vanadium based mixed oxide nanomaterials. Although it has been previously documented that new or different properties could be reached by reducing their particle dimensions to 1–100 nm (nanoscale).

Electrospinning is a simple and versatile technique that has emerged in the last decade as powerful tool to prepare a wide range of nanostructured metal oxide materials, from zero-dimensional nanoparticles (electrospraying) to one-dimensional nanofiber or nanotubes. Then, the objective of this work has been the preparation and characterization of different vanadium oxide-based nanofibers and the study of their catalytic possibilities. The oxide fibers (of nominal composition: V_2O_5, V_3O_7, $SbVO_4$, $Mo_6V_3Nb_1Te_1$, $Mo_5V_4Nb_1Te_1$) were prepared by electrospinning of suitable metallic salt/PVP solutions in ethanol, followed by their calcination up to different temperatures. On the other hand, carbon fiber-supported VPO catalysts were prepared by electrospinning, stabilization and carbonization of P-containing fibers followed by vanadium salt precursor deposition and decomposition. For comparison purposes, powdery catalysts of similar composition were prepared and studied. After washing and drying, the fibers were characterized by TEM, XRD, Raman, XPS and N_2 gas adsorption at -196 ºC.

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EFECTO DE LA ADICIÓN DE ZEOLITA Y A UN CATALIZADOR DE PtPd/FCC EN EL HIDROTRATAMIENTO DE BIO-OIL

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Palabras Clave: *Bio-oil, Hidrotratamiento, Hidrodesoxigenación*

Introducción. El aceite de pirólisis de biomasa lignocelulósica es una de las potenciales fuentes renovables de energía capaces de sustituir a los combustibles fósiles, aunque, debido a su alto contenido en compuestos oxigenados, es necesario su tratamiento para conferirle una mayor estabilidad térmica a altas temperaturas [1]. En este trabajo, se propone el hidrotratamiento de bio-oil con el fin de obtener un combustible líquido asimilable por la industria petrolera existente en la actualidad.

Experimental. El hidrotratamiento se ha llevado a cabo en un reactor de lecho fijo de 15 cm^3. Las condiciones de operación han sido: 65 bar, WHSV, 2.6 h^{-1}; relación H_2/Alimentación, 2000 (v/v) y TOS, 10 h. La temperatura de reacción se ha variado desde 450 °C hasta 400 °C y vuelta a 450 °C. Los líquidos han sido recogidos y analizados en un sistema GC. Los gases han sido analizados en línea mediante un MicroGC. Los catalizadores usados han sido: PtPd (Pt 0.5%, Pd 0.5%) soportado en un catalizador FCC y mezcla de ese catalizador con zeolita Y (SiO_2/Al_2O_3 = 5.2).

Resultados. La Figura 1 muestra los rendimientos obtenidos, en base seca, para las diferentes fracciones. El efecto de la temperatura es similar en ambos casos, siendo máximo el rendimiento a nafta a 400 °C.

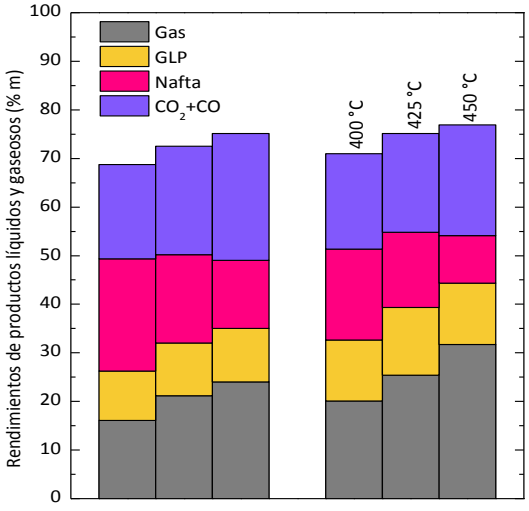

Figura 1. Rendimientos, en base seca, a fracciones gaseosas y líquidas.

Estudiando el efecto de añadir zeolita Y al catalizador, se observa que aumenta la formación de gases ligeros y GLP en detrimento de la fracción nafta.

Evaluando la composición de las fracciones, destacar que la composición de los gases y GLP prácticamente no se ve afectada. En cambio, con la mezcla física se obtiene una nafta menos aromática y más parafínica.

El grado de hidrodesoxigenación [2] ha sido muy elevado en ambos casos con valores medios cercanos al 96%.

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GeSAC-CONSERVA: GESTIÓN SOSTENIBLE DE LA ANCHOA DEL CANTABRICO: ESTRATEGIAS LOCALES PARA UN DESARROLLO GLOBAL

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Palabras Clave: *anchoas, industria conservera, análisis de ciclo de vida, mejores técnicas disponibles, gestión sostenible.*

INTRODUCCIÓN

El proceso de elaboración de la conserva de Anchoa del Cantábrico incluye las etapas de presalado, descabezado, fileteado y lavado, entre otras, en las cuales gran parte de este recurso es desaprovechado generando una cantidad considerable de flujos residuales líquidos (aguas y aceites) y sólidos (residuos de pescado).

La gestión de estos efluentes industriales constituye un problema ambiental que requiere una gestión sostenible que considere los aspectos locales para su desarrollo global. Para alcanzar este objetivo, diferentes directivas como la Directiva de Prevención y Control Integrados de la Contaminación (IPPC) [1], que propone el uso de las Mejores Técnicas Disponibles (BAT), y la Política de Productos Integrada (IPP) [2] ayudan a promover modelos más sostenibles de producción y consumo, bajo un enfoque de Análisis de Ciclo de Vida (ACV).

EL PROYECTO GeSAC-CONSERVA

Dentro de este marco, el proyecto GeSAC-Conserva, Gestión Sostenible de la Anchoa del Cantábrico: estrategias locales para un desarrollo global, tiene como objetivo principal el diseño e implementación de estrategias para una gestión sostenible del sector de la Anchoa del Cantábrico bajo una visión de ciclo de vida. La metodología del proyecto se basa en, por un lado, aplicar metodologías ya testadas (ACV, BAT, Ecodiseño, Huellas Ambientales) y por otro lado, en las opiniones y experiencias de los representantes del sector. Se pretende contribuir al desarrollo sostenible del sector conservero en Cantabria y promover la competitividad de la Anchoa del Cantábrico aplicando las BAT tanto en la pesca como en su transformación. Los resultados obtenidos serán de gran utilidad tanto para los fabricantes como para los consumidores puesto que se analizan los impactos ambientales, sociales y económicos asociados al ciclo de vida de la anchoa, desde su captura hasta que llega al consumidor final y su envase se convierte en un residuo Otro resultado con valor añadido es el desarrollo e implementación de Reglas de Categoría de Producto para la elaboración de Huellas Ambientales del Producto “conserva de anchoa”, que podrán ser extrapoladas a otros productos pesqueros de conserva.

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EVALUACIÓN AMBIENTAL DE LA OBTENCIÓN DE CLORURO SÓDICO EN LA INDUSTRIA CLORO-ÁLCALI

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Palabras Clave: *análisis de ciclo de vida, proceso cloro álcali, cloruro sódico*

La industria de cloro-álcali es aquella que produce mediante la electrolisis de una salmuera, cloro y álcali, hidróxido de sodio (Na(OH)) y en menor medida, cloruro de potasio (KCl). En la actualidad hay tres técnicas diferentes de electrolisis que son aplicadas en este sector: pilas de mercurio, pilas de diafragma y tecnologías de membranas [1], las cuales utilizan principalmente cloruro de sodio (NaCl) como material de alimentación [2].

La sal utilizada en este proceso puede provenir de varias fuentes, destacando la sal de roca de minas subterráneas, la salmuera procedente de pozos subterráneos, la sal solar de pozos de evaporación de agua de mar y la sal de vacío. Sin embargo, en algunas plantas está sal se está obteniendo mediante la purificación de residuos del procesado de minerales de potasa, los cuales actualmente se están descargando en escombreras, vertiendo en ríos y el mar o utilizado como relleno en minas de potasa abandonadas.

Es necesario por tanto evaluar desde un punto de vista ambiental las diferentes fuentes de obtención de la sal, ya que la reutilización de estos residuos puede suponer una ventaja económica y ambiental.

Para ello, en este trabajo se propone el uso de la metodología de análisis de ciclo de vida (ACV) para determinar las ventajas, desventajas e impactos ambientales de la extracción y/o producción de sal. Mediante el uso de esta herramienta se evaluará el comportamiento ambiental de los procesos desde la cuna a la tumba, es decir, desde la extracción de materias primas hasta el fin de vida del producto [3].

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DESCONTAMINACIÓN DE AGUAS MEDIANTE NANOPARTÍCULAS DE HIERRO OBTENIDAS POR SÍNTESIS VERDE

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Palabras Clave: *nanopartículas, hierro, síntesis verde, arsénico*

El estudio de la nanotecnología ha llevado al descubrimiento de numerosas aplicaciones de las NPs en campos tan diversos como la electrónica, la cosmética o el medio ambiente. El principal objetivo de este trabajo es la obtención de nanopartículas (NPs) de hierro mediante síntesis verde para su utilización en la eliminación de arsénico en disoluciones acuosas.

Normalmente la síntesis de NPs se lleva a cabo mediante la reducción de sales metálicas y el uso de agentes estabilizantes para evitar que dichas partículas se agreguen. Actualmente, se han desarrollado métodos de síntesis alternativos para reducir el uso de sustancias químicas. Estas nuevas técnicas consisten en utilizar extractos vegetales que contienen compuestos como polifenoles y terpenos para conseguir la reducción y estabilización de las NPs. En este trabajo se lleva a cabo la optimización de esta síntesis verde para la obtención de NPs de hierro y su posterior aplicación en la eliminación de metales pesados en aguas [1,2].

Se han utilizado distintos biomateriales para la obtención de los extractos optimizando parámetros como la temperatura, el tiempo de contacto o el tipo de agente extractante. La elección del extracto con mayor capacidad reductora se realiza mediante el análisis de los polifenoles totales, del potencial redox y de la capacidad antioxidante de los mismos.

Tras la caracterización del extracto se lleva a cabo la síntesis de las nanopartículas mediante la mezcla del mismo con una sal de hierro (III). Al poner en contacto la sal de hierro con el extracto vegetal la disolución adquiere un color negro de manera instantánea. Este cambio de color es una muestra de la formación de las NPs. Se han realizado medidas de microscopía de transmisión electrónica (TEM) sobre las mezclas para conocer el tamaño y la forma de las nanopartículas sintetizadas.

Las mezclas de nanopartículas obtenidas se han utilizado para la eliminación de arsénico de disoluciones acuosas. El pequeño tamaño de las NPs de hierro dificulta mucho su separación de la disolución, para solventar este inconveniente se ha llevado a cabo la inmovilización de las nanopartículas en una matriz de quitosano. Se han obtenido buenos datos de eliminación de arsénico con los materiales sintetizados.

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SÍNTESIS DE CATALIZADORES DE HIERRO OBTENIDOS DE SEMILLAS DE UVA PARA SU EMPLEO EN REACCIONES CWPO DE BISFENOL A

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Palabras Clave: *bisfenol A, CWPO, semillas de uva, catalizadores de Fe*

El trabajo estudia la oxidación húmeda catalítica con peróxido de hidrógeno (CWPO) de bisfenol A (BPA), monómero de resinas epoxi y policarbonato, utilizando catalizadores de Fe soportados en semillas de uva pirolizadas y activadas. Recientemente se ha estudiado la valorización de estos residuos para la producción de adsorbentes o soportes catalíticos y su empleo en tratamiento de aguas contaminadas con herbicidas clorados [1].

La CWPO de BPA (100 mg/L) se realizó en un reactor mezcla perfecta (50-80 ºC, 1 atm, 600 rpm, [catalizador]: 500 mg/L, $[H_2O_2]_0$: 265-530 mg/L, pH_0: 3) empleando catalizadores de Fe (4 % wt.) soportado sobre semillas de uva (SU), previamente sometidas a pirólisis (Q_{N2}: 1 L/min, 600 ºC, 2 h) y activación con aire (Q_{aire}: 2 L/min, 400 ºC, 2 h) (Fe-SU-1) o activación con aire y lavado con ácido nítrico (Fe-SU-2). La estabilidad de los catalizadores se evaluó mediante ensayos de larga duración (100 h; 4,7 $kg_{cat}\cdot h\cdot mol^{-1}$). La cuantificación del BPA y de los intermedios de reacción se realizó por HPLC-UV-VIS y cromatografía iónica y el grado de mineralización a través de la medida del COT. Se emplearon métodos colorimétricos para la determinación de la concentración de H_2O_2 y de Fe lixiviado. La caracterización de los catalizadores se realizó mediante adsorción de CO_2 a 273 K, TXRF, XPS y SEM.

En todos los ensayos realizados se consiguió conversión completa de BPA, mientras que el grado de mineralización aumentó significativamente con la temperatura y la concentración de H_2O_2, alcanzándose las mayores conversiones de COT (60 %) con el catalizador Fe-SU-1 (80 ºC; $[H_2O_2]_0$: 530 mg/L). Como intermedios de reacción se detectaron 4-hidroxiacetofenona, p-benzoquinona y ácidos orgánicos de cadena corta. La mayor actividad del catalizador Fe-SU-1 frente al catalizador Fe-SU-2 se asoció a la mejor distribución de la fase activa sobre el soporte carbonoso.

En el ensayo de estabilidad con el catalizador Fe-SU-1 se observó que tras un primer periodo de 15 h de inestabilidad, debido a la lixiviación de Fe (~20%), la actividad, evaluada en términos de conversión de bisfenol A y COT, se mantuvo constante durante más de 80 h.

Los resultados obtenidos muestran que la síntesis de catalizadores soportados sobre semillas de uva resultó efectiva para su empleo en reacciones CWPO.

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CARBON DIOXIDE ELECTROCHEMICAL REDUCTION INTO HYDROCARBONS

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Keywords: *electrochemistry, CO_2, reactor, hydrocarbons.*

One of the most important challenges considered in the 21st century is the global warming reduction. Carbon dioxide (CO_2) is the main compound in the global warming generation. In order to reduce the amount of CO_2 in the atmosphere, the development of different technologies capable of capturing and transforming CO_2 into valuable products is emerging. In this sense, the electrochemical reduction of CO_2 represents a good alternative due to their environmental and economic benefits associated [1].

Hydrocarbons could be an interest product for the electrochemical reduction of carbon dioxide due to their different uses such as the possibility of heat and electricity production and their utilization as a substitute for gasoline because of their high fuel capacity [2]. Furthermore, aliphatic hydrocarbons are also the starting compounds of the value chain in chemical industry and can be used for the storage of intermittent renewable energy [3].

The aim of this study is the analysis of the different possible alternatives of electrochemical reactors in order to reduce CO_2 into hydrocarbons. The results reported for the different catalysts and reactors are compared in terms of the specific hydrocarbons obtained, the current density applied and the Faradaic efficiency observed. For the electrochemical reduction of CO_2 to hydrocarbons, most of the cathodes reported in the literature are formed by copper-based catalysts, with which methane and ethylene are the main hydrocarbons obtained with Faradaic efficiencies that can reach 60 % and 20 %, respectively [4].

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EVALUACIÓN DE RIESGOS DE CONTAMINACIÓN EN ALIMENTOS POR ENVASES DE CARTÓN RECICLADO. MIGRACIÓN DE FOTOINICIADORES DE CARTÓN RECICLADO A LOS ALIMENTOS

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Palabras Clave: *fotoiniciadores, benzofenona, migración, cartón reciclado*

Los fotoiniciadores, empleados en las tintas de impresión y barnices de curado ultravioleta, pueden estar presentes en los envases alimentarios de cartón reciclado, por lo que pueden migrar a los alimentos desde la cara interna del cartón. El fotoiniciador más común es la benzofenona (BP), que de hecho es considerado en un significativo número de artículos como un subrogado, es decir un modelo de fotoiniciador contaminante.

La migración, transferencia de sustancias desde el envase a los alimentos, depende, fundamentalmente de las propiedades físicoquímicas del migrante, de las características de los alimentos o simulantes alimentarios, de la temperatura y del tipo de envase. En este trabajo se ha estudiado la migración de benzofenona desde cartón utilizado en embalaje alimentario dopado en función del tiempo de contacto y de la temperatura (desde 70 hasta 190ºC) utilizando tilosa, un simulante alimentario de alimentos secos. Se ha estudiado también el porcentaje de migración en presencia de barreras plásticas de diferente naturaleza.

El análisis de benzofenona en el cartón y en el simulante alimentario se ha llevado a cabo mediante HPLC con detección fotométrica, y también se ha desarrollado un método electroquímico (de stripping adsortivo de onda cuadrada) de análisis de BP utilizando el electrodo de mercurio.

Asimismo, se ha analizado el contenido en BP en tres tipos de cartón, llevando a cabo una evaluación de riesgo mediante la determinación del límite específico de migración (SML), que es la cantidad máxima permitida de una sustancia que puede ser transferida a un alimento o a un simulante alimentario. Los valores de SML determinados son inferiores al máximo permitido de 0.6 mg/Kg según el Reglamento (UE) No 10/2011 (Directiva de Plásticos).

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WATER SORPTION ISOTHERMS MODELLING OF *FUCUS vesiculosus* SEAWEED

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Keywords: adsorption, desorption, equilibrium, Halsey model, temperature

Fucus vesiculosus is a dominant species of macro alga in the northern Atlantic Ocean and, ecologically, it is the most important seaweed, providing shelter and food for associated flora and fauna. The seaweed composition shows high polyphenol and carbohydrates (mainly mannitol, fucoidan and alginates) content [1]. Water removal is necessary to preserve the seaweed during long periods and water sorption characteristics must be determined in order to design drying equipment and to define storage conditions.

Equilibrium moisture content, EMC, of *Fucus vesiculosus* at several temperatures (5, 25, 45 and 65ºC) were determined using static gravimetric method. Samples (< 0.8 g) were introduced into sealed jars, provided with different saturated salt (LiCl, $MgCl_2$, $Mg(NO_3)_2$, NH_4NO_3, NaCl, KCl and $BaCl_2$) solutions to generate different water activities, a_w, until samples reached equilibrium. Fresh seaweed samples were used for desorption experiments and for adsorption, seaweed samples were previously dried at 40ºC until constant weight (app 3 days). EMC was reached within 6 months. All experiments were carried out in duplicate.

Water sorption isotherms corresponded to type III at low temperatures (< 25 ºC) while at high temperatures (> 45 ºC) belonged to type II. EMC increased as temperature decreased from 65 to 5ºC at low a_w (< 0.5), but this behaviour was reversed at high a_w. As result, crosspoints at intermediate a_w for water adsorption and desorption were observed. At low a_w (< 0.5), hysteresis cycles among water adsorption and desorption isotherms were observed. At low temperatures (< 25ºC), desorption isotherms showed higher water content than adsorption isotherms at the same a_w. This behaviour disappeared at 45ºC and was reversed at 65ºC.

Several models were tested for water sorption modelling. After statistical analysis of the mathematical fittings, Halsey model was selected as the most adequate for modelling the tested seaweed. Both two-parameters model were linearly correlated with temperature, T (K), for adsorption and desorption experiments, in order to reproduce successfully (R^2 > 0.99 and E_{RMS} < 0.075) the experimental data. The resulting equations were:

Water adsorption:

$$EMC = \left(\frac{-(-284.01 + 1.108 \cdot T)}{T\ln(a_W)}\right)^{(-4.04+0.018 \cdot T)}$$

Water desorption:

$$EMC = \left(\frac{-(-295.17 + 1.13 \cdot T)}{T\ln(a_W)}\right)^{(-5.82+0.023 \cdot T)}$$

Authors acknowledge the financial support to MINECO of Spain and FEDER by the project (CTQ 2013-43616/P).

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S15: *Ingeniería Química y Medioambiente*

SÍNTESIS VERDE DE NANOPARTÍCULAS METÁLICAS PARA LA ELIMINACIÓN DE CONTAMINANTES

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Palabras Clave: *nanopartículas, plata, hierro, fenton, azul de bromotimol.*

La presencia de sustancias químicas tales como colorantes, en los medios acuosos constituye un grave problema medioambiental dada su elevada toxicidad y baja biodegradabilidad.

En las últimas décadas la síntesis de nanopartículas ha experimentado un gran avance debido al gran número de aplicaciones de las mismas en campos como la cosmética, la industria y en especial el medioambiente.

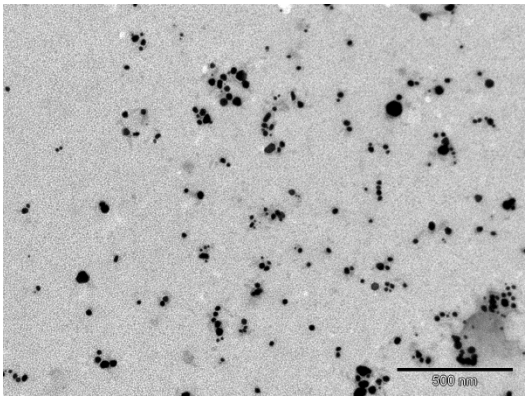

Figura 1. Imagen TEM de nanopartículas de plata.

En el presente estudio se lleva a cabo la síntesis de nanopartículas empleando sustancias químicas de origen natural como los extractos de algunas plantas en vez de reductores peligrosos como borohidruro sódico ($NaBH_4$). El principal objetivo en la obtención de nanopartículas de Fe (FeNPs) y de plata (AgNPs) mediante la reducción de sales metálicas con extracto de eucalipto. La caracterización de las partículas se realiza con las técnicas de Microscopía electrónica de transmisión (TEM), Espectroscopía Ultravioleta-Visible, turbidimetría y estimación del tamaño de partícula.

Se evalúa el efecto de las FeNPs y AgNPs en el proceso de degradación de colorantes en medios acuosos, también se ensayan procesos de oxidación tipo Fenton mediante la adición de peróxido de hidrógeno a la mezcla de nanopartículas. Además se llevan a cabo diversos estudios cinéticos para optimizar los parámetros de interés en la degradación del colorante como concentración de peróxido de hidrógeno o cantidad de nanopartículas.

De este modo, se observa que el uso de tecnologías avanzadas de oxidación como las reacciones tipo Fenton puede poseer un elevado número de aplicaciones y así fomentar el empleo de química verde.

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DETERMINACIÓN DEL TIPO DE ATRICIÓN DE ARENAS FINAS A BASE DE COLORANTE ALIMENTARIO

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Palabras Clave: *Atrición, arena fina, spouted bed, colorante.*

Para un buen diseño de cualquier proceso es indispensable conocer la evolución del material a tratar trabajando con largos tiempos de residencia. Uno de los fenómenos más comunes en tiempos de residencia grandes y que pueden condicionar el tiempo de residencia óptimo de un material es la disminución del tamaño de partícula por atrición. Siendo generalmente un fenómeno no deseado, conocer su origen puede ser la base para lograr prevenirlo. En este trabajo se ha podido obtener conclusiones acerca del tipo de atrición de arenas finas en un contactor tipo spouted bed mediante la coloración de la arena con colorante alimentario. Este trabajo está enmarcado en el proyecto conjunto del grupo de investigación Procesos Catalíticos y Valorización de Residuos (Universidad del Pais Vasco, UPV/EHU) y la empresa de desarrollo tecnológico Novattia Desarrollos S.L. con el objetivo de diseñar un nuevo secadero de arenas finas y ultrafinas basado en tecnología spouted bed.

El material utilizado en el estudio fueron aproximadamente 5 kg de arena fina con una distribución de tamaño de partícula entre 0 y 800 µm que se han dividido por tamaño en 5 grupos. Cada grupo se ha coloreado con un color diferente usando un colorante alimentario puro o mezcla de varios (Figura 1). La arena se mantuvo durante 8 horas fluidizando en un contactor tipo spouted bed. El resultado más importante del ensayo es que gracias a la coloración de las partículas, al volver a separar la arena en grupos se ha observado que en cada uno aparecen partículas del color pertenecientes a todos los grupos de tamaños más grandes, lo que indica que el fenómeno más importante acaecido fue la rotura, y no el redondeo, de partículas por fricción.

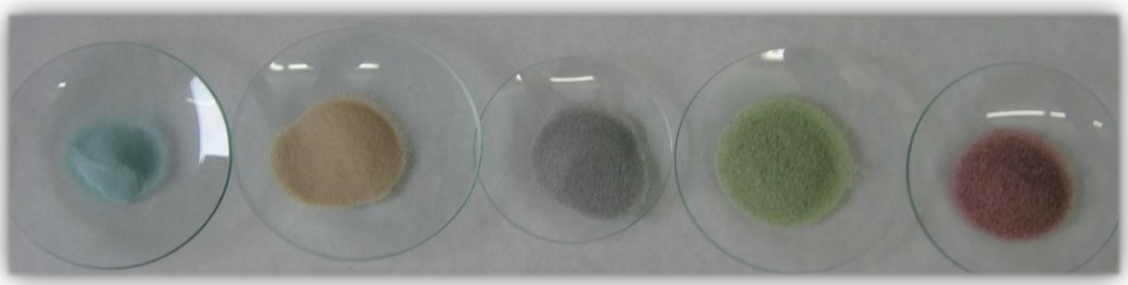

Fig. 1: Arena coloreada utilizada en el estudio. Azul, 0-100 µm; naranja-marrón, 100-200 µm; gris, 200-300 µm; verde, 300-500 µm y rojo, 500-800 µm.

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EFECTO DE LA RELACIÓN SiO_2/Al_2O_3 DEL CATALIZADOR DE ZEOLITA HZSM–5 EN LA TRANSFORMACIÓN DE DME EN OLEFINAS

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Palabras Clave: *DME, olefinas, zeolita*

La transformación de dimetil éter (DME) en olefinas ligeras recibe una creciente atención [1,2], en paralelo al interés por la síntesis de DME en una etapa, a partir de carbón, biomasa o gas natural (shale gas) vía gas de síntesis [3]. La síntesis de DME presenta importantes ventajas respecto a la de metanol, por las menores limitaciones termodinámicas y en consecuencia la disponibilidad futura de DME es mayor que la de metanol.

En este trabajo se ha explorado la posibilidad de aumentar el rendimiento de olefinas, modulando la acidez mediante la selección de la adecuada relación SiO_2/Al_2O_3 de la zeolita HZSM-5.

Los catalizadores se han preparado con zeolitas HZSM-5 (*Zeolyst Int.*) de relación SiO_2/Al_2O_3 30, 80 y 280; las cuales se han aglomerado con bentonita (30% en masa) y α-Al_2O_3 (45 %), para aportar a la partícula de catalizador una matriz con meso- y macroporos. Las propiedades físicas de los catalizadores (superficie BET, volumen de microporos y mesoporos) se han determinado mediante isotermas de adsorción-desorción de N_2; y la acidez mediante la adsorción–desorción (craqueo) de amoniaco, por combinación de técnicas termogavimétricas y calorimetría diferencial de barrido. Los experimentos se han llevado a cabo en un reactor de lecho fijo isotermo a diferentes temperaturas (350 y 400 ºC), con un tiempo espacial de 1.25 $g_{zeol}hmol_C^{-1}$, una duración de 4 h y a presión atmosférica. Los productos de reacción se han analizado de forma continua en un cromatógrafo de gases (*Micro-GC Agilent 490)*.

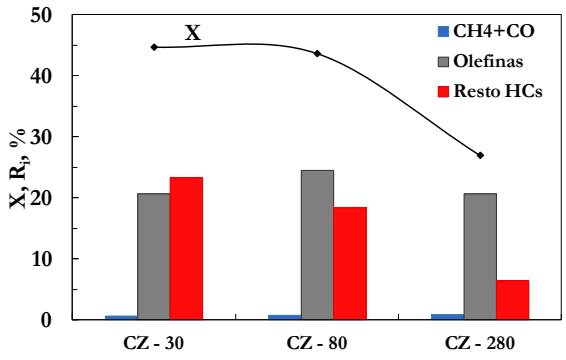

Figura 1. Efecto de la relación SiO_2/Al_2O_3 en la transformación catalítica de DME. Condiciones de reacción: 350 ºC, tiempo espacial 1.25 $g_{zeol}hmol_C^{-1}$.

En la Figura 1 se observa que al aumentar la relación SiO_2/Al_2O_3, como consecuencia de la disminución de la acidez del catalizador, es menor el avance en el esquema de reacción, disminuyendo los rendimientos de las olefinas (productos primarios) y del resto de hidrocarburos (productos secundarios), y siendo más notable este efecto al aumentar la relación de 80 hasta 280. Para esta relación la fracción mayoritaria es la de olefinas ligeras y el rendimiento del resto de hidrocarburos es inferior al 10 %. Además, el aumento en la relación SiO_2/Al_2O_3 conlleva una atenuación en la desactivación del catalizador, al disminuir la deposición de coque.

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ESTUDIO DEL ENVEJECIMIENTO DE VERTIDOS DE HIDROCARBUROS EMPLEANDO ÍNDICES DE INFRARROJO Y MAPAS AUTO-ORGANIZATIVOS DE 3-VÍAS

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Palabras Clave: *Vertidos, índices, infrarrojo, Redes neuronales de Kohonen de 3 vías.*

La entrada mundial anual de petróleo para el medio marino se estima entre 1 y 3,2 MTm. Las fuentes mayoritarias son los efluentes urbanos e industriales (aproximadamente 30%), operaciones de buques tanque (22%) y los accidentes de petroleros (13%). Aunque el número de derrames disminuyó en los últimos años, accidentes como el hundimiento del petrolero Prestige frente a las costas de Galicia y el accidente de la plataforma Deepwater Horizon en el Golfo de México, siguen ocurriendo. Estos constituyen una importante amenaza para los ecosistemas marinos y costeros, causando fuertes daños en el medio ambiente y la economía.

Una vez vertidos, los hidrocarburos sufren gran variedad de procesos, incluyendo evaporación, disolución, dispersión, emulsión, oxidación fotoquímica, biodegradación microbiana, adsorción de materia suspendida y deposición en el fondo marino. Todos ellos complican la identificación de vertidos. De ahí la necesidad de disponer de metodologías analíticas rápidas y eficaces.

Para realizar este estudio, se llevó a cabo el vertido en condiciones controladas de 6 tipos de hidrocarburos, los cuales se dejaron envejecer durante 4 meses. Las muestras fueron medidas mediante espectrometría ATR en la región infrarrojo media. Se han calculado 10 índices entre bandas espectrales para tratar de diferenciar los vertidos. Se propone el uso de una técnica quimiométrica novedosa de 3-vías denominada MOLMAP ('Matrix reOrganization Layout to Map Analytical Parameters'). Emplea las redes neuronales de Kohonen (o mapas autoorganizativos) para extraer los 'MOLMAP-scores' y a continuación emplea los 'MOLMAP-scores' como entradas para aplicar o bien técnicas de reconocimiento de pautas o bien técnicas de clasificación. En este caso se empleó PCA (análisis de componentes principales). Los cubos de datos se organizaron en forma de productos × envejecimiento × variables y envejecimiento × productos × variables.

Agradecimientos

M.P.G.C. agradece la ayuda posdoctoral del plan I2C (modalidad B), Xunta de Galicia, con participación FEDER.

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ENHANCED PHOTOCATALYTIC DEGRADATION OF ORGANIC COMPOUNDS USING GRAPHENE OXIDE/tITANIUM DIOXIDE (gO/TIO_2) COMPOSITES

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Keywords: *Photocatalysis, graphene oxide, titanium dioxide, organic compounds degradation*

Photocatalysis is an emerging technology for the removal of organic and inorganic pollutants from water but it has not been deeply developed yet. TiO_2 is the most popular catalyst; however, its photocatalytic activity is limited [1]. Graphene oxide is a new material that can overcome some of the limitations of TiO_2 [2].

Graphene oxide/titanium dioxide composites (GO/TiO_2) were synthesized by three methods: hydrothermal (H), solvothermal (S) and mechanical (M) method with a weight ratio GO/TiO_2 of 5%. Nanocomposites were characterized by several techniques including thermogravimetric analysis (TGA) and Fourier-transformed infrared spectroscopy (FT-IR). Dichloroacetic acid (DCA) was used as a model organic compound to assess the photocatalytic activity through its degradation and mineralization.

TGA results showed that the composite is thermally more stable than graphene oxide and a significant loss of oxygen groups was observed through FT-IR spectroscopy, which confirmed the reduction of graphene oxide during the synthesis process. The experimental data of DCA degradation and mineralization were fitted to a pseudo-first order kinetic model. Figure 1 shows that compound removal as well as mineralization were better for all the composites than for TiO_2 alone. Moreover, the composite synthesized by hydrothermal method has greater kinetic constant for both degradation and mineralization, in these working conditions, asserting that the synthesis method may influence the characteristics of the composite and subsequently their photocatalytic behavior.

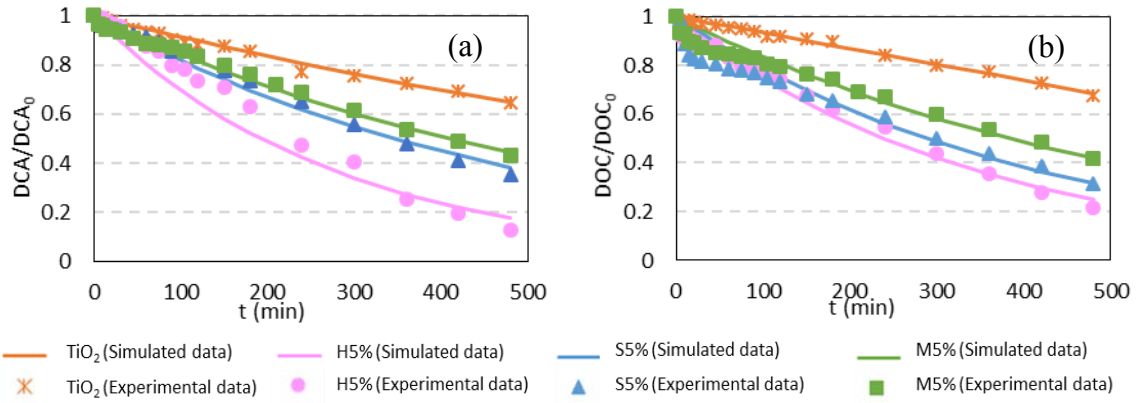

Figure 2. Experimental and simulated results of DCA degradation (a) and mineralization (b)

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CATALIZADORES DE Pd, Pt Y Cu SOPORTADOS EN ARCILLAS PILAREADAS PARA LA REDUCCIÓN CATALÍTICA DE NITRATO

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Palabras Clave: *Reducción catalítica, nitrato, Pd, Pt, Cu, arcillas pilareadas*

En los últimos años la contaminación de aguas subterráneas por nitrato se ha convertido en un problema creciente debido a la intensificación de cultivos y crecimiento de las explotaciones ganaderas. Entre las diferentes tecnologías desarrolladas para su eliminación, la reducción catalítica de nitrato (RCN) es una de las que ha dado lugar a resultados más prometedores. Los catalizadores bimetálicos, especialmente aquéllos que combinan Pd con otros metales de transición, son los que mejores resultados han proporcionado [1,2]. En este trabajo se estudia el uso de catalizadores Pd/Cu, Pt/Cu y Pd-Pt/Cu soportados en arcillas pilareadas Al-PILC para la reducción de nitrato.

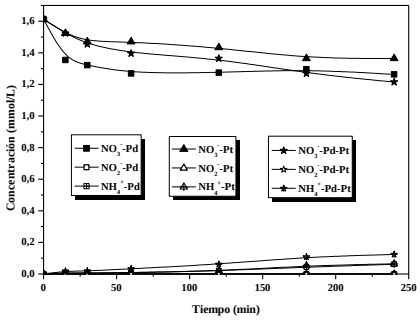

Fig. 1. RCN con catalizadores de Pd, Pt y Pd-Pt.

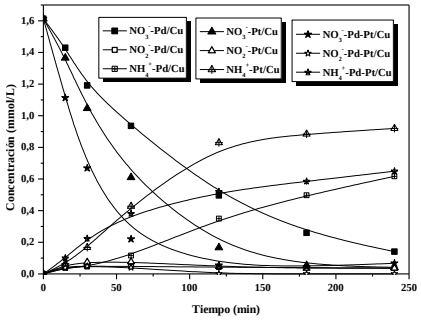

Fig. 2. RCN con catalizadores de Pd, Pt y Pd-Pt con Cu.

Las fases activas metálicas se introdujeron en la estructura de Al-PILC por impregnación húmeda con disoluciones acuosas de H_2PtCl_6, $CuCl_2$ y $PdCl_2$ (HCl 1 M). Los sólidos se secaron 14 h a 110 ºC y se calcinaron 2 h a 500 ºC. El contenido metálico de Pd y Pt fue 5 % en peso y para Cu fue del 2,5 % en peso. Los experimentos catalíticos se realizaron en un reactor tanque agitado en discontinuo (25 °C, 1 atm) y los catalizadores fueron previamente reducidos 2 h a 90ºC. Las concentraciones de nitrato y nitrito se determinaron por cromatografía iónica y la de amonio con una sonda selectiva de amonio.

Los catalizadores estudiados en todos los casos mostraron actividad frente a la reducción de nitratos. Los nitratos fueron transformados en nitrito, nitrógeno gas o amonio. En la Fig. 1 puede observarse cómo los catalizadores que únicamente contenían metales preciosos dieron lugar a bajas conversiones de NO_3^-, inferiores al 25%. Cuando se introdujo Cu en estos materiales se alcanzó la casi total eliminación de NO_3^- en todos los casos (Fig. 2), observándose una mayor actividad al emplear Pt/Cu que Pd/Cu respecto al NO_3^- y una mayor producción de NH_4^+ (producto no deseado) con Pt/Cu. La cantidad de NO_2^- obtenido en todos los casos fue inferior a 2 mg/L. El catalizador Pd-Pt/Cu dio lugar a los mejores resultados con una total eliminación de NO_3^- tras 2 h de reacción y una producción de amonio similar al catalizador Pd/Cu, alrededor de 0,6 mmol/L (selectividad a NH_4^+ del 37,5%).

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SÍNTESIS DE CATALIZADORES VPO MÁSICOS CON ELEVADA POROSIDAD. REACCIÓN ODH DE PROPANO

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Palabras Clave: *VPO Másico, Porosidad, ODH de propano, Propileno*

Los catalizadores de VPO son de elevado interés industrial por sus propiedades de activación de hidrocarburos y presentan un gran potencial para la obtención de etileno y propileno a partir de alcanos mediante la reacción ODH (deshidrogenación oxidativa de hidrocarburos). No obstante, estos óxidos mixtos presentan una baja superficie específica, lo que limita, en cierta medida, sus propiedades catalíticas para este tipo de reacciones. En este trabajo se plantea una nueva estrategia para sintetizar catalizadores másicos VPO con una relativamente elevada superficie específica mediante el uso de moldes de sacrificio de base carbonosa.

Se han preparado catalizadores másicos de VPO mediante el método de nanomoldeo [1] usando residuos lignocelulósicos. En este sentido, se prepararon distintos carbones activos que se usaron como molde de sacrificio y sobre los que se depositó la fase metálica de vanadio y fósforo. Las matrices carbonosas se prepararon mediante activación química de hueso de aceituna con H_3PO_4, y por infiltración-carbonización de lignina sobre zeolitas [1]. Para depositar la fase activa metálica sobre los materiales carbonosos se ha usado el metavanato amónico y el H_3PO_4, los cuales se disuelven en ácido oxálico y se introducen en un sistema rotavapor para infiltrar toda la estructura porosa de las matrices carbonosas. Finalmente, se calcinan las muestras impregnadas para eliminar la matriz y obtener, así, el catalizador másico VPO. Estudios anteriores mostraron que los catalizadores VPO son apropiados para la obtención de propileno a partir de propano [2], por ello se analiza la capacidad catalítica de los materiales obtenidos en la reacción ODH de propano, variando la temperatura de reacción entre 400 y 600 ºC y la relación C_3H_8/O_2 entre 0.5 y 4.

Los resultados muestran catalizadores másicos VPO con una alta superficie específica y una estructura mesoporosa. Mediante las técnicas de caracterización empleadas se corrobora la presencia de fases características del catalizador VPO. Los catalizadores obtenidos presentan conversiones de propano de hasta el 25% y selectividades a propileno de hasta 80%.

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CORRELACIÓN EXPERIMENTAL PARA LA ESTIMACIÓN DEL COEFICIENTE DE TRANSFERENCIA DE CALOR

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Palabras Clave: *spouted bed, transferencia de calor, serrín*

Los estudios encaminados a medir el coeficiente de transferencia de calor en lechos de arena y biomasa operando en régimen de spouted bed son escasos en la bibliografía y las propuestas de correlaciones empíricas son aún más difíciles de encontrar. La mayoría de los trabajos de modelización matemática de la transferencia de calor en el secado de partículas en spouted bed emplean las correlaciones propuestas por Kmiec[1,2]. El estudio de la transferencia de calor se ha realizado sobre lechos de serrín, arena y mezclas de ambos. Ambos materiales corresponden al grupo A de la clasificación de Geldart. El contactor está fabricado en polimetilmetacrilato, con un diámetro de columna, D_c, de 0.304 m, un ángulo de cono, γ, de 28° y un diámetro de entrada del gas, D_o, de 0.05 m. Se ha trabajado con tres alturas de lecho, H_o, 0.10, 0.20 y 0.30 m, introduciendo la sonda en las tres posiciones disponibles: 0.10, 0.20 y 0.35 m. Para la altura menor se tomaron dos medidas, una en la pared y otra introduciendo la sonda 2 cm. Para las otras dos alturas se tomaron tres medidas: junto a la pared e introduciendo la sonda 1 y 3 cm respectivamente. El ajuste se ha llevado a cabo en Scilab minimizando el error relativo promedio (ASRE). En la Figura 1 y Tabla 1 se observa que el ajuste es razonablemente bueno para todos los valores, por lo que se puede afirmar que la correlación propuesta es válida para toda la zona anular y que ésta se puede emplear para estimar el valor del coeficiente de transferencia de calor en lechos de arena y serrín en spouted bed, implementándola en herramientas de modelización complejas.

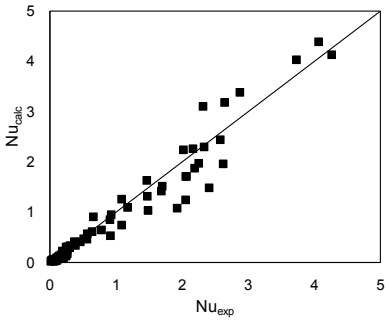

Figura1. Gráfico de paridad correspondiente al reajuste.

$$Nu = a\mathrm{Re}^{b} Pr^{c} Ar^{d} (\tan(\gamma/2))^{e} \left(\frac{H_o}{d_p}\right)^{f} \phi^{g} \left(\frac{r}{R}\right)^{i} \left(\frac{z}{H_o}\right)^{j}$$

a	$4.31\ 10^{-7}$	**f**	1.05
b	3.43	**g**	7.28
c	0.660	**h**	-0.481
d	0.200	**i**	-0.204
e	6.58	**j**	1.61
ASRE			**0.110**

Tabla 1. Ecuación y coeficientes de mejor ajuste.

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S15: *Ingeniería Química y Medioambiente*

SYNTHESIS AND CHARACTERIZATION OF HMDI-MODIFIED CELLULOSE ACETATE/CASTOR OIL FORMULATIONS FOR WOOD BONDING APPLICATIONS

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Keywords: *Adhesives, cellulose acetate, diisocyanate, vegetable oil, rheology, peel strength, tension loading*

The substitution of non-renewable raw materials in industrial processes has become the currently target of many researches, trying to find eco-friendly alternatives. Nowadays, different types of natural substances such as sugars, starch, cellulose and their derivatives are widely used as renewable raw materials. [1] In this regard, vegetable oils have been considered as promising products to be used in the synthesis of high quality products in different applications, in the adhesive field among them. [2] Some studies reveal interesting properties of polyurethane adhesives obtained by reacting castor oil (CO) and diols with different diisocyanates. [3, 4] According to this, several bio-based formulations were synthesized by inducing first the functionalization of cellulose acetate with 1,6-hexamethylen diisocyanate (HMDI) and then, the resulting biopolymers were mixed with a variable amount of castor oil, from 20 to 70% (wt). These bio-based adhesives were rheologically characterized by means of dynamic oscillatory torsional tests, at different temperatures, mechanical standaridized tests to evaluate tension loading (ASTM D906) and peel strength (ASTM D903). In addition, thermal properties and stability of the synthesized biopolyurethane formulations were also analyzed through thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). As a result, the performance of these bio-polyurethane products as wood adhesives were compared and analyzed.

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S15: *Ingeniería Química y Medioambiente*

DESARROLLO DE LA TECNOLOGIA DE SPOUTED BEDS PARA EL PROCESO DE DIGESTION ANAEROBIA DE LODOS DE DEPURADORA

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Palabras Clave: *digestion anaerobia, spouted beds cónicos, lodos de depuradora, lodos residuales, spouted beds*

La gran cantidad de lodos de depuradora producidos requiere alternativas de valorización agrícola y energética. Además, el alto contenido de humedad que de estos lodos sólidos (mayor del 50 % en base húmeda), aumenta los costes de transporte para valorización agrícola y dificulta la posible valorización energética posterior.

El método de contacto en Spouted Beds es especialmente útil para aplicaciones que requieren un movimiento vigoroso del sólido como en el tratamiento de sólidos adherentes, de textura irregular o con amplia distribución de tamaño de partícula. La tecnología de Spouted Bed se ha aplicado satisfactoriamente en el tratamiento de residuos por secado [1-4] y por tratamiento térmico [5-7].

Con objeto de llevar a cabo el proceso de digestión de lodos residuales de depuradora (WWTP) para la producción de biogas en un reactor cónico mediante la tecnología de spouted bed, en este trabajo se han determinado las condiciones de estabilidad, así como el rango de condiciones de operación que optimiza las condiciones del proceso.

Se ha probado que los contactores spouted beds cónicos presentan un buen comportamiento para la producción de biogas por tratamiento anaerobio de lechos de lodos industriales de depuradora de diferente diámetro de partícula. Por lo que podrían ser empleados en aplicaciones industriales como para lodos de depuradora.

Agradecimientos al Ministerio de Economía y Competitividad por la financiación del Proyecto CTQ2014-59312-P y a la Unión Europea por la cofinanciación con fondos FEDER.

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S15: *Ingeniería Química y Medioambiente*

VALORACIÓN DE LAS CONCENTRACIONES DE Al, Fe, Mn, Cu Y Zn DISUELTOS EN UN ARROYO DE CABECERA EN RELACIÓN CON LA CALIDAD DEL AGUA

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Palabras Clave: *metales disueltos, cuenca rural, arroyo de cabecera, calidad del agua.*

En medios acuáticos los metales en forma disuelta generalmente presentan mayor biodisponibilidad y toxicidad a elevadas concentraciones que aquellos que se encuentran adheridos a otras moléculas o partículas en suspensión.
El objetivo de este estudio se centra en analizar las concentraciones de metales disueltos (Al, Fe, Mn, Cu y Zn) en un arroyo de cabecera del Río Mero (A Coruña, NO España), fuente de recarga del Embalse de Cecebre, del cual se extrae el agua para abastecer a la población de A Coruña y áreas metropolitanas. El arroyo discurre por un área rural en la que los usos del suelo predominantes son el forestal y el agrícola.
En el transcurso de cuatro años hidrológicos se tomaron muestras de agua bajo diferentes condiciones de flujo (flujo base y episodios de escorrentía). Los metales se cuentificaron mediante ICP-MS. Se encontraron las siguientes concentraciones medias de metales disueltos: [Al]: 18,3 µg L^{-1}, [Fe]: 53,9 µg L^{-1}, [Mn]: 1,1 µg L^{-1}, [Cu]: 0,5 µg L^{-1} y [Zn]: 1,8 µg L^{-1}.
Las concentraciones de Al, Fe, Mn, Cu y Zn excedieron en un 13%, 53%, 0,6%, 1% y 64% de las muestras los valores propuestos por Meybeck et al. (1992)[1] para aguas prístinas a nivel mundial. Sin embargo, las concentraciones de estos metales cumplieron los parámetros de calidad para el consumo humano establecidos por la Directiva de la Unión Europea (EU Directive 98/83/EC)[2] excepto el Fe, que en 6 muestras recogidas en episodios de escorrentía superó el valor límite permitido (200 µg L^{-1}).

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S15: *Ingeniería Química y Medioambiente*

(PEG-SULFATE SALTS) AQUEOUS TWO-PHASE SYSTEMS

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Palabras Clave: *Aqueous Two-Phase System, extraction, polymer, phase diagram, Liquid-liquid equilibrium*

Aqueous two phase systems (ATPS) were discovered by Beijerinck in 1896. But only in 1950 a successful application was found as extraction media in biotechnology, when Albertsson proposed their use for the separation of biomolecules [1]. These biotechnological applications are feasible due to the high percentage of water present in both equilibrium phases, which avoids denaturalization of proteins. Indeed, these systems have been successfully applied to separate a wide variety of solutes, such as proteins, antibodies or antibiotics, but also for the recovery of viruses, cells or cell's organelles [1].

ATPS are obtained mixing in water certain pairs of polymers, or a polymer and a salt, above some critical compositions and temperatures [1, 2]. Recently, the possibility of combining an ionic liquid and an inorganic salt has also been raised [3]. Although both components are soluble in water, when mixed they produce a phase splitting into two (aqueous) phases. One phase will be enriched in one of the components, while the other phase is enriched in the other. In general, polymer-salt ATPS are preferred for industrial applications for economical reasons.

In this work, phase diagrams for polymer-salt ATPS have been characterized. The selected polymer is PEG 8000, which is a low toxicity polymer, included in the FDA's GRAS List (***G***enerally ***R***ecognized ***A***s ***S***afe), and with high biocompatibility (proteins are generally stable in PEG aqueous solutions). On the other side, sulfate salts have been selected for their low cost and wide availability. Phase diagrams have been obtained by analysis of the phases in equilibrium, using physical properties such as density and refraction index. This allows for experimental quantification of the ends of the tie-lines. The phase diagrams obtained have been compared, and the effect of the salt cation is discussed. Differences in the ATPS phase behavior where explained with differences in the hydration shell of the salt cation.

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NOVEL BIOLUBRICANT FORMULATIONS BASED ON CHEMICALLY MODIFIED LIGNOCELLULOSIC MATERIALS AND CASTOR OIL

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Keywords: *castor oil; isocyanate; lignocellulose; oleogel; rheology*

In the frame of environmental protection, different strategies for the replacement of non-renewable raw materials by renewable resources are targeted to reduce the impact that process technologies and products of different industrial sectors cause in the environment. In this sense, the concept of biorefinery arises as an integrated industrial metabolism able to produce chemical intermediates, end-use materials and energy based on the principles of the green chemistry and Engineering [1]. On the other hand, one example of industrial sector with particular environmental awareness is the lubricant industry [2]. Thus, the substitution of traditional thickening agents, such as metallic soaps, by others derived from renewable resources is still a non-totally solved issue, mainly due to the high technical efficiency achieved with the traditional ones. In this work several lignocellulose pulps from different origin and/or submitted to different treatments were crosslinked with HMDI in order to induce the formation of a physically and mechanically stable three-dimensional network with enhanced hydrophobic interactions once dispersed in castor oil. The rheological properties and microstructure as well as lubricant performance of the different products were then evaluated. In general, HMDI-crosslinked lignocellulose gel-like dispersions attained fit the rheological and tribological properties requirements as well as suitable physical and mechanical stability to be proposed as efficient biodegradable alternatives to traditional lubricating greases. In particular, both the thermo-rheological response, which evidences a softening temperature of around 100ºC, and the microstructural morphology, composed of long and entangled fibers, are extremely similar to that found in lithium greases. Mechanical stability of HMDI-crosslinked lignocellulose-based oleogels, evaluated as the loss of consistency after submitting the sample to a working test, was significantly improved respecting non-crosslinked lignocellulose gel-like dispersions previously studied. Moreover, friction coefficient and resulting wear mark diameters obtained in a ball-on-disc contact lubricated with these ecofriendly formulations were, in most cases, comparable to that obtained with commercial lubricating greases. The HMDI/cellulose pulp weight ratio applied in the crosslinking reaction can be used to modify and modulate the consistency and the values of rheological functions and parameters of these gel-like dispersions.

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S15: *Ingeniería Química y Medioambiente*

DESARROLLO DE MATERIALES SOPORTE PARA LA ADSORCIÓN DE HIERRO Y POSTERIOR APLICACIÓN EN LA ELIMINACIÓN DE DIVERSOS TIPOS DE CONTAMINANTES

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Palabras Clave: *Eliminación contaminantes, adsorción de hierro, materiales soporte, isoterma.*

El posible uso de materiales de bajo coste para la eliminación de contaminantes en efluentes acuosos resulta interesante a la vez que económico frente a los métodos tradicionales, más costosos, complejos y largos en el tiempo de aplicación.

Por ello el presente trabajo fue pensado para desarrollar materiales adsorbentes de bajo coste y estudiar métodos de inmovilización para garantizar su estabilidad estructural y que faciliten su posterior separación del medio.

Este estudio se centró en materiales que contangan hierro inmovilizado en los siguientes soportes:

- Pastillas de gel de sílice.
- Pastillas de gel de sílice + Ludox
- Beads de alginato.

Todos estos materiales se caracterizan por tener en su estructura grupos funcionales capaces de fijar, en este caso el hierro, que a continuación será empleado para la eliminación de diferentes contaminantes.

Se realizaron estudios previos para la obtención de las pastillas de silicato y de los beads de alginato y se comparó su efectividad para la eliminación de hierro. Para ello se obtuvieron las isotermas de adsorción de los tres materiales por separado.

Los resultados muestran que el material con mayor capacidad para la eliminación de hierro en disoluciones acuosas es el silicato, seguido del silicato + ludox y finalmente el alginato.

Después del tratamiento con hierro se probó la eficacia de los distintos materiales frente a la eliminación de diversos contaminantes en disolución acuosa.

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REMEDIACIÓN DE LA CONTAMINACIÓN DE FOSFATOS MEDIANTE MÉTODOS DE ADSORCIÓN

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Palabras Clave: *Eliminación fosfatos, adsorción, lodo rojo, residuo industrial, alúmina granulada, cinética, estudio pH, isoterma.*

Los compuestos de Fósforo juegan un papel crucial en los ciclos energéticos: En la fotosíntesis transforman la energía solar en energía química y en la biosíntesis de las plantas actúan como proveedores de energía química. Esto, además de su baja concentración y su baja solubilidad en suelos, lo convierten en un nutriente de vital importancia y clave en la limitación del crecimiento de las plantas tanto en suelos como en aguas. El exceso de fosfatos en el medio ambiente puede tener efectos perjudiciales, principalmente la eutrofización de las aguas.

En este estudio se han seleccionado diversos biomateriales y materiales inorgánicos y se ha ensayado su capacidad de eliminación de fosfatos en medio acuoso. En base a los resultados obtenidos se han seleccionado dos de ellos para su estudio en profundidad: el Lodo Rojo y la Alúmina granulada.
El Lodo Rojo es un residuo de la industria del Aluminio. Se produce en la obtención de la alúmina, precursor de Aluminio, a partir de la bauxita mediante el proceso Bayer.
La Alúmina granulada es un material comercial empleado en el relleno de las columnas cromatográficas.

En la parte experimental se ha realizado un estudio de pH, en el cual se han obtenido los intervalos óptimos de eliminación de fosfatos para el Lodo Rojo y la Alúmina granulada, siendo 4-5 y 3-7, respectivamente.
A continuación, se ha llevado a cabo un estudio cinético, a los pHs óptimos de cada material, con el fin de conocer el tiempo de reacción necesario para que se alcance el equilibrio. Los resultados fueron: 24 horas para el Lodo Rojo y 30 minutos para la Alúmina Granulada empleando una relación de 2,5 g adsorbente/L y una concentración inicial de 10 mg P/L.
Por último, sabiendo el pH óptimo y el tiempo necesario para que se alcance el equilibrio, se han realizado las isotermas correspondientes para determinar la capacidad máxima de adsorción de Fosfatos.

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EXPERIMENTAL MEASUREMENTS AND ESTIMATION BY QUANTITATIVE STRUCTURE-ACTIVITY RELATIONSHIPS (QSAR) OF (ECO) TOXICITY OF IONIC LIQUIDS

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Keywords: *ionic liquids, (eco) toxicity, Vibrio Fischeri,* Microtox®, QSAR.

Ionic liquids (ILs) have interest because constitute a new group of polar and non-aqueous solvents whose most important advantage is their negligible vapor pressure. Mainly, for this reason they are considered green solvents compared to the conventional volatile organic solvents. While ILs are nonvolatile, they do not affect to atmospheric pollution [1]. However, they have significant solubility in water and high stability so they could become persistent pollutants in waste waters. For this reason, in order to get industrial applications of the ILs it is crucial to know the ILs environmental fate and toxicological behavior by means of toxicological parameters such as (eco) toxicity obtained by *Vibrio Fischeri* toxicity test. According to Parvez *et al* [2], *Vibrio Fischeri* luminescence inhibition test is the most common bacterial bioassay. In addition, it constitutes a standard (eco) toxicological bioassay in Europe (DIN EN ISO 11348). Specifically, ILs (eco) toxicity has been determined by Microtox® Toxicity Test. Light emission is directly proportional to the metabolic activity of the bacterial population and any inhibition of enzymatic activity causes a corresponding decrease in luminescence. In the last years, some authors have developed mathematical models based on the structural features of the ILs to predict their toxicity. These models are called Quantitative Structure-Activity Relationships (QSAR) and consist of group contribution methods [3].

The aim of this work has been to obtain the experimental and estimated values of the *Vibrio Fischeri* toxicity (EC_{50}) for a set of ten chloride anion-based ILs.

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S16. Química y Cristalografía: Materia y Vida con Precisión Atómica (CRIS) / Chemistry and Crystallography: Matter and Life with Atomic Precision

"El simposio pretende mostrar los avances recientes en el campo de la Cristalografía, y cómo los estudios estructurales están siendo claves para entender aspectos diversos de la química de la vida y de la materia. Química biológica y estructural, diseño de fármacos y química supramolecular, ingeniería cristalina, estudios de densidad de carga, cristalografía en condiciones extremas y estructuras magnéticas tienen cabida entre la temática de nuestro simposio."

"This symposium intends to present the State-of-the-Art of Crystallography and shows how structural studies are key to understand the Chemistry of Life and Matter. Chemical biology and structural chemistry, drug design and supramolecular chemistry, crystal engineering, charge density studies, extreme conditions crystallography and magnetic structures are within the scope of this symposium."

Organizadores:

Laura Bayés García (UB)

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Mª José Sánchez Barrena (CSIC)

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Simposio patrocinado por el Grupo Especializado de Cristalografía y Crecimiento Cristalino y PANalytical

Miércoles 22 de Julio 2015

Chairwoman: Lourdes Infantes

15:30 – 16:15	**S16-IL-01**	**Colin Groom** *"Drug Discovery by Design: Using Every Small Molecule Crystal Structure ever Published"*
16:15 – 16:30	**S16-OC-01**	**Concepción González-Bello** *"Structure-based Design of Inhibitors for Antibiotic Drug Discovery"*
16:30 – 17:00		Pausa Café

Chairwoman: Mª Jose Sánchez Barrena

17:00 – 17:45	**S16-IL-02**	**Ignacio Fita Rodríguez** *"Chemistry and Macromolecular Crystallography: A most Fruitful Partnership"*
17:45 – 18:00	**S16-OC-02**	**Carlos Martí-Gastaldo** *"Peptide-based Poprous Materials by Sidechain Engineering"*
18:00 – 18:15	**S16-OC-03**	**M. S. M. Abdelbaky** *"Metal-Organic Frameworks Based on Lanthanide and Carboxylate Ligands: Synhtesis Structure and Properties"*
18:15 – 18:30	**S16-OC-04**	**Carlos Fernández-Tornero** *"Crystal Structure of RNA Polymerase I"*

18:30	***Sesión de Pósteres***

19:30	**Asamblea Ordinaria del Grupo Especializado GE3C**

Jueves 23 de Julio 2015

08:40 – 09:40	**PL-5**	***Conferencia Plenaria*** (Común a todos los simposios) **Avelino Corma Canós** *"Intentos para Establecer Puentes entre la Catásisis Homogénea y Heterogénea"*

Chairman: Santiago García Granda

10:00 – 10:45	**S16-IL-03**	**Kenneth Harris** *"Structure Determination of Organic Materials from Powder X-Ray Diffraction Data: Current Opportunities and State-of-Art"*
10:45 – 11:00	**S16-OC-05**	**Jordi Rius** *"Caracterización de Microvolúmenes Cristalinos en Láminas Delgadas por Microdifracción TTS"*
11:00 – 11:30		Pausa Café

Chairman: Fernando Lahoz

11:30 – 12:15	**S16-IL-04**	**Wolfgang Scherer** *"Charge Density and Bonding in Inorganic Molecules & Materials"*
12:15 – 12:30	**S16-OC-06**	**Felipe Gándara** *"Control de la Actividad Catalítica de una Nueva Familia de Metal-Organic Frameworks Preparados con Múltiples Cationes Metálicos"*
12:30 – 12:45	**S16-OC-07**	**Begoña Bazán** *"Transformación Estructural Reversible en una Red Sólida de Coordinación de Cu^{II} con Piridin-2,5-dicarboxilato y Di-2-piridilcetona: Análisis con Radiación Sincrotrón"*
12:45 – 13:00	**S16-OC-08**	**Teresa Calvet** *"Dynamic Thermal Treatments for the Development of New Textures of Chocolate"*
13:00 – 13:10		**Entrega de Premios a los Mejores Posters (PANalytical)**
13:10 – 13:30	**S16-OC-09**	**Entrega del Premio "*Xavier Solans*" (BRUKER):** **Antonio Chaves** *"Structural Basis of the Regulatory Mechanism of the Plant CIPK Family of Protein Kinases Controlling Ion Homeostasis and Abiotic Stress"*

13:30	***Ceremonia de Clausura***

Comunicaciones Invitadas (IL)

S16: *Química y Cristalografía: Materia y Vida con Precisión Atómica*

DRUG DISCOVERY BY DESIGN: USING EVERY SMALL MOLECULE CRYSTAL STRUCTURE EVER PUBLISHED

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Keywords: *cristal, structure, drug*

The modern drug discovery scientist is bathed in structural information. Crystal structures of molecular targets are available for almost every target class, often with ligands of interest. But whilst many drug discovery stories tell of the involvement of structural biology, the contribution of structural chemistry is often overlooked.

This presentation, timed to coincide with the 50th anniversary of the Cambridge Structural Database, will touch on the contribution of Spanish crystallographers, before outlining the tremendous contribution structural chemistry makes to affinity optimisation, selectivity, bioavailabilty and most particularly solubility.

S16: *Química y Cristalografía: Materia y Vida con Precisión Atómica*

CHEMISTRY AND MACROMOLECULAR CRYSTALLOGRAPHY: A MOST FRUITFUL PARTNERSHI

Ignacio Fita
(IBM-CSIC)

After many years of successful collaborations between Chemistry and Macromolecular Crystallographic the relationship between them appears stronger than ever, as reflected for example in the truly astonishing number of protein crystallographers that have been awarded with the Nobel Prize in Chemistry since the year 2000. Will this continue? Some lessons from and reasons for this long and most fruitful partnership will be commented. A couple of challenging chemical processes, where enlightenment provided by macromolecular crystallography appears mostly irreplaceable, will also be presented.

S16: *Química y Cristalografía: Materia y Vida con Precisión Atómica*

STRUCTURE DETERMINATION OF ORGANIC MATERIALS FROM POWDER X-RAY DIFFRACTION DATA: CURRENT OPPORTUNITIES AND "STATE OF THE ART"

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Keywords: *powder X-ray diffraction, structure determination, organic materials*

Knowledge of crystal structure is a prerequisite for understanding the fundamental properties and potential applications of crystalline materials. Although single-crystal X-ray diffraction (XRD) is the most powerful technique for determining the structures of crystalline materials, the requirement for a single crystal specimen imposes severe limitations on the scope of this technique. For materials that cannot be grown as suitable single crystals, it is necessary to tackle structure determination instead using *powder* XRD data [1]. However, carrying out structure determination from powder XRD data is significantly more challenging than structure determination from single-crystal XRD data, particularly for organic materials. Indeed, as recently as the early 1990s, no organic crystal structure had ever been determined directly from powder XRD data. During the intervening time, we have focused on the development, implementation and optimization of new techniques for carrying out crystal structure determination of organic materials directly from powder XRD data. Our techniques are based on the direct-space strategy for structure solution [2], in which a hypersurface defined by the powder profile *R*-factor (R_{wp}) is searched using a global optimization algorithm, with current focus on the use of Genetic Algorithms. Using our techniques, crystal structures of organic materials of moderate complexity can now be determined directly from powder XRD data. The lecture will give an overview of the current opportunities for carrying out structure determination of organic materials from powder XRD data, emphasizing that the structure determination process can often be enhanced by making use of information from other experimental (especially solid-state NMR) and computational techniques. Recent results from the application of our direct-space methodology will be presented, with examples from several different fields within chemical, materials and biological sciences [3,4].

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S16: *Química y Cristalografía: Materia y Vida con Precisión Atómica*

CHARGE DENSITY AND BONDING IN INORGANIC MOLECULES & MATERIALS

W. Scherer[1], G. Eickerling[1], Andreas Fischer[1] , Andrew Dunbar[1], Dominik Schmitz[1], Petra Meixner[1]

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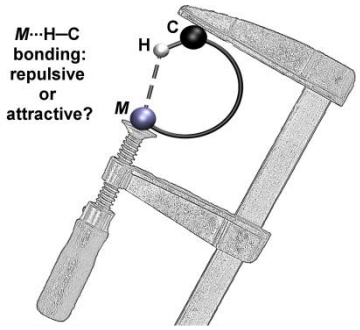
Keywords: *charge density, bond activation, high pressure, superconductivity*

Since the theoretical prediction and experimental verification of Charge Concentrations (CCs) in the valence shell of main group elements and transition metals several attempts have been undertaken to understand their origin and relevance in chemistry and physics. In pioneering studies we could demonstrate that these CCs not only influence the geometry of coordination compounds and solids but also serve as controlling parameters for important chemical reactions like the activation of C-H bonds in catalytic reactions [1] and under extreme conditions [2] (Scheme). Furthermore, in covalent solids such as transition metal oxides and carbides they appear to signal even subtle electron localization phenomena which might induce metal-to-insulator transitions or effect the onset of superconductivity [3]. The complex interplay between valence shell charge concentrations and chemical properties of molecules and solids will be the central topic of this contribution with the focus on (i) unusual bonding scenarios displayed by solid state compounds [4] and the (ii) control of geometry and bond activation processes in molecules.



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Comunicaciones Orales (OC)

S16: *Química y Cristalografía: Materia y Vida con Precisión Atómica*

STRUCTURE-BASED DESIGN OF INHIBITORS FOR ANTIBIOTIC DRUG DISCOVERY

Concepción González-Bello[1]

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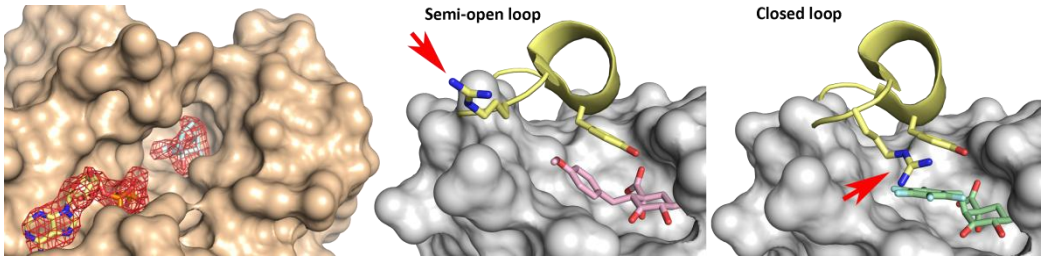
Keywords: *Type II dehydroquinase, Shikimate Kinase, Drug Discovery, Antibiotics*

The decreased effectiveness of antibacterial agents against infectious diseases caused by the development of drug resistance has become one of the most important public health issues of the early 21st century. Therefore, the discovery of novel drugs and therapies to treat antibiotic-resistant infections and, particularly of compounds with new mechanisms of action is urgently needed. A promising approach in the search of new antimicrobial agents is a detailed knowledge of the catalytic mechanism and the binding determinants of enzymes involved in biosynthetic pathways that no have mammalian homologues but they are essential for bacterial survival. That is the case of the shikimic acid pathway enzymes, through which chorismic acid is biosynthesized. The talk will be focused in two essential bacterial enzymes that are recognized to be attractive targets for the development of new antibacterial agents, type II dehydroquinase and shikimate kinase. Based on the mode of action of the enzyme, structural, molecular modeling and dynamic simulations studies and by creating favorable interactions with key residues in the enzymatic mechanism, several potent inhibitors were designed and identified. The talk will show how the resolution of several crystal structures of enzyme/inhibitors complexes proved to be a key tool for drug discovery.



Financial support from the Spanish Ministry of Economy and Competitiveness (SAF2013-42899-R), Xunta de Galicia (GRC2013-041) and the European Regional Development Fund (ERDF) is gratefully acknowledged.

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S16: *Química y Cristalografía: Materia y Vida con Precisión Atómica*

PEPTIDE-BASED POROUS MATERIALS BY SIDECHAIN ENGINEERING

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Keywords: *Metal-Organic Frameworks, Peptide porous materials, Flexible porosity*

Peptides have recently emerged as naturally occurring linkers for the design of metal organic frameworks (MOFs) provided their multiple coordination modes, torsional adaptability and chirality. The use of peptide struts provides unprecedented guest adaptability,[1] modulation of the framework's flexibility[2] and control over its chemical and mechanical stabilities[3] triggered by suitable choice of the amino acids in the peptidic sequence.

We have recently demonstrated that these porous crystal also show well-ordered porosity closure controlled by the peptide's side chain.[4] $Zn[Gly\text{-}Ser]_2$ evolves from a solvated porous into a non-porous desolvated state as result of ordered displacive and conformational changes of the peptide that suppress the void space in response to guest loss. This cooperative closure, which recalls the folding of proteins, retains order in three-dimensions and is driven by the hydroxyl groups from the sidechain of the serine residue acting as H-bond donors in the peptide sequence. This ordered closure is also displayed by multipeptide solid solutions in which the combination of different sequences of amino acids controls guest response in a non-linear way.

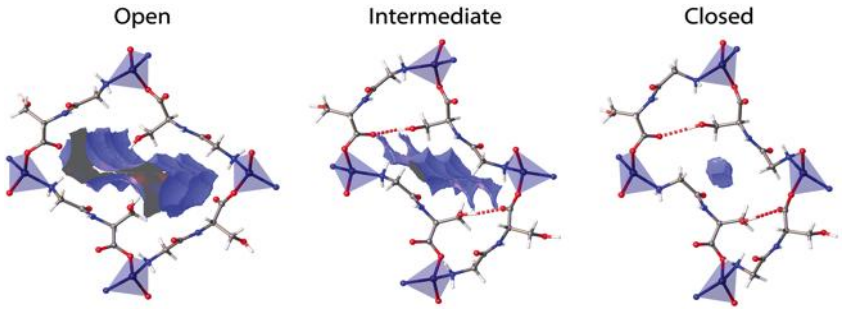

Figure 1: Porosity closure in $Zn(Gly\text{-}Ser)_2$ induced by cooperative folding of the peptide enabled by conformational change.

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S16: *Química y Cristalografía: Materia y Vida con Precisión Atómica*

METAL-ORGANIC FRAMEWORKS BASED ON LANTHANIDE AND CARBOXYLATE LIGANDS: SYNTHESIS, STRUCTURE AND PROPERTIES

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Keywords*: MOFs, Lanthanide,* Carboxylate, *Porosity, Luminescence*

Metal-organic frameworks (MOFs) are considered nowadays as the most promising class of materials ideal for various relevant applications such as gas storage and separation, catalysis, drug delivery and chemical sensing due to the inherent structural modularity [1]. In particular, lanthanides-organic frameworks (LOFs) in which the intrinsic chemical character, magnetic and optical properties of lanthanides (Ln^{3+}) cations are often not matched by other transition metal cations. Thus, synthesis of LnOFs is an attractive subject of great interest both from a fundamental scientific standpoint and also for different practical applications [2,3]. Carboxylate linkers are of particular interest to design LnOFs due to their structural rigidity, diversity of coordination geometries, possibility of facilitating the formation of porous structures [4], and high affinity toward Ln^{3+} cations.

In this communication, we give an overview of our ongoing research concerning the synthesis of novel LOFs by using rigid carboxylate linkers, such as dianion BDC (1,4-benzenedicarboxylate acid) [5] and PDC (2,5-pyridinedicarboxylic acid), and trianion BTB (1,3,5-benzene(tris)benzoic acid).

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S16: *Química y Cristalografía: Materia y Vida con Precisión Atómica*

CRYSTAL STRUCTURE OF RNA POLYMERASE I

Carlos FERNÁNDEZ-TORNERO[1], María MORENO-MORCILLO[2], Umar J. RASHID[2], Nicholas M. I. TAYLOR[1], Federico M. RUIZ[1], Tim GRUENE[3], Pierre LEGRAND[4], Ulrich STEUERWALD[2]

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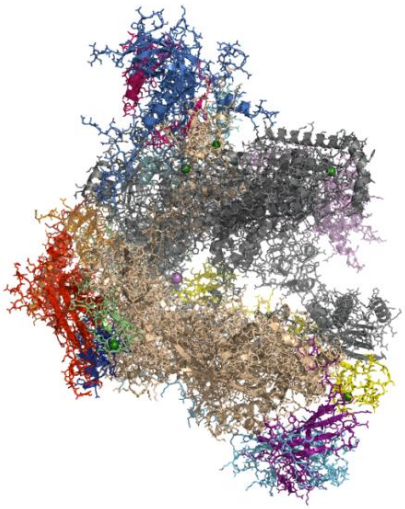
Keywords: *X-ray crystallography, enzyme mechanism, in vivo RNA synthesis*

Biosynthesis of the eukaryotic ribosome starts with ribosomal RNA production by RNA polymerase I (Pol I), a process that is critical to regulate cell growth and proliferation. We were able to obtain the crystal structure of yeast Pol I, a 14-subunit complex composed of more than 80,000 atoms with a total mass of 590,000 Da, at 3.0 Å resolution [1]. The structure represents the latent state of the enzyme, characterized by three major features. First, it forms dimers that involve the C-terminal tail of the stalk subunit A43. Second, the two enzyme halves pivot along the DNA-binding cleft to produce an open cleft and an unfolded bridge helix. Third, an extended loop in subunit A190 mimics the DNA backbone along the cleft, hampering nucleic acid binding. The Pol I crystal structure also reveals intrinsic modules that only bind transiently in other RNA polymerases, such as a TFIIS-like zinc ribbon in subunit A12.2 and a TFIIF-like dimerization module in the A49/A34.5 heterodimer.



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S16: *Química y Cristalografía: Materia y Vida con Precisión Atómica*)

CARACTERIZACIÓN DE MICROVOLÚMENES CRISTALINOS EN LÁMINAS DELGADAS POR MICRODIFRACCIÓN TTS

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Palabras Clave: *microdifracción-tts, lámina delgada pulida, radiación sincrotrónica, Patterson-function direct methods, modo transmisión*

Hace unos cuatro años se introdujo la técnica de microdifracción-*tts* (*tts*-μXRD; *tts*= through-the-substrate) [1]. En dicha técnica el experimento de difracción se efectua por transmisión a través de la lámina delgada pulida objeto del estudio que se encuentra adherida a un sustrato de vidrio. Debido a los espesores involucrados (del orden de 0,9 a 1,5 mm para el sustrato y unas 30 μm para la lámina), la radiación sincrotronica (λ < 0.5Å) con su alta capacidad de penetración y su posibilidad de focalización (15 x 15 μm^2 en la estación de microdifracción de MSPD) es ideal. En [1] la aplicación de la técnica *tts*-μXRD se restringió a las zonas policristalinas de la lámina delgada. Posteriormente los datos de difracción de polvo obtenidos se procesan con los 'Patterson-function direct methods' para la determinación de las correspondientes estructuras cristalinas [2].

Más recientemente la técnica *tts*-μXRD (combinada con radiación sincrotrónica) se ha extendido a la caracterización de microcristales incrustados en secciones delgadas pulidas de materiales compactos [3]. El procedimiento resultante consta de los siguientes pasos básicos: i. Registro de un número limitado de patrones de difracción 2D (frames) para cada uno de los microcristales escogidos y orientados al azar (entre 5 y 10 microcristales); ii. Afinamiento de la métrica a partir del patrón de difracción 1D obtenido promediando cricularmente la suma de los frames registrados; iii. Determinación de la orientación del retículo recíproco para cada microcristal lo cual permite asignar a las manchas los índices *hkl*, y por consiguiente, combinar las intensidades de los diferentes frames del cristal en un juego final de intensidades (frame merging); iv. Combinación de los juegos de intensidades finales de varios cristales (multicrystal merging) para la obtención de un juego de intensidades más completo (tipo monocristal) apropiado para la determinación/afinamiento estructural. Su viabilidad se demuestra con algunos ejemplos representativos de petrologia en que se han usado sustratos de vidrio de varios espesores. Gracias a su versatilidad y simplicidad experimental esta metodologia deberia ser de gran utilidad en disciplinas tan distantes como la petrologia, la ciencia de materiales y patrimonio cultural. Esta investigación forma parte del proyecto NANOXRED (MAT2012-35247) del MINECO.

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S16: *Química y Cristalografía: Materia y Vida con Precisión Atómica*

CONTROL DE LA ACTIVIDAD CATALÍTICA EN UNA NUEVA FAMILIA DE METAL-ORGANIC FRAMEWORKS PREPARADOS CON MÚLTIPLES CATIONES METÁLICOS

L. M. Aguirre-Díaz, F. Gándara, M. Iglesias, N. Snejko, E. Guitérrez-Puebla, M. A. Monge

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Palabras Clave: *MOFs, Catálisis heterogénea,*

Los metal-organic Frameworks, MOFs, son una clase de materiales cristalinos formados por la unión de centros metálicos a través de ligandos orgánicos. Estos materiales poseen alto interés por sus aplicaciones en campos diversos como son el almacenamiento y separación de gases, la catálisis heterogénea, liberación de fármacos, luminiscencia, etc.[1]

En el presente estudio, hemos establecido cómo MOFs formados por distintos cationes metálicos que ocupan la misma posición cristalográfica, que denominamos soluciones sólidas, poseen actividad catalítica que es diferente a la de sus equivalentes monometálicos. Además, demostramos como la actividad de estos materiales como catalizadores heterogéneos en reacciones multicomponentes puede ser controlada gracias modificaciones en la proporción de los distintos cationes empleados. En particular, hemos preparado una nueva familia de MOFs isoestructurales usando aluminio, galio, indio, y mezclas de indio y galio en distintas proporciones. La actividad catalítica de estos materiales ha sido probada en la reacción Strecker, una reacción de tres componentes y que se lleva a cabo en un solo paso. Nuestros resultados demuestran el gran potencial en usar soluciones sólidas de MOFs para controlar los distintos pasos en reacciones multicomponente.[2]

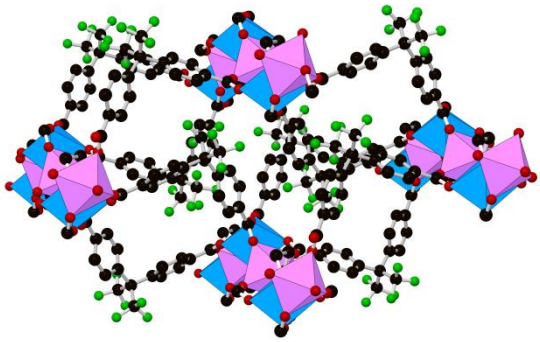

Figura 1. Representación de la nueva familia de MOFs. Poliedros azules y rosas representan los cationes metálicos (Al, Ga o In), esferas negras, rojas y verdes representan átomos de carbono, oxígeno y flúor, respectivamente.

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S16: *Química y Cristalografía: Materia y Vida con Precisión Atómica*

TRANSFORMACIÓN ESTRUCTURAL REVERSIBLE EN UNA RED SÓLIDA DE COORDINACIÓN DE Cu^{II} CON PIRIDIN-2,5-DICARBOXILATO Y DI-2-PIRIDILCETONA: ANÁLISIS CON RADIACIÓN SINCROTRÓN

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Palabras Clave: *SCFs, cristalografía, transformación estructural, radiación sincrotrón.*

Las redes sólidas de coordinación (solid coordination frameworks) han experimentado un gran desarrollo a lo largo de la última década gracias a la infinidad de complejos metálicos obtenidos gracias al gran abanico existente de ligandos orgánicos disponibles. Su porosidad y/o flexibilidad estructural ante la desorción/adsorción de diferentes moléculas han hecho de ellos unos materiales con importantes aplicaciones en el ámbito de almacenamiento de gases, catálisis y sensores químicos, entre otros.

En este sentido, se ha sintetizado un nuevo compuesto de fórmula general $[Cu(PDC)((py)_2C(OH)_2)(H_2O)]$ (**1**) (PDC= piridin-2,5-dicarboxílato ,$(py)_2C(OH)_2$= dipiridil cetona). El mismo se ha caracterizado mediante difracción de rayos-X en monocristal, IR, TG/DSC y TDX. El estudio térmico ha revelado la existencia de una transformación estructural a 98°C ante la pérdida de una molécula de agua de coordinación. La estructura de alta temperatura, $[Cu(PDC)((py)_2C(OH)_2)]$ (**2**), se ha resuelto a partir de datos de difracción de radiación sincrotrón. Así mismo, se ha analizado la reversibilidad de la transformación mediante un ciclo de histéresis.

Agradecimientos

Los autores agradecen al Ministerio de Ciencia e Innovación (MAT2013-42092-R), al Gobierno Vasco (Grupo Consolidado, IT-630-13) y a la UPV/EHU (UFI11/15) la financiación. Se agradece el soporte técnico y humano proporcionado por los SGIker por las medidas realizadas. F. Llano-Tomé agradece al Ministerio de Ciencia e Innovación su beca de formación (BES-2011-045781).

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S16: *Química y Cristalografía: Materia y Vida con Precisión Atómica*

DYNAMIC THERMAL TREATMENTS FOR THE DEVELOPMENT OF NEW TEXTURES OF CHOCOLATE

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Keywords: *polymorphism, kinetics, lipids, food products*

Dynamic thermal treatments are highly significant to obtain specific polymorphic forms of lipids [1, 2]. In this study, we examined the influences of dynamic thermal treatments on the development of new textures of chocolate revealing soft mouthfeel (velvet effect), which can be obtained by tailoring rapid cooling and subsequent heating treatments. Fluidized chocolate (tempered mixture of chocolate and cocoa butter) was sprayed on two different substrates (metal and tempered chocolate) at different substrate temperatures (4°C, 12°C, 16°C and 18°C). Polymorphic crystallization and transformation was in-situ monitored by using laboratory-scale X-ray diffraction. Thermal treatments enabled the formation of thin layers of cocoa butter crystals with much small particle sizes and low melting point compared to normally-tempered chocolate, leading to create soft-mouth feeling. The results confirmed the template effect caused by substrate of chocolate, as polymorphic transformations occurred more rapidly than metallic substrate.

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STRUCTURAL BASIS OF THE REGULATORY MECHANISM OF THE PLANT CIPK FAMILY OF PROTEIN KINASES CONTROLLING ION HOMEOSTASIS AND ABIOTIC STRESS

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Keywords: *signaling, ion transport, abiotic stress*

The regulation of ionic transport in plants is essential because it establishes the key physicochemical parameters for cell function. Under abiotic stress, the intracellular levels of pH, potassium and toxic cations, such as sodium, change and this affect multiple cellular systems. Consequently, the knowledge of the molecular mechanism that regulates the ionic transport is fundamental and provides opportunities to use plants to our benefit [1].

The plant cells use calcium-signaling pathways, in which calcium sensors and kinases are involved in the regulation of certain ion channels to provide the correct response to each particular stress situation. CIPKs are a family of multidomain protein kinases that play an essential role in the regulation of these calcium-signaling pathways since they interact with both, the calcium sensors and the ion channels (Fig. 1 a) [2].

We have carried out structural studies with the kinase domain of the CIPKs to understand at molecular level the regulation this family of protein kinases. The structures determined in this work (Fig. 1 b) provide the molecular basis to identify or design more resistant plant species and to develop small compounds that help to protect crops [3].

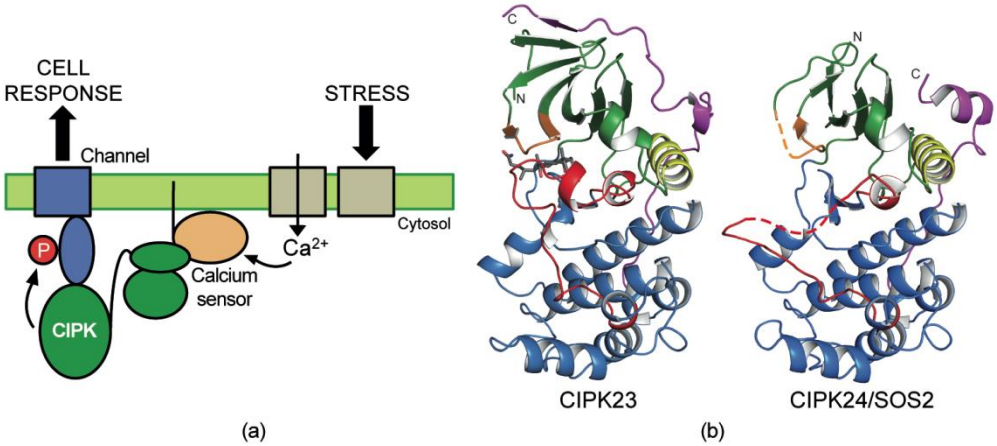

Figure 1. Regulation of CIPKs. (a) Schematic representation of the activation of the response that restores ion homeostasis under abiotic stress. (b) Crystallographic structures of CIPK23 and CIPK24/SOS2.

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Presentaciones Póster (PP)

ESTUDIO DE DENSIDAD ELECTRÓNICA DEL COMPLEJO DE RODIO [[Rh [κ^2-(bmpza)] [η^4-(C_7H_8)]]·[CH_3OH]]

M.J. Artigas

CATÁLISIS HETEROGENEA EN REDES METALOPORFÍRINiCAS: SISTEMA Mn^{II}-TPPS (TPPS= MESO-TETRA(4-SULFONATOFENIL)-PORFIRINA)

G. Barandika

HALOGEN BONDING BASED ORGANOMETALLIC NETWORKS: SOLID STATE AND SOLUTION STUDIES

Irene Egido

COMPUESTOS DE Pd(II) DERIVADOS DE N-CINAMILIDEN IMINAS. APLICACIONES EN CATÁLISIS.

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RELACIÓN ESTRUCTURA-PROPIEDADES CATALÍTICAS EN COMPLEJOS [(η^n-anillo)M(L)L]$^{+n}$. INTERACCIONES INTRA- E INTERMOLECULARES.*

P. García-Orduña

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C.A. Jiménez

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F. Lucio

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M. Martínez-Ripoll

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M. Moreno Alvero

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N. Parra

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Jorge Pasán

ESTUDIO DE LA REACTIVIDAD DE UN COMPLEJO BINUCLEAR κ^2*N,Ge-AMIDINATOGERMILENO DE RUTENIO(0)*

Enrique Pérez Carreno

ESTUDIO ESTRUCTURAL DE DIFERENTES COMPUESTOS DE TRICARBONIL RENIO (I) CON UN LIGANDO DERIVADO DE BENZOTIAZOL

Arantxa Pino-Cuevas

NEW COBALT (II) COORDINATION POLIMERS BASED ON FLEXIBLE TRIAZINE DERIVATIVES

Beatriz Rasines

FREQUENIN/NCS-1 AS A PHARMACOLOGICAL TARGET FOR SYNAPSE REGULATION IN X-LINKED MENTAL RETARDATION AND AUTISM

M.J. Sánchez-Barrena

SSNMR, CRYSTALLOGRAPHY AND COMPUTATIONAL STUDIES OF 1H-BENZOTRIAZOLE AND 5,6-DINITRO-1H-BENZOTRIAZOLE

D. Santa María

ESTUDIO MAGNETO-ESTRUCTURAL DE POLÍMEROS DE COORDINACIÓN DE COBRE(II) CON LIGANDOS TERPIRIDINA SUSTITUIDOS

D.Toledo

S16: *Química y Cristalografía: Materia y Vida con Precisión Atómica*

ESTUDIO DE DENSIDAD ELECTRÓNICA DEL COMPLEJO DE RODIO

[[Rh [κ^2-(bmpza)] [η^4-(C_7H_8)]]·[CH_3OH]]

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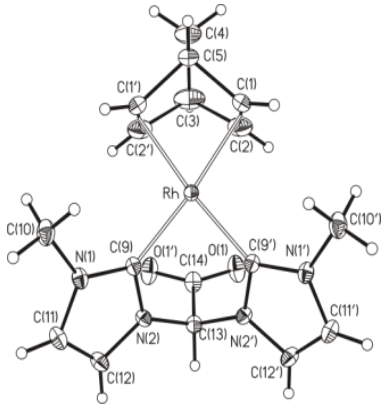
Palabras Clave: *densidad electrónica, compuesto organometálico, Rodio, interacciones intermoleculares*

El compuesto [Rh [κ^2-(*bis*(3-metil)pirazol-1-yl)acetato][η^4-(C_7H_8)]] es un precursor catalítico en reacciones orgánicas específicas. Este trabajo expone el análisis de la densidad electrónica experimental de este complejo de un metal de segunda serie de transición con el objetivo de caracterizar la coordinación del metal, los enlaces interatómicos y las interacciones intermoleculares.



El estudio de densidad electrónica del complejo de Rodio fue llevado a cabo mediante medidas experimentales de difracción de rayos-X a alta resolución (sin θ/λ=1.06 $Å^{-1}$) a una temperatura de 100K. La unidad asimétrica contiene media molécula de complejo (el centro metálico, cuatro carbonos y sus hidrógenos se encuentran sobre un plano de simetría) y una molécula de metanol. Tras un refino estructural convencional, se realizó un refino multipolar usando el modelo propuesto por Hansen y Coppens[1] con el software MoPro[2,3]. El modelo de densidad experimental ha sido interpretado topológicamente de acuerdo a la teoría de "Quantum Theory of Atoms in Molecules"[4]. La caracterización de las interacciones intra- e intermoleculares, especialmente la coordinación del metal y la interacción intermolecular entre el fragmento acetato del complejo metálico y una molécula de metanol serán discutidos.

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S16: *Química y Cristalografía: Materia y Vida con Precisión Atómica*

CATÁLISIS HETEROGENEA EN REDES METALOPORFÍRINiCAS: SISTEMA Mn^{II}-TPPS (TPPS= MESO-TETRA(4-SULFONATOFENIL)-PORFIRINA)

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Palabras Clave: *metaloporfirinas, redes sólida de coordinación, catálisis heterogénea*

Las entidades supramoleculares basadas en el auto-ensamblaje de metaloporfirinas son ejemplos paradigmáticos de la gran eficiencia de los biodispositivos utilizados por los sistemas naturales en la fotosíntesis, transporte de oxígeno, la transferencia de electrones y catálisis, entre otras.[1] Así, algunos catalizadores basados en metaloporfirinas e inmovilizados en los poros de redes sólidas de coordinación pueden llegar a ser altamente eficientes [2]. Nuestro grupo de investigación viene investigando desde hace varios años sobre un enfoque alternativo: utilizar las metaloporfirinas en un doble rol como unidades estructurales en redes sólidas de coordinación y como catalizadores [3].

Con este enfoque, los resultados que aquí se presentan corresponden a un compuesto Mn-TPPS-bipy (TPPS= *meso*-tetra(4-sulfonatofenil)-porfirina y bipy= 4, 4'-bipiridina) obtenido mediante síntesis hidrotermal en microondas. La estructura cristalina consiste en monómeros MnTPPS, donde el átomo metálico se encuentra en un entorno octaédrico con dos moléculas de agua en las posiciones axiales. Los huecos generados entre estos monómeros se ocupan con bipy y agua. La estabilidad térmica del compuesto se basa a una red de enlaces de hidrógeno cuya flexibilidad le permite actuar eficientemente como catalizador heterogéneo en la oxidación de diferentes alcoholes.

Agradecimientos

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HALOGEN BONDING BASED ORGANOMETALLIC NETWORKS: SOLID STATE AND SOLUTION STUDIES

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Keywords: *Halogen Bonding, Polyhalide Redox Reactivity, Crystal Engineering*

Halogen bonding (XB) is an interaction whose importance has been particularly acknowledged since the early years of this century. [1] XB interactions can be strong enough to direct the aggregation of molecules rendering them a useful tool in crystal engineering. In recent years, the attention on XB keeps growing due to the broad array of areas where their influence is evident, ranging from material science to biology. [2]

One of our ongoing research areas is focused on the use of these interactions to generate supramolecular organometallic networks, containing either main group or transition metal complexes.[3] In this communication we present our results for octahedral ruthenium derivatives of formula $[Ru(X)_2(CNR)_4]$. When the XB donor is the species 1,4-$C_6F_4I_2$ the generation of the synthon M—Cl···X—C is observed generating a monodimensional zig-zag arrangement (figure 1a). Changing the XB donor to X_2 (I_2 or Br_2) allowed us to generate bidimensional honey-comb networks. As well the modifications of the ligand R group from alkyl to aryl rendered the formation of a monodimensional network where the organometallic units are connected by the unprecedented Cl···I—I···I—I···Cl moiety (figure 1b). We have also performed NMR studies in solution to analyze the presence of these interactions when dissolved and their implications in the reactivity of these ruthenium compounds.

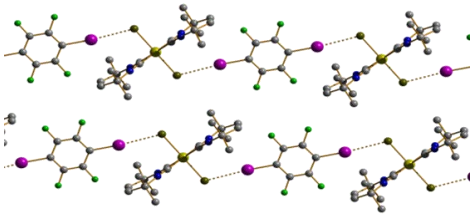

Figure 1 a)

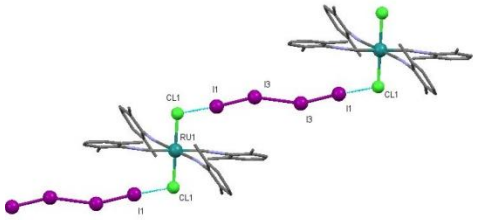

Figure 1 b)

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COMPUESTOS DE Pd(II) DERIVADOS DE *N*-CINAMILIDEN IMINAS. APLICACIONES EN CATÁLISIS.

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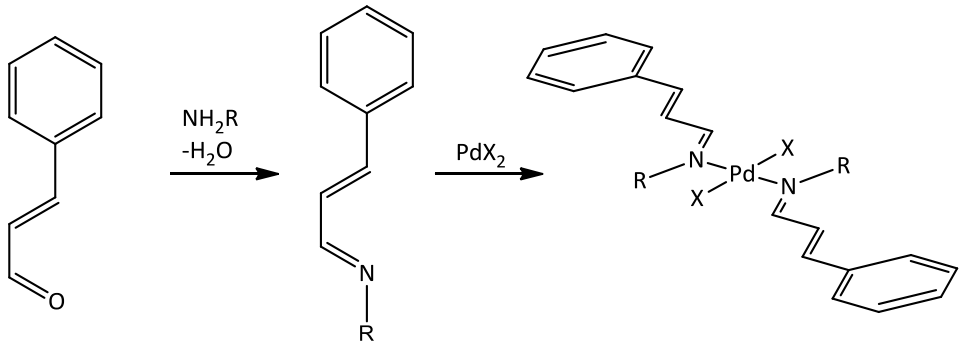
Palabras Clave: *paladio (II), catálisis, reacción de Suzuki, reacción de Heck.*

El cinamaldehído es un precursor adecuado para la síntesis bases de Schiff que pueden actuar como ligandos en la síntesis de paladaciclos; la metalación transcurre mediante ataque electrofílico a un carbono sp^2 no aromático por síntesis directa [1]. No obstante este proceso es complicado y en algunos casos lleva a la formación de complejos de coordinación con estructura de tipo $[PdX_2L_2]$. Este resultado, en principio adverso, resulta sin embargo muy interesante ya que existen estudios en los que se muestra que estos compuestos tienen actividad catalítica en las reacciones de acoplamiento C–C de Suzuki y de Heck [2]. Algunos de los resultados obtenidos en nuestro laboratorio se presentan en esta comunicación. Para la preparación metalaciclos con enlaces $C(sp^2)$–metal en carbonos no aromáticos existen alternativas a la metalación directa[3].



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RELACIÓN ESTRUCTURA-PROPIEDADES CATALÍTICAS EN COMPLEJOS $[(\eta^n\text{-anillo})M(L^*)L]^{+n}$. INTERACCIONES INTRA- E INTERMOLECULARES.

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Palabras Clave: *Estructura, Catálisis, Enantioselectividad, Compuestos Organometálicos, Interacciones Interatómicas.*

El uso de ácidos de Lewis, basados en complejos metálicos, como catalizadores en la síntesis de compuestos quirales enantiopuros se ha revelado como uno de los métodos más versátiles, ya que la modificación del metal o de sus ligandos permite modular ampliamente sus propiedades. El estudio de dos familias de catalizadores metálicos conteniendo metales del segundo periodo y con diferentes ligandos P,P-, N,N- y P,O- dadores nos ha permitido poner en evidencia que sus propiedades catalíticas estereoselectivas quedan estrechamente ligadas a las interacciones de tipo intra- e intermolecular que se establecen.

En concreto, en una familia de complejos del tipo $[(\eta^n\text{-anillo})M(PP^*)(substrato)]^{+n}$ ('$(\eta^n$-anillo)M' = $(\eta^5\text{-}C_5Me_5)Rh$, $(\eta^6\text{-}C_6Me_6)Ru$ o $(\eta^6$-*p*-cymene)Ru) se ha identificado claras interacciones intramoleculares de tipo CH/π. Se ha llevado a cabo un estudio sistemático en estos complejos de tipo semi-sandwhich, con el centro metálico como centro quiral, y conteniendo diversos difosfanos o (imidazolil)iminas como ligandos quirales y Cl, H_2O, metacroleína y cetonas α-β insaturadas, como ligandos fácilmente desplazables. El análisis de las interacciones intramoleculares permite entender la estereoselectividad obtenida en su aplicación como catalizadores asimétricos en reacciones de Diels-Alder [1].

En el caso de complejos metálicos de tipo $[(\eta^n\text{-anillo})Ru(POH)]^{+n}$ (POH: (S_{C1},R_{C2})-$Ph_2PC)Ph)HC(OH)\text{-}HCH_2OMe$), las diferentes formas de coordinación κ^1P, κ^2P,O y κ^3P,O,O' del ligando POH incrementan sucesivamente las propiedades ácidas del grupo hidroxilo. Su estudio estructural ha puesto de manifiesto que como consecuencia, este grupo tiene capacidad para establecer enlaces de hidrógeno intermoleculares facilitando la actuación del complejo como especie catalítica en procesos Diels-Alder o Friedel-Crafts. [2]

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S16: *Química y Cristalografía: Materia y Vida con Precisión Atómica*

EXPLORACIÓN ESTRUCTURAL DE METALOSUPRAMOLÉCULAS BASADAS EN LIGANDOS ACIL- Y NITROSOPIRAZOLONAS

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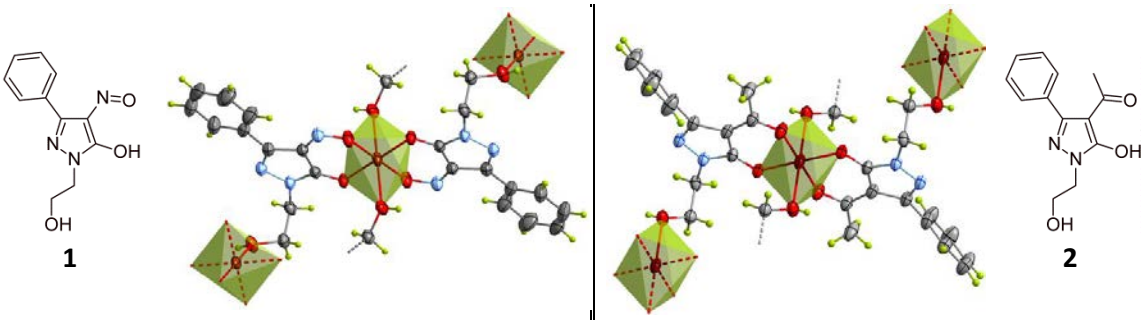
Palabras Clave: *Metalosupramoléculas, acilpirazolonas, nitrosopirazolonas*

A la fecha, existe escasa evidencia en la literatura de metalosupramoléculas basadas en ligandos orgánicos que utilicen el anillo de pirazolona como unidad coordinante. El más destacable corresponde al clúster octamérico reportado por Raymond, donde un derivado de acilpirazolona y Ln, generan un ensamble supramolecular 0D [1]. El hecho de que sean pocos los reportes bibliográficos de metalosupramoléculas basados en esta clase de ligandos orgánicos, transforma su obtención en un desafío. Las pirazolonas poseen ciertas ventajas, frente a otros ligandos, como; alta capacidad de funcionalización, buena solubilidad y alta disponibilidad. En este trabajo se describe la síntesis de nuevos ligandos multitópicos derivados de 1-(2-hidroxietil)-3-fenil-4-hidroxiimino o acetil-5-pirazolona y sus respectivos complejos de Cu(II). Las hidroxialquilpirazolonas se obtuvieron por condensación entre un β-cetoéster con 2-hidroxietilhidracina [2]. La posterior nitrosación o acetilación permite obtener los distintos ligandos en rendimientos de regulares a buenos. La síntesis de los respectivos complejos de Cu(II) muestra para los ligandos **1** y **2**, la formación de dos polímeros coordinación 1D isoestructurales (Figura), lo que confirma la similitud electrónica entre acil- y nitrosopirazolonas. El plano ecuatorial del metal se encuentra coordinado por dos *bis*quelato en posición *anti*, uno con respecto al otro y las posiciones axiales están ocupadas por los grupos hidroxilos anclados a N1. Ambos complejos muestran una marcada distorsión Jahn-Teller dando lugar a una octaedro elongado axialmente [3].



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DISEÑO DE COMPUESTOS ORGANOMETÁLICOS MIXTOS TRANSICIONALES / NO TRANSICIONALES

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Palabras Clave: *paladaciclo, DFT, éteres corona.*

Estudios previos del grupo han demostrado la capacidad catalítica de los paladaciclos y platinociclos con ligandos tiosemicarbazona y fosfinas[1]. Además, dado que los éteres corona se pueden usar como ligandos neutros para coordinar metales no transicionales[2] se genera la posibilidad de incluir en un metalaciclo otro metal, no transicional, dando como resultado compuestos polimetálicos mixtos.

El primer compuesto ciclometalado con éter corona fue sintetizado en 2001 por Bezosoudnova *et al.*[3] y a partir de entonces se han intentado sintetizar compuestos polimetálicos de esta naturaleza[4].

Esta comunicación tiene por objeto presentar una serie de paladaciclos con grupo funcional éter corona; así como un estudio para la optimización de los ligandos mediante cálculos DFT.

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IRREVERSIBLE COVALENT MODIFICATION OF *SALMONELLA TYPHI* TYPE I DEHYDROQUINASE BY A STABLE SCHIFF BASE: OPPORTUNITIES FOR ANTIVIRULENCE DRUG DISCOVERY

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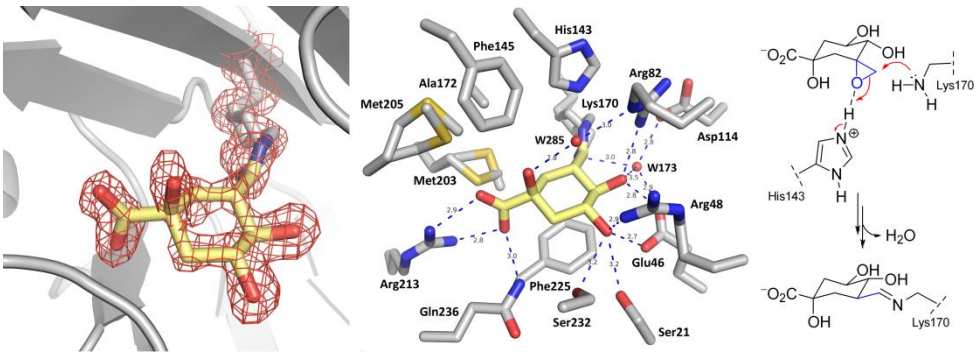
Keywords: *Bacterial Type I dehydroquinase, Schiff base, covalent modification*

The irreversible inhibition of type I dehydroquinase (DHQ1), the third enzyme of the shikimic acid pathway, has been investigated by structural, biochemical and computational studies [1,2]. Two epoxides, which are mimetics of the natural substrate, were designed as irreversible inhibitors of the DHQ1 enzyme and to study the binding requirements of the linkage to the enzyme. The epoxide with *S* configuration caused the covalent modification of the protein whereas no reaction was obtained with its epimer. The first crystal structure of DHQ1 from *Salmonella typhi* covalently modified by the *S* epoxide, which is reported at 1.4 Å, revealed that the modified ligand is surprisingly covalently attached to the essential Lys170 by the formation of a stable Schiff base. The experimental and Molecular Dynamics simulation studies reported here highlight the huge importance of the conformation of the C3 carbon of the ligand for covalent linkage to this type of aldolase I enzyme, revealed the key role played by the essential His143 as a Lewis acid in this process and show the need of a neatly closed active site for catalysis [3].



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IS CRYSTALLOGRAPHY PROPERLY TAUGHT AND LEARNED?

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Keywords: *crystallography, teaching, learning*

Crystallography is a vital part of much modern research into the structure and properties of materials ranging across many scientific fields like Chemistry, Biology, Biomedicine, Physics, Materials Science, Engineering and Mineralogy. However, although it underpins nearly all of the sciences today, it remains relatively unknown to the general public and it still seems to remain an unresolved matter in academic environments of even some developed countries. The American Crystallographic Association and the US National Committee for Crystallography suggested in 2006 that "perhaps due to rapid technological advances in the field of modern crystallography, there appears to be a declining number of professional crystallographers, as well as a lack of sufficient education and training in crystallography…" Indeed, as it occurs in Spain, this is very probably due to the fact that crystallography is erroneously considered as a minor technical issue, whose application and interpretation is trivial.

A website [1] is presented (http://www.xtal.iqfr.csic.es/Cristalografia/), designed not only to attract beginners to the fascinating world of crystals, but also as a tool for learning the skills needed to understand the science that tells us about the nature of crystals, and how they can show us the shape and dimensions of molecules, hormones, nucleic acids, enzymes, proteins... what their properties are and how they work in a chemical reaction, in a test tube, or inside of a living being. The different chapters of this website present the fundamental concepts of Crystallography, illustrated with numerous figures and animations, as well as hundreds of external links to reliable resources of information. This work, the result of an early essay by M. Martinez-Ripoll and F.H. Cano at the dawn of the 1990s, now appears as a live and frequently updated web, written in two languages (Spanish and English), receiving over 1,000 visitors a day from all countries, but especially US, Europe, India and Latin America. It was announced by the International Union of Crystallography (http://bit.ly/dHj0Q0) and selected by this institution as one of the most interesting sites for learning crystallography (http://bit.ly/1zCsBOX). It was offered as such in the commemorative web for the 2014 International Year of Crystallography (http://bit.ly/1BYMGyd), and suggested as the educational website to learn about crystals, diffraction and crystal structure determination in the brochure (http://bit.ly/1DXoqxP) prepared for the Crystal-Growing competition for UNESCO Associated Schools.

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ON THE CHEMICAL CONTROL OF THE PLANT RESPONSE TO ABIOTIC STRESS

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Keywords: *Cristalografía, Química Biológica, Bilogía de Plantas.*

Plants have to endure adverse environmental conditions due to their sessile nature, for that reason evolution has provided specialized protein networks to resist abiotic stress. The research on the molecular mechanism underlying these networks is important since it provides opportunities to generate or manage crops with enhanced resistance for our benefit.

The plant stress hormone abscisic acid (ABA) regulates many of the stress adaptive plant processes by the interaction with the PYR family of protein ABA receptors. This in turn, tunes the cell response by the inhibition of the family of PP2C protein phosphatases and the activation of the family of SnRK2 protein kinases. Biochemical, cellular and structural studies have shown that ABA triggers the PP2C inhibition by the formation of a ternary stable complex PYR-ABA-PP2C [1].

The generation of agonist and antagonist molecules of ABA has been revealed as a very interesting chemical approach to control plants response in stress situations [2]. To gain knowledge in this subject, we have solved the crystal structure of various crop plant receptors and its complexes with phosphatase and ABA and the agonist Quinabactin. Our data provide a totally new framework for the design of antagonist molecules using the geometrical restrains of the ABA binding pocket.

In addition, the knowledge of the different genomes of crops plants allows the identification and characterization of ABA receptors and phosphatases in plants with commercial value. Our work shows the potential applications of this knowledge to enhance plants abiotic stress resistance.

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ENSAMBLES METALOSUPRAMOLECULARES DE PLATA (I): INFLUENCIA DEL CONTRAIÓN EN LA DIVERSIDAD ESTRUCTURAL

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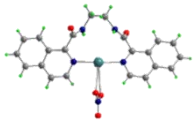
***Palabras Clave**: Ingeniería Cristalina, Bis(isoquinolina), Complejos de plata (I).*

La ingeniería de cristales consiste en el diseño y síntesis de materiales cristalinos mediante el auto-ensamblaje de unidades moleculares como iones metálicos o *cluster* y ligandos orgánicos con la finalidad de fabricar materiales multifuncionales [1]. Se sabe que las propiedades en el estado condensado están estrechamente relacionados con la forma en que las moléculas se empaquetan en el estado sólido [2]. Por este motivo es importante conocer como la estructura cristalina se modela bajo ciertas alteraciones.

En este trabajo nuestro interés está enfocado en el estudio de la variación estructural de una serie homologa de compuestos de coordinación de plata (I), [Ag(L)]X (X=NO_3^- (**1**), CF_3COO^- (**2**) y ClO_4^-(**3**)) y L= *N,N'*-Bis(1-isoquinolincarboxamido)etano). Los compuestos **1** y **2** son 0D y cada monómero se conecta a través de interacciones de enlace hidrógeno del tipo $NH^{\cdots}O_{(NO3^-\ o\ CF3COO^-)}$ para construir el empaquetamiento cristalino. **3** presenta una propagación del enlace coordinativo en 1D y cada cadena se une a través de enlaces $NH^{\cdots}O_{(clo4-)}$ para construir el cristal en 3D. Los complejos **1**, **2** y **3** presentan una configuración eclipsada en el puente alcano con ángulos de torsión de 65°, 60° y 65° respectivamente. Existe una pérdida de planaridad entre los anillos de isoquinolina en los complejos en el orden **3** >**2** >**1**, además en **3** el ángulo generado entre el plano del grupo amida y el plano del anillo de isoquinolina está 20° aproximadamente por encima de **1** y **2**. Esto permite entender por qué la red extendida 1D en **3** se transforma en 0D para **1** y **2.** Con el objetivo de estudiar la estructura electrónica de los complejos se evaluaron las propiedades fotoluminiscentes. Se observó una disminución en la intensidad de las bandas en relación al ligando aislado y la presencia de dos bandas con dos longitudes diferentes de emisión para los complejos.



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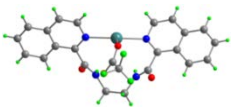
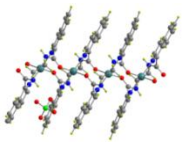


2-0D



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TUNING THE MAGNETIC BEHAVIOR IN MOF SOLID SOLUTIONS $[M_XCO_{1-X}(BTA)]_N$ M = MN^{II} & FE^{II}

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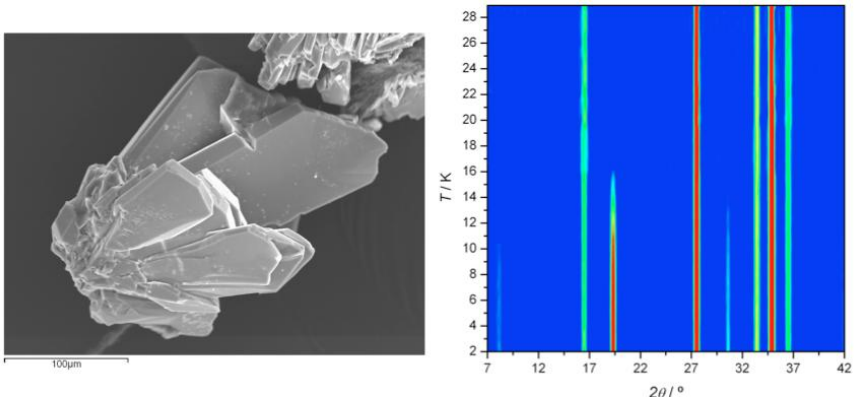
Keywords: *Solid Solutions, Molecular Magnetism, Neutron Diffraction*

The coordination polymers are crystalline materials formed by the combination of metal ions or clusters and organic spacers. Among the properties exhibited by these materials, magnetism is one of the most intriguing. To establish magneto-structural correlations in complex systems, the knowledge of the magnetic structure through neutron diffraction experiments (NPD) is of great importance. In this sense, we have recently reported a detailed study on the magnetic properties of the $[Co_2(bta)]_n$ (H_4bta = 1,2,4,5-benzenetetracarboxylic acid) compound [1]. It has also been reported that the Mn(II) and Fe(II)-based bta compounds are isomorphous [2] but the T_N temperatures are completely different, and therefore we decided to extend our neutron diffraction studies to these two complexes.

We also propose the study of the hybrid Mn^{II}-Co^{II} and Fe^{II}-Co^{II} metal-organic solid solutions (MOSS). The concentration of Co^{II} versus Mn^{II} and Fe^{II} has been confirmed via Dispersive X-ray Spectroscopy (EDS) (Fig. 1-left) and high-resolution neutron diffraction. The magnetic structure of the homometallic $[M_2(bta)]_n$ (M = Mn^{II} and Fe^{II}) and the MOSS have been studied via neutron diffraction measurements at different temperatures (Fig. 1-right). Funds from the Ministerio de Economía y Competitividad through MAT2014-57465-R are acknowledged.



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ESTUDIO DE LA REACTIVIDAD DE UN COMPLEJO BINUCLEAR κ^2N,Ge-AMIDINATOGERMILENO DE RUTENIO(0)

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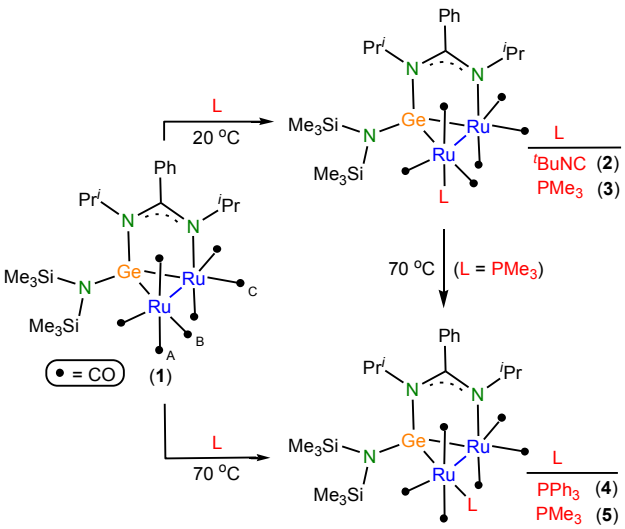
Palabras Clave: *complejos organometálicos, amidinatogermilenos, cálculos DFT*

Los compuestos divalentes de silicio, germanio, estaño y plomo, también conocidos como análogos pesado de los carbenos, metalenos del grupo 14 o tetrilenos pesados, son especies de gran interés en la química de los elementos representativos. Son moléculas muy reactivas capaces de coordinarse a metales de transición, activar moléculas pequeñas, insertarse en enlaces tipo sigma, formar aductos donor-aceptor, unirse a sustratos insaturados, promover cicloadiciones, etc. Sin embargo, debido a la inestabilidad de estos compuestos en presencia de aire o humedad, son todavía escasos los estudios de sus complejos con metales de transición y su posible actividad catalítica. Una forma de mejorar la estabilidad de estos tetrilenos es hacerlos formar parte de ligandos bidentados, en nuestro caso **amidinatogermilenos**.

En este trabajo se estudia la reactividad del complejo [Ru2{μ–κ^2Ge,N-Ge(^{i}Pr$_2$bzam)(HMDS)}(CO)$_7$] (**1**) en reacciones de sustitución de CO con ^{t}BuNC y varias monofosfinas.



Se observó que a temperatura ambiente se produce la sustitución de un CO axial de **1** (complejos 2 y 3), mientras que a 70^{0}C se obtiene la sustitución en posición ecuatorial (complejos 4 y 5). Un estudio teórico, mediante cálculos DFT, ha permitido determinar la estabilidad relativa de las especies **3** y **5** y el mecanismo de la isomerización axial-ecuatorial que transforma **3** en **5** a 70^{0}C.

S16: *Química y Cristalografía: Materia y Vida con Precisión Atómica*

ESTUDIO ESTRUCTURAL DE DIFERENTES COMPUESTOS DE TRICARBONIL RENIO (I) CON UN LIGANDO DERIVADO DE BENZOTIAZOL

Arantxa Pino-Cuevas[1], Rosa Carballo[1], Ezequiel M. Vázquez-López[1]

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Palabras Clave: *Benzotiazol, carbonil complejos, renio.*

La enfermedad de Alzheimer es una de las formas de demencia más comunes en los últimos años [1]. Desafortunadamente, el diagnóstico correcto de esta enfermedad es difícil, pudiéndose confirmar solo mediante la realización de un examen del tejido cerebral después del fallecimiento.

Por otra parte, se sabe que los pacientes afectados por esta enfermedad presentan depósitos anormalmente frecuentes de placas de β-amiloide en el cerebro [2], los cuales presentan afinidad por cierto tipo de compuestos. Un ejemplo de estos compuestos son los derivados de Benzotiazol [3].

En este trabajo se ha sintetizado y caracterizado un ligando thiosemicarbazona y se ha estudiado su reacción con el fragmento $[Re(CO)_3]^+$, que es un eficaz modelo de $[^{99m}Tc(CO)_3]^+$ actualmente usado en radiodiagnosis.

La reacción se ha realizado en diferentes medios de reacción obteniéndose compuestos de coordinación diferentes.

Todos los compuestos han sido caracterizados por diferentes técnicas espectroscópicas y a excepción del compuesto monomérico, también se han podido estudiar estructuralmente por difracción de rayos X de monocristal (Figura 1).

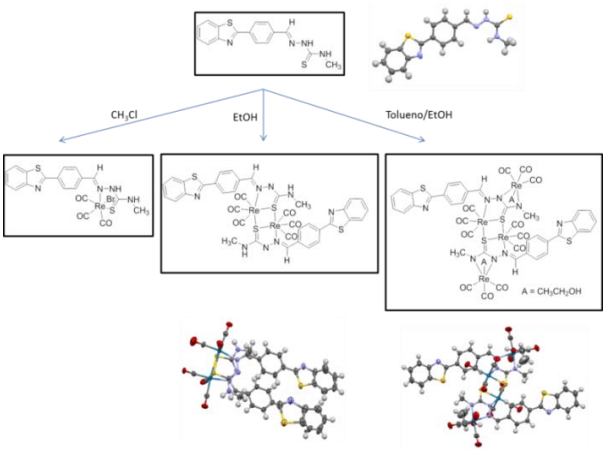

Figura 1: Esquema de los compuestos obtenidos.

Agradecimientos

A. P. C. agradece a la Universidad de Vigo por el contrato predoctoral.

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S16: *Química y Cristalografía: Materia y Vida con Precisión Atómica*

NEW COBALT (II) COORDINATION POLIMERS BASED ON FLEXIBLE TRIAZINE DERIVATIVES

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Keywords: *Metal-organic frameworks (MOF´s), Triazine, Cobalt, Hydrothermal synthesis.*

Metal-organic frameworks (MOF´s) are an emerging class of interesting molecular materials that have been extensively studied in the last decades[1]. They present great applications in gas storage, chemical sensing, catalysis and drug delivery due to the high porous hybrid structure. MOF´s are composed of metal ions or secondary building units (SBU) connected through organic linkers. The great advantage of MOF´s materials is that their properties can be tailored by the thoughtful selection of the organic ligand.

Our research deals with the synthesis and characterization of porous and magnetic MOF´s based on s-triazine derivatives. These ligands can be prepared from the cheap and commercially available cyanuric chloride (2,4,6-trichloro-1,3,5- triazine). Tri-substituted triazines have been extensively studied and porous MOF´s with high adsorption capacities have been constructed. The selective nucleophilic substitution of two chlorides with two 1,4-aminobenzoic groups (Fig. 1) is less explored and, upon MOF´s fabrication it shall be modified by the substitution of the remnant chloride of the triazine group by a specific functional group. The high spin state and large magnetic anisotropy of the Co(II) ion[2] adds promising magnetic properties to construct a multifunctional material.

Here we present the synthesis and structural characterization of a new cobalt metal-organic framework based on a flexible organic ligand containing the 1,3,5-triazine scaffold.

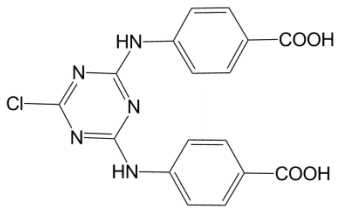

Fig.1. Triazine derivative ligand with two aminobenzoic acid subtituents.

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S16: *Química y Cristalografía: Materia y Vida con Precisión Atómica*

FREQUENIN/NCS-1 AS A PHARMACOLOGICAL TARGET FOR SYNAPSE REGULATION IN X-LINKED MENTAL RETARDATION AND AUTISM

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Keywords: *Calcium sensor, synapse regulation, drug desing, Fragile X, autism*

Pathologies such as X-linked mental retardation and autism result from abnormal synapse number and probability of neurotransmitter release per synapse. Recently we have described the mechanism by which these neuronal characteristics are co-regulated by the conserved Ca^{2+}-binding protein Frequenin/Neuronal Calcium Sensor 1 (Frq/NCS-1) and its binding partner Ric8, a receptor-independent activator of G protein complexes. Crystallographic studies with Drosophila Frq2 followed by site directed mutagenesis demonstrated that amino acids R94 and T138 are essential for Ric8 interaction and that Frq2 binds Ric8 through a surface-exposed hydrophobic crevice. Human Frq and Ric8 reproduce the binding and maintain the structural requirements. Thus, our structural data expose the Frq-Ric8 interacting surface as a potential pharmacological target for NCS-1 related diseases [1,2].

Virtual screening calculations have identified a family of small compounds as potential blockers of the NCS-1/Ric8 complex. *In vitro* binding studies show that these molecules are able to disrupt the NCS-1/Ric8 complex. The high-resolution X-ray structure of dFrq2 bound to one of the candidate molecules shows the mechanism of recognition and explains the activity of these compounds. Furthermore, *in vivo* data with Fragile X model Drosophila indicate that the crystallized compound is able to restore synapse number to healthy-flies levels. Taken together, our multidisciplinary approach demonstrates the potential use of this compound as a therapeutic drug against Fragile X Syndrome. Our crystallographic data will be key to improve the pharmacological properties of the candidate molecules for future development of lead regulators of mental disorders.

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S16: *Química y Cristalografía: Materia y Vida con Precisión Atómica*

SSNMR, CRYSTALLOGRAPHY AND COMPUTATIONAL STUDIES OF 1*H*-BENZOTRIAZOLE AND 5,6-DINITRO-1*H*-BENZOTRIAZOLE

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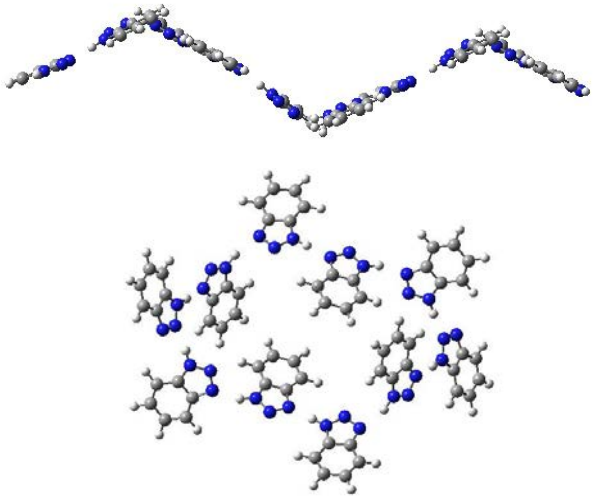
Keywords: *benzotriazoles, self-assembly, polymorphism, NMR, B3LYP/6-311++G(d,p)*

Amongst the three benzazoles, benzotriazoles are the least studied, even if they have many important properties [1]. They are also very different from the two others having much lower basicity and much higher acidity. The study of the two polymorphs of 1*H*-benzotriazole, α and β [2,3], as well as the crystal and molecular structures of 5,6-dinitro-1*H*-benzotriazole obtained in various conditions has been approached by a combination of solid state NMR (SSNMR), and X-ray crystallography [4]. DFT calculations have been carried out on both polymorphs of 1*H*-benzotriazole, the α an infinite chain (catemer) and the β a very unusual ten-membered ring.



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S16: *Química y Cristalografía: Materia y Vida con Precisión Atómica*

ESTUDIO MAGNETO-ESTRUCTURAL DE POLÍMEROS DE COORDINACIÓN DE COBRE(II) CON LIGANDOS TERPIRIDINA SUSTITUIDOS

D.Toledo[1], Y.Moreno[2], O.Peña[3], T. Roisnel[3], J-Y. Pivan[3,4].

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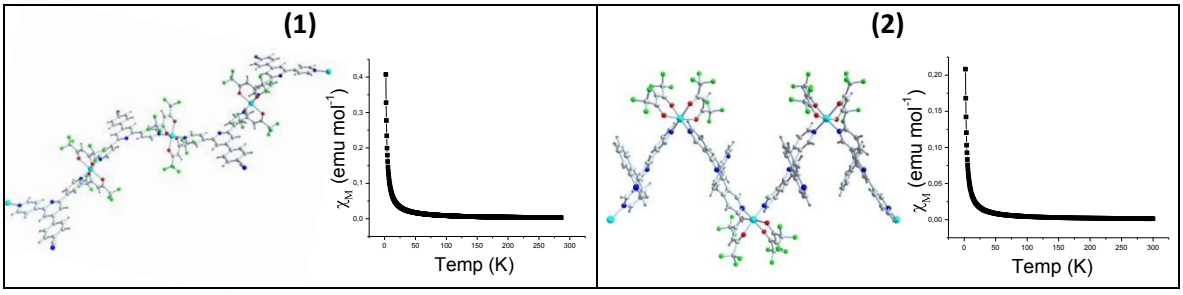
Palabras Clave: *Terpiridinas, Estructura Cristalina, Propiedades Magnéticas.*

Los ligandos terpiridina sustituidos son bloques de construcción ideales para ensambles moleculares y/o polímeros con interesantes propiedades magnéticas, luminiscentes, de absorción, catálisis, etc. [1,2]. Estos ligandos son capaces de formar sistemas 1D, 2D o 3D y ofrecen una gran capacidad de coordinación gracias a la disposición divergente de los átomos N-dadores en la terpiridina y a la variada gama de grupos funcionales que pueden ser incorporados como sustituyentes. En este trabajo, presentamos la síntesis y caracterización de dos nuevos polímeros de coordinación 1-D: $[Cu_2(hfac)_4(\mathbf{L1})_2]_n$ **(1)** y $\{[Cu(hfac)_2(\mathbf{L2})]\cdot CHCl_3\}_n$ **(2)**, los cuales fueron obtenidos de la reacción de $Cu(hfac)_2$ (hfac=hexafluoroacetilacetonato) con los ligandos 4'-(4-cianofenyl)-4,2':6',4''-terpiridina **(L1)** y 4'-(4-quinolinyl)-3,2':6',3''-terpiridina **(L2).** El sistema **1** es una cadena ondulada 1-D de nodos octaédricos trans-$\{CuN_2(hfac)_2\}$. Las cadenas se unen en el espacio por diversos enlaces hidrógeno: CH···O y CH···F, debido a la presencia del grupo CF_3. El sistema **2** consiste en una cadena zig-zag de nodos octaédricos cis-$\{CuN_2(hfac)_2\}$; las cadenas adyacentes se unen por interacciones CH···N, CH···O, CH···F. CH···π y π-π, que involucran a los sustituyentes de quinolina y el grupo CF_3. La presencia de más de un centro paramagnético nos llevó a indagar posibles interacciones cooperativas, por lo que hemos realizado mediciones de susceptibilidad; mediante ajuste de modelos teóricos, se determinaron los parámetros ***g, J*** y χ_{PIT}.



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S17. Otros Ámbitos de la Química (OAQ) / Other topics in Chemistry

Este simposio está destinado a la presentación de contribuciones de cualquier ámbito de la Química no contemplado en los restantes simposios".

Todas las contribuciones son en formato póster

This symposium will be devoted to the presentation of contributions in any topic of Chemistry that does not fit in the different symposia.

All contributions are presented as posters

Organizadores:

Moisés Canle López (UDC)

Emilia Iglesias Martínez (UDC)

José Pérez Sestelo (UDC)

Darío Prada Rodríguez (UDC)

María Teresa Rodríguez Blas (UDC)

Juan Arturo Santaballa López (UDC)

e-mail de contacto: congreso.bienal.rseq2015@udc.es

Lunes 20, Martes 21 y Miércoles 22 de Julio 2015

18:30	***Sesión de Posters***

Nota: Todas las contribuciones de este simposio se presentan en formato póster y permanecerán expuestos durante toda la duración del Congreso. Se defenderán en las tres sesiones previstas para ello.

Presentaciones Póster (PP)

Listado de presentaciones póster

ESTUDIO DE LA REACTIVIDAD ATMOSFÉRICA DE $C_6F_{13}CH=CH_2$ CON OZONO

J. Albaladejo

FUNCIONALES DE LA DENSIDAD Y CORRECCIÓN DEL ERROR DE SUPERPOSICIÓN DE BASES. UN ESTUDIO COMPARATIVO EN EL DÍMERO DEL AGUA.

José M. Alía

ESTUDIO DE LA ALTERACIÓN DEL ENTORNO OCTAÉDRICO DEL CROMÓFORO (N) DE CADA SISTEMA $Y_{2-x}M_xN_yO_3$ AL VARIAR N (Ca (II) O Ba(II))

A. Antón

COMPARACIÓN DE NIVELES DE LITIO SÉRICO POR DOS MÉTODOS COMERCIALES FRENTE A DETERMINACIÓN POR ABSORCIÓN ATÓMICA

Laura Barrenechea

ACTIVIDAD CATALASA DE COMPLEJOS DE METALES DE TRANSICIÓN CON UN NUEVO LIGANDO AZAMACROCÍCLICO trans-SUSTITUIDO

Rufina Bastida

APPLICATION OF OPEN SOURCE MOLECULAR MODELLING AND VIRTUAL SCREENING SOFTWARE TO MOLECULAR IMPRINTING

F. Bates

HYDROLYSIS OF AROMATIC ESTERS IN MICELLAR MEDIA

I. Brandariz

PROCESOS DE GUANILACIÓN DE AMINAS EMPLEANDO UN CATALIZADOR NO METÁLICO

Rafael Fernández-Galán

TRANSPORTE DE ACIDOS NUCLEICOS A TRAVÉS DEL COMPLEJO DEL PORO NUCLEAR

M.A. Freire-Picos

SÍNTESIS DE NUEVOS COMPEJOS CICLOMETALADOS DE Pt(II) CON LIGANDOS HIDRAZONA

P. Gaudino

SIMULTANEOUS MERCURY AND SELENIUM SPECIATION IN MARINE SEAFOOD BY HPLC-ICP-MS

J.L. Gómez-Ariza

NITROEPOXIDES AS STARTING MATERIALS FOR THE PREPARATION OF VICINAL DIAMINES AND 1,4-DIAMINO HETEROCYCLIC COMPOUNDS

F. V. González

ESPECIACIÓN NO CROMATOGRÁFICA DE MERCURIO EN AGUAS Y ACEITES COMESTIBLES MEDIANTE MICROEXTRACCIÓN CON NANOPARTÍCULAS MAGNÉTICAS FUNCIONALIZADAS SEGUIDA DE ETAAS

M. Hernández Córdoba

NUEVO PIGMENTO ROJO MULTIFUNCIONAL BASADO EN LA RED HUÉSPED $Y_2Zr_2O_7$ DOPADO CON LOS IONES Tb^{+3} y Fe^{+3}

M. Jovaní

UN COMPLEJO BIMETÁLICO DE Pd(II) CON ENTORNO DE COORDINACIÓN INUSUAL

J. Lado

INTERACCIONES π-π ENTRE ANILOS QUELATO ORGANOMETÁLICOS EN COMPLEJOS DE Pd(II) y Pt(II)

I. Marcos

DEGRADACIÓN ATMOSFÉRICA DE VINIL ÉTERES: REACTIVIDAD CON ÁTOMOS DE CLORO DE BUTIL VINIL ÉTER Y PROPIL VINIL ETER

E. Martínez

DETERMINACIÓN DE ALQUILFENOLES Y BISFENOL A EN MUESTRAS DE AGUA MEDIANTE EXTRACCIÓN EN FASE SÓLIDA Y CROMATOGRAFÍA LÍQUIDA ACOPLADA A ESPECTROMETRÍA DE MASAS EN TÁNDEM

J.A. Martínez-Pontevedra

BORON – THE FORGOTTEN ELEMENT? CLUSTERIZATION OF PHYSICAL-CHEMISTRY, MATERIALS SCIENCE, BIOCHEMISTRY AND MATHEMATICS

Josep M. Oliva

POLYDIMETHYLSILOXANE (PDMS)-THYMOL/NITROPRUSSIDE DELIVERY COMPOSITE SENSOR FOR RAPID ANALYSIS OF AMMONIUN IN WINES

M. C. Prieto-Blanco

COMPLEJOS DE LOS LANTÁNIDOS DERIVADOS DE PLATAFORMAS MACROCÍCLICAS PARA APLICACIÓN EN IMAGEN MOLECULAR

R. Pujales-Paradela

REARRANGEMENT OF A KREBS-TYPE POLYOXOMETALATE UPON COORDINATION OF N,O-BIS(BIDENTATE) LIGANDS

S. Reinoso

H_2 GENERATION MECHANISMS IN THE REACTION OF Al CLUSTERS WITH WATER MOLECULES: A THEORETICAL STUDY

U. Rivero-González

EVALUATION OF THE TEMPLATE ACTIVITY OF Sr(II), Ca(II) AND Mg(II) IN THE SYNTHESIS OF LATERAL MACROBICYCLES DERIVED FROM 4,13-DIAZA-18-CROWN-6: WHAT THE INTERMEDIATES TELL US

Teresa Rodríguez-Blas

A DFT STUDY OF THERMAL AND PHOTOCHEMICAL CYCLIZATION OF 1,2-DI-THIENYLETHENES (DTEs)

J.A. Santaballa

CHELATION ASSISTANCE AS A TOOL FOR THE SELECTIVE PREPARATION OF MESOIONIC CARBENES

Juan Tejeda

TIME COURSE OF THE FRACTIONAL MODIFICATION OF THE MONOCYCLIC ENZYME CASCADES, DEFINED IN AN ALTERNATIVE WAY INVOLVING THE TWO FORMS OF THE MODIFIED PROTEIN

R. Varón

INTEGRACIÓN DE NANOTUBOS DE CARBONO EN DISPOSITIVOS ELECTROANALÍTICOS COMO HERRAMIENTAS PARA LA CLASIFICACIÓN DE VINOS BLANCOS BASADA EN EL CONTENIDO DE POLIFENOLES ESTIMADO MEDIANTE DETECCIÓN AMPEROMÉTRICA

A. Zapardiel

NACIMIENTO DE UN NUEVO ECOSISTEMA: EVOLUCIÓN DE LA CALIDAD FÍSICO-QUÍMICA Y BIOLÓGICA DEL LAGO DURANTE EL LLENADO DEL HUECO MINERO DE AS PONTES

Alfredo Suárez

S17: *Otros Ámbitos de la Química*

ESTUDIO DE LA REACTIVIDAD ATMOSFÉRICA DE $C_6F_{13}CH=CH_2$ CON OZONO

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Palabras Clave: *química física atmosférica, hidrofluoroolefinas (HFOs), ácidos carboxílicos perfluorados (PFCAs), cinética.*

Los ácidos carboxílicos perfluorados (PFCAs) han demostrado ser bioacumulativos y potencialmente tóxicos. Los tejidos humanos y muestras de animales recogidos en zonas geográficamente remotas contienen este tipo de compuestos [1-3]. Sólo se conocen emisiones directas de PFCAs a través de procesos industriales. Por otro lado, además se ha observado que los PFCAs pueden originarse a partir de sustancias precursoras mediante procesos atmosféricos de oxidación con los principales radicales troposféricos [4]. Estos precursores son las hidrofluoroolefinas (HFO, $C_xF_{2x+2}CH=CH_2$) que se han propuesto como sustitutos de los hifrofluorocarbonados (HFC) en espumas de expansión o en unidades móviles de climatización. En el presente trabajo se ha realizado el estudio completo de la reacción en fase gas del $C_6F_{13}CH=CH_2$ con uno de los oxidantes troposféricos, el ozono. Se ha determinado la constante de velocidad mediante técnicas cinéticas relativas en dos cámaras de simulación atmosférica de vidrio, una de 264 L de capacidad que utiliza SPME/GC-MS como técnica de detección, y otra cámara de 16 L acoplada a un FTIR [5]. Dichas cámaras permiten trabajar en las condiciones ambientales de presión y temperatura, 720 Torr y 298 K, utilizando aire como gas portador.

También se ha realizado el estudio de productos formados en la reacción con SPME/GC-MS [5] lo que permite proponer un mecanismo para la reacción de $C_6F_{13}CH=CH_2$ con Ozono en condiciones atmosféricas.

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S17: *Otros Ámbitos de la Química*

FUNCIONALES DE LA DENSIDAD Y CORRECCIÓN DEL ERROR DE SUPERPOSICIÓN DE BASES. UN ESTUDIO COMPARATIVO EN EL DÍMERO DEL AGUA.

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Palabras Clave: *DFT, corrección BSSE, dímero del agua, enlace de hidrógeno.*

Se estudia el rendimiento de cuarenta funcionales de la densidad (incluyendo GGA y mGGA puros, híbridos y doble-híbridos) en combinación con la base 6-311++G(3df,2p), calculando aspectos energéticos, geométricos y vibracionales del dímero del agua, tanto en la superficie de energía potencial normal (espacio normal, EN) como en la corregida para el error de superposición de bases (espacio *counterpoise*, ECP). Las referencias de comparación son de origen teórico (CCSD(T)/aug-cc-pVTZ) y experimental.

En promedio, los funcionales estudiados subestiman la energía de interacción del dímero. Los resultados correspondientes al dímero optimizado en el ECP son prácticamente idénticos a los que se obtienen mediante el método tradicional (optimización normal seguida de la corrección BSSE). Es preferible, en general, emplear la energía electrónica (1.0 kJ/mol de error promedio) que la energía ZPE corregida (3.0 kJ/mol de error promedio). Por familias, los funcionales GGA puros y los doble-híbridos son los que mejores resultados proporcionan. No hay grandes diferencias entre puros meta GGA, híbridos GGA e híbridos metaGGA, aunque los segundos son los que se aproximan más al valor objetivo. El empleo de correcciones (dispersión empírica o larga distancia) implica, salvo en el caso del funcional wB97X, un incremento de la energía de interacción, que se sitúa en valores muy próximos al objetivo en APFD, CAM-B3LYP y B2PLYPD.

La geometría del dímero es bastante bien reproducida por los funcionales, si bien ninguno de ellos supera en calidad a los métodos correlacionados (MP2 y CCSD(T)). La geometría optimizada en el ECP mejora un 40% con respecto a la optimizada en el EN y dicha mejora se produce en la mitad de los funcionales.

Los modos vibracionales del dímero del agua, sobre todo en la zona de bajas frecuencias, son reproducidos correctamente por los funcionales y superan en precisión a los obtenidos empleando MP2 en 23 de los funcionales estudiados. En general, sólo presentan errores significativos algunos miembros de los grupos mGGA, tanto funcionales puros como híbridos, siendo llamativos los pobres resultados de los funcionales muy parametrizados (M06 en sus diferentes variantes y BMK). De nuevo, los resultados vibracionales en el ECP son ligeramente mejores que los calculados en el espacio normal.

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ESTUDIO DE LA ALTERACIÓN DEL ENTORNO OCTAÉDRICO DEL CROMÓFORO (N) DE CADA SISTEMA $Y_{2-x}M_xN_yO_3$ AL VARIAR N (Ca (II) O Ba(II))

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Palabras Clave: *óxido de itrio, mecanismo de coloración, Pechini.*

En los últimos años se ha producido un aumento del estudio del óxido de itrio (Y_2O_3) debido a que sus propiedades refractarias y su alta estabilidad térmica hacen de este óxido un ideal candidato para numerosas aplicaciones. En este trabajo, en concreto, se ha estudiado la influencia en la coloración del Y_2O_3 codopado con Ba(II) o Ca(II) usando como cationes cromóforos Cr(III), Fe(III), Ni(II), Co(III) y Cu(II) y también se utilizaron los lantánidos Eu(III) y Er(III). El mecanismo de coloración se estableció a partir de los resultados obtenidos. Utilizando una modificación del método Pechini se sintetizaron y caracterizaron varios tipos de disoluciones sólidas. El sistema sintetizado fue $Y_{2-x}M_xN_yO_3$ donde M es igual al elemento cromóforo, N es igual a Ba(II) o Ca(II) y la x toma valores comprendidos entre 0,14 y 0,06. A 1200^{o}C se obtuvo una única fase cristalina de Y_2O_3. Se estudiaron las diferencias que ocurrían en el entorno octaédrico de los cromóforos al dopar el sistema con Ba(II) o Ca(II) mediante el uso de técnicas de caracterización como difracción de rayos X, espectroscopia de UV-Vis y de emisión y medidas colorimétricas.

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COMPARACIÓN DE NIVELES DE LITIO SÉRICO POR DOS MÉTODOS COMERCIALES FRENTE A DETERMINACIÓN POR ABSORCIÓN ATÓMICA

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Palabras Clave: *Litio, suero, plasma, Absorción Atómica, método colorimétrico.*

Objetivo: Sustituir la determinación de concentración sérica de *litio* realizada actualmente mediante un método de *Absorción Atómica* con llama (Perkin Elmer 1100 B) por métodos *colorimétricos* automáticos (ADVIA® 2400, Dimension® Siemens) para determinaciones urgentes, se procedió al estudio de correlación de los tres métodos.[1]

Material y métodos: Alícuotas de 200 µL de muestras séricas. Estas alícuotas son analizadas por metodología de *Absorción Atómica* con llama y *colorimetría* (que se basa en la formación de complejos de los iones de *litio* con un cromoionóforo específico). Fueron analizadas dos veces por semana por ambos métodos y se efectuó el control de calidad en cada uno de ellos según sus respectivos protocolos, comenzando el estudio a mediados de abril y abierto a fecha de hoy.

Resultados: De las primeras cuarenta muestras de *suero* se obtuvieron los resultados que se expresan en la ilustración 1. Su precisión por Control bajo: 0.71 meq/L, CV: 4.1%, Control alto: 1.36 meq/L, CV: 2.7%.

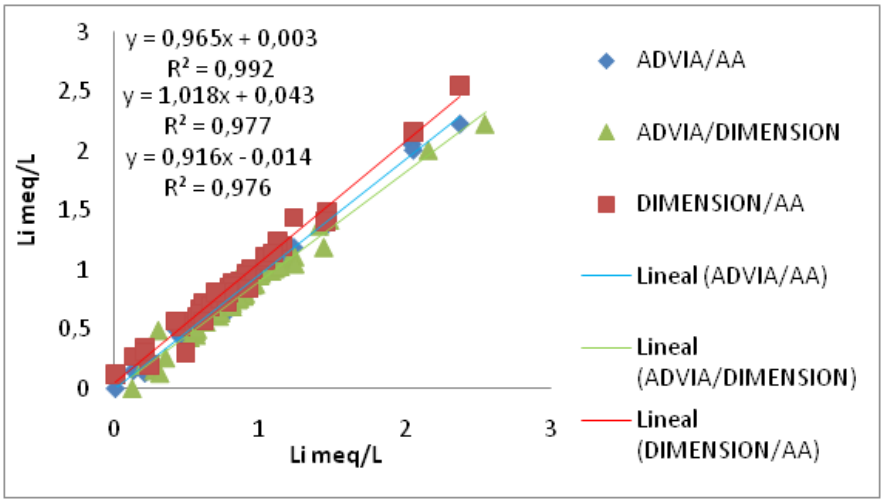

Ilustración 1: Correlación del *Litio* en *suero*.

Discusión y conclusiones: Se observa una muy buena correlación. Una vez cerrada la fase de análisis los datos se estudiarán estadísticamente por regresión Passing-Bablok y Bland-Altman para poder concluir si los valores por uno u otro método son intercambiables.

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ACTIVIDAD CATALASA DE COMPLEJOS DE METALES DE TRANSICIÓN CON UN NUEVO LIGANDO AZAMACROCÍCLICO *trans*-SUSTITUIDO

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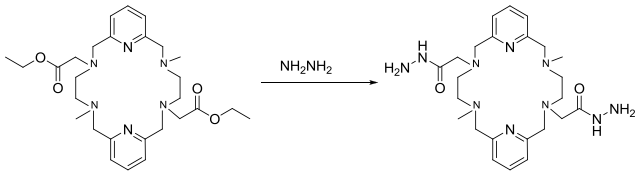
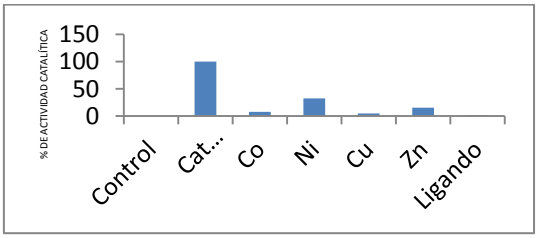
Palabras Clave: *macrociclos, complejos metálicos, actividad catalasa*

La síntesis de ligandos azamacrocíclicos Py_2N_4, derivados del precursor 2,6-diformilpiridina, funcionalizado con *pendant-arms* acetohidrazona, permite la obtención de ligandos con un mayor número de átomos dadores.[1] Asimismo, este nuevo tipo de ligandos presenta propiedades interesantes, como la variación de su solubilidad en disolución acuosa. Este comportamiento los hace potencialmente adecuados para el estudio de sus aplicaciones bioanalíticas y bioinorgánicas.



Se analizó el poder catalítico de un nuevo ligando *trans*-sustituido con grupos acetohidrazona y la de sus nitrato-complejos con metales de transición, evaluándose su actividad respecto al de catalasa de hígado bovino. Para ello se utilizó el reactivo comercial Amplex-Red® con el H_2O_2 presente en la reacción de oxidación.[2]

Se estudiaron los complejos de cobalto, cobre, cinc y níquel, evidenciándose una mayor actividad como catalasa para el complejo de níquel. Comprobado el efecto antioxidante del ligando y sus complejos, se realizarán ensayos de supervivencia celular, valorando su eficacia como neutralizadores de estímulos tóxicos que provocan el envejecimiento celular.



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APPLICATION OF OPEN SOURCE MOLECULAR MODELLING AND VIRTUAL SCREENING SOFTWARE TO MOLECULAR IMPRINTING

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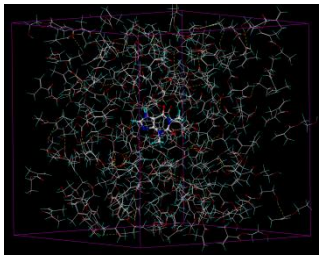
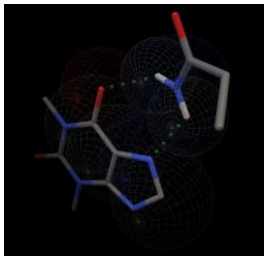
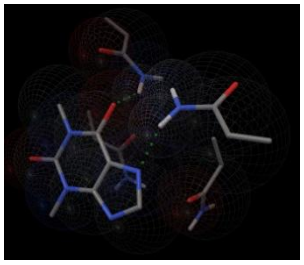
Keywords: *molecularly imprinted polymers (MIPs), computational modelling, high throughput virtual screening,*

Molecular imprinted polymers (MIPs) have experienced exponential growth in popularity and research interest over the past several decades. Determination of optimal protocols for these porous imprinted polymers has long been done practically via laboratory experimentation which can be both expensive and laborious.

Virtual modelling and screening allows this design to be drastically shortened through computer-aided monomer selection (high throughput virtual screening) , template-monomer ratio determination (stoichiometry and molecular dynamics) and composition design (primary, co- and ter-polymer affinity analysis) [1]. Along with replication of the conventional screening events, herein is also presented a 'rebinding' docking procedure using the open source molecular docking suite, AutoDock [2]. This can be used to rank structural analogues as potential dummy templates for target molecules which are not suitable for imprinting due to sensitivity, price. A preliminary study based of methylxanthines with commonly used functional monomers MAA, acrylimide and HEMA was used to confirm the efficacy of the model; screen captures of this (Theophylline-Acrylamide) are displayed below.







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HYDROLYSIS OF AROMATIC ESTERS IN MICELLAR MEDIA

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Keywords: *hydrolysis, ion-exchange equilibrium,mass action model, micelle*

Micelles are supramolecular assemblies that have been widely used as drug delivery systems [1]. The hydrophobic part of the surfactant constitutes the inner core of these aggregates, that are stabilized because the hydrophilic part of the molecules is oriented towards the aqueous solvent. In this work, two drugs have been studied, 2-naphthyl acetate (2NA) and phenyl acetate (PhA), both with a hydrophobic aromatic ring that, in solution, is included in the core of the micelles, while the ester moiety is localized in the interface, where it can be hydrolyzed by OH^- ions. This fact allows the kinetic method to be used and the variation in the rate of the alkaline hydrolysis yields the association constants of both compounds with micelles. The cationic surfactants used were: dodecyltrimethylammonium bromide (DTABr), tetradecyl-trimethylammonium bromide (TTABr), and hexadecyltrimethylammonium bromide (CTABr) and the corresponding hydroxides (DTAOH, TTAOH and CTAOH) at 25ºC. The pseudo-first order rate constants increase with surfactant concentration when the counter-ions are OH^- ions. On the contrary, a maximum is reached for bromide surfactants, at constant hydroxyl ion concentration, because there is a competition between OH^- and Br^- attracted toward the surface of the micelle. The adsorption equilibrium of OH^- to the micelles has been used to calculate the concentration of these ions in the micelle surface, this is known as the mass action model [2], that has been used satisfactorily to explain experimental data and yields, as fitting parameters: 1) the adsorption equilibrium constants of both esters with micelles, that can be considered equal with different counter-ion, for the same substrate, and 2) the rate constant in micellar medium, demonstrating that the more important effect in the micellar catalysis is the concentration of reactants in the micelles[3].

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PROCESOS DE GUANILACIÓN DE AMINAS EMPLEANDO UN CATALIZADOR NO METÁLICO

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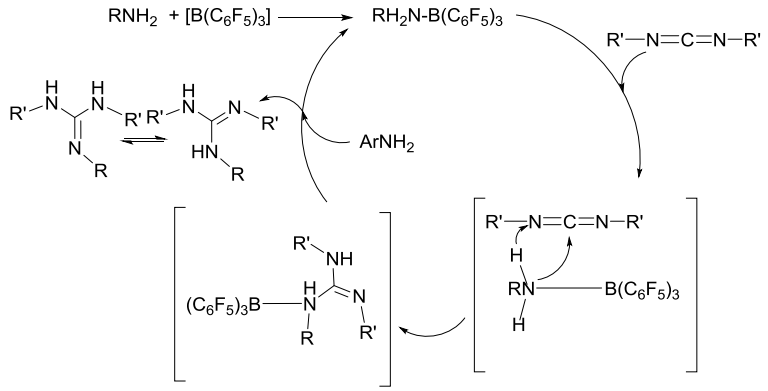
Palabras Clave: *borano/guanidina/catálisis*

Los enlaces carbono-nitrógeno constituyen uno de los enlaces más importantes en la química orgánica y las ciencias de la vida. Entre las metodologías disponibles para obtener este tipo de enlaces se utilizan principalmente catalizadores metálicos cuya reconocida toxicidad y alto precio están dando lugar al desarrollo de nuevos métodos alternativos. En este sentido, las reacciones de hidrofuncionalización proporcionan una eficiencia atómica del 100%, un proceso libre de residuos, son de relativamente bajo coste y materiales de partida asequibles.

Actualmente, el tris(pentafluorofenil)borano [$B(C_6F_5)_3$] está adquiriendo un importante protagonismo como ácido Lewis no convencional, no tóxico y estable. [1] Como parte de nuestro continuo estudio en la química de guanidinas y complejos guanidinato,[2] presentamos aquí el uso de este borano como un excelente catalizador para la adición tanto de aminas aromáticas como alifáticas a carbodiimidas.



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TRANSPORTE DE ACIDOS NUCLEICOS A TRAVÉS DEL COMPLEJO DEL PORO NUCLEAR

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Palabras Clave: *RNA, transporte, Complejo de Poro Nuclear*

En las células eucariotas, el transporte del ácidos nucleicos y más concretamente de RNA mensajero (mRNA) del núcleo al citoplasma a través del Complejo del Poro Nuclear (NPC) es un proceso clave en la regulación de la expresión génica que en último término, determina que proteínas van a ser sintetizadas por las células. El NPC se organizan en 5 sub-complejos proteicos, incluido Nup84 o complejo Y. El NPC está además implicado en la regulación transcripcional y el procesamiento de RNA [1,2]. El complejo Y está constituido por 7 proteínas (Nup84, Seh1, Sec13, Nup85, Nup120, Nup133 y Nup145c) y se localiza simétricamente en las caras citoplasmática y nuclear del NPC, en los anillos externos [3].

Para nuestro estudio obtuvimos mutantes que tienen anulados los genes *NUP84* y *SEH1* que codifican para componentes del NPC. Con éstas cepas analizamos la expresión de genes con procesamiento 3´alternativo de RNA utilizando como modelo la levadura *Saccharomyces cerevisiae*. Los genes *RNA14* y *CBP1* son transcritos dando lugar a 3 iso-formas de mRNA pero pertenecientes a dos grupos de genes poliadenilados. *RNA14* con dos mRNAs truncados (respecto a la región codificadora) y *CBP1* con las 3 iso-formas no truncadas. Se investigaron el efecto de la fase de cultivo y del cambio de la temperatura de crecimiento (el mutante *⊿seh1* es incapaz de crecer a 37^{o}C). Las diferencias encontradas en la predominancia de los transcritos de *CBP1* y *RNA14* en ambos mutantes sugieren un efecto gen-específico de cada componente del complejo Nup84 que no había sido descrito previamente, y ha sido posible descubrir gracias a la utilización de genes con poliadenilación alternativa.

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SÍNTESIS DE NUEVOS COMPEJOS CICLOMETALADOS DE Pt(II) CON LIGANDOS HIDRAZONA

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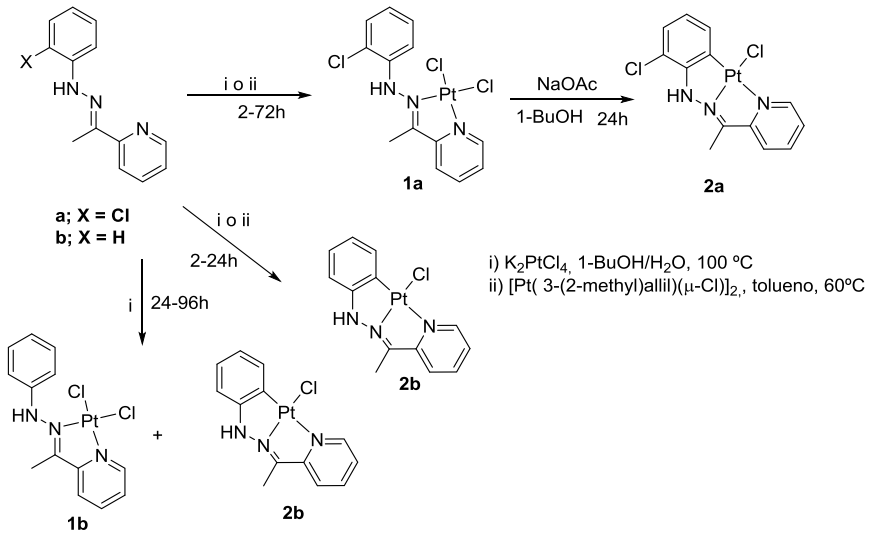
Palabras Clave: *Ciclometalación, Ligandos hidrazona, platino.*

En los últimos años nos hemos interesado en las reacciones de preparación de compuestos de Pd(II) derivados de ligandos hidrazona y hemos podido comprobar que estos últimos forman fácilmente compuestos ciclometalados [1]. En esta comunicación mostramos el comportamiento de los mismos ligandos (**a** y **b**) frente a compuestos de platino (II).

Como se puede apreciar en el esquema de reacción el comportamiento de ambos ligandos frente a la reacción de ciclometalación es completamente distinto.

Así la hidrazona **a** reacciona tanto con K_2PtCl_4 como con [Pt(η^3-(2-methyl)allil)(μ-Cl)]$_2$ para formar un complejo en el que el ligando actúa como bidentado quelato, pero en el que no se ha producido la metalación del anillo aromático (**1a**). La formación del complejo ciclometalado solo se consigue por reacción de **1a** con acetato sódico a fin de neutralizar el cloruro de hidrógeno formado.



El comportamiento del ligando **b** es, sin embargo, muy diferente. La reacción de **b** con sales de Pt(II) en las mismas condiciones conduce a la obtención del complejo ciclometalado **2b**; el compuesto con la hidrazona actuando como quelato **1b** solo se obtiene mediante reacción prolongada (24-96h) y siempre mezclado con el ciclometalado **2b**. A falta de estudios mecanísticos, la mayor reluctancia de **a** para experimentar la formación del anillo ciclometalado probablemente se debe a la desactivación del anillo frente al ataque electrófilo del átomo de Pt.

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SIMULTANEOUS MERCURY AND SELENIUM SPECIATION IN MARINE SEAFOOD BY HPLC-ICP-MS

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Keywords: mercury speciation, marine food

Our understanding about the mechanisms of biological activities and biogeochemical cycling of mineral and trace element species has been substantially advanced during recent years with the help of chemical speciation studies. The safety and nutritional quality of food are determined by both the total level and the speciation, i.e. chemical form(s), of trace elements in foods.

The European Commission recommends restrict the consumption of large fish (including swordfish, tuna) to pregnant women, nursing mothers and young children because they may contain high levels of mercury (Hg). In this sense, the European Community establishes maximum total mercury in fish of 0.5 mg / kg, although in some species of fish the limit of Hg concentration is set at 1.0 mg/kg (such as swordfish and tuna). The Agency for Toxic Substances and Disease Registry (ATSDR) includes mercury as the third of 275 potentially hazardous substances to human health present in the environment, based on their abundance, their toxicity and potential exposure levels that can be achieved in humans. The toxicity of mercury depends not only of the total concentration but also on the chemical form (species) in which it is found. In the case of organic species of mercury, methylmercury (MeHg+) is more toxic than inorganic forms. MeHg+ primarily affects the nervous system and causes irreversible damage in the brain, and others deleterious effects.

Despite this fact, several studies show that selenium (Se) affects in the toxicity of Hg, as demonstrated in 1967 in an experiment with rats treated with mercuric chloride and selenite.

The present study considers the study of selenium:mercury ratio in the fish studied, to evaluate the antagonistic action between these elements and the possible toxic effects of the intake of seafood in the human health. For this purpose we have optimized a method for multielement determination in fish muscle by HPLC coupled to ICP-ICP-MS equipped with a collision/reaction cell. This method has been validated using certified reference materials. It has also been optimized and validated a method for speciation of mercury in muscle extracts from different species of fishes commonly consumed in Spain using HPLC-ICP-MS.

The highest concentration of mercury was found in swordfish and tuna (5.86 ± 0.2 and 1.58±0.02 μg g^{-1} dry weight, respectively), these being those with larger and in turn predators of smaller fishes, which also contain this toxic element (biomagnification). In the case of selenium, the highest concentrations were found also found in tuna and swordfish (3.79 ± 0.13 and 2.27 ± 0.08 μg g^{-1} dry weight, respectively).

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NITROEPOXIDES AS STARTING MATERIALS FOR THE PREPARATION OF VICINAL DIAMINES AND 1,4-DIAMINO HETEROCYCLIC COMPOUNDS

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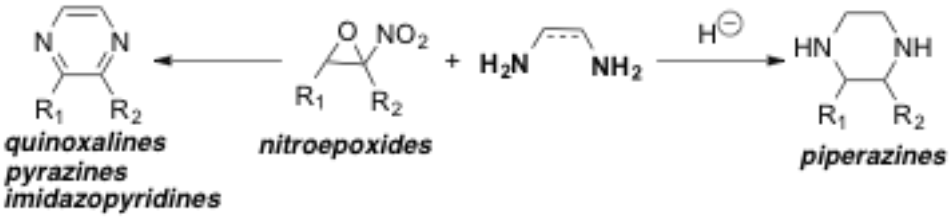
Keywords: *Diamines, quinoxalines, pyrazines, piperazines, tetrahydroquinoxalines*

Vicinal diamines can be accessed in a highly diastereoselective fashion by the treatment of nitroepoxides with primary amines and then a reducing agent. When using a chiral primary amine, racemic nitroepoxides are transformed into chiral diamines as a single enantiomers (>95:5 er) through a dynamic kinetic asymmetric transformation (DYKAT). The overall process is a one-pot procedure combining the exposure of nitroepoxides to chiral amines to afford diastereomeric mixtures of aminoimines and subsequent stereoselective imine reduction.[1]

Nitroepoxides are easily transformed into 1,4-diamino heterocycles such as quinoxalines and pyrazines by treatment with 1,2-benzenediamines and ammonia, respectively. Additionally, related saturated heterocycles, such as piperazines and tetrahydroquinoxalines, can be accessed by treatment with 1,2-diamines and a reducing agent. These transformations are efficient, provide access privileged, bioactive structures, and produce minimal waste. [2]



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S7: *Otros Ámbitos de la Química*

ESPECIACIÓN NO CROMATOGRÁFICA DE MERCURIO EN AGUAS Y ACEITES COMESTIBLES MEDIANTE MICROEXTRACCIÓN CON NANOPARTÍCULAS MAGNÉTICAS FUNCIONALIZADAS SEGUIDA DE ETAAS

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Palabras Clave: *mercurio, agua, aceites, especiación, nanopartículas funcionalizadas, ETAAS.*

Se presenta un procedimiento sencillo para la determinación de mercurio inorgánico y mercurio total basado en su diferente retención sobre nanopartículas de ferrita recubiertas de Ag nanomérica (Fe_3O_4@Ag) y funcionalizadas con, bien 2-mercaptoetano sulfonato sódico (MESNa), bien L-Cisteína (Cys), respectivamente.

Los datos experimentales muestran el Hg(II) presente en una disolución es retenido por Fe_3O_4@Ag@MESNa, mientras que otras formas de mercurio como MeHg, Me_2Hg, EtHg, PhHg, Ph_2Hg no interaccionan con las nanopartículas. Sin embargo, cuando la funcionalización se realiza con L-cisteína todas las formas de mercurio son retenidas cuantitativamente. Este comportamiento permite cuantificar las especies de mercurio inorgánicas, metiladas y aromáticas en aguas y en el importante caso de muestras de aceite comestible.

Tras la separación de las nanopartículas magnéticas con ayuda de un campo magnético intenso, se puede retroextraer el mercurio a un microvolumen de fase acuosa conteniendo ioduro potásico. La cuantificación se consigue llevando una porción de este extracto acuoso al detector de ETAAS. La retención es cuantitativa y, en las condiciones optimizadas se consigue un factor de enriquecimiento (FE) de aproximadamente 200.

Para la discriminación entre mercurio inorgánico y las principales especies orgánicas de mercurio se combina el proceso con el empleo de cartuchos de separación en fase sólida y elución selectiva. Con ello se consigue el fraccionamiento entre mercurio inorgánico, metilado y fenilado. De esta forma resulta posible el fraccionamiento en aceites comestibles, aceites de pescado utilizados en dietas y aceites vegetales sobrenadantes de conservas de pescado sin necesidad de tratamiento previo.

El procedimiento propuesto se ha validado con empleo de materiales de referencia y mediante ensayos de recuperación de las distintas formas de mercurio.

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NUEVO PIGMENTO ROJO MULTIFUNCIONAL BASADO EN LA RED HUÉSPED $Y_2Zr_2O_7$ DOPADO CON LOS IONES Tb^{+3} y Fe^{+3}

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Palabras Clave: *pigmentos cerámicos, cool pigments, sol-gel.*

Los óxidos con estructura pirocloro son unos materiales que presentan una gran variedad de aplicaciones en diversos campos de la tecnología, tales como luminiscencia, fotocatálisis, conductores iónicos, etc [1]. En este sentido el campo de los pigmentos cerámicos no es una excepción. La estructura pirocloro posee la capacidad de incorporar una gran variedad de elementos en su estructura, los cuales pueden jugar el papel de cromóforos. Siguiendo esta tendencia son muchas las investigaciones dirigidas a introducir cromóforos en la estructura pirocloro, si bien es cierto en la mayoría de los casos se trata de iones que presentan una gran toxicidad. La normativa actual requiere la búsqueda de nuevos sistemas pigmentantes que eviten el uso de cromóforos tóxicos. En el presente trabajo se sintetizó la disolución solida $Y_{2-x}Tb_xZr_{2-y}Fe_yO_{7-\delta}$ (x=0;0.25 y=0;0.15;0.25;0.35) mediante el método de síntesis sol-gel polimérico. Se obtuvieron muestras con una coloración rojiza sin el uso de cromóforos tóxicos.Las muestras que contenían terbio presentaron fase única, así como unas excelentes coloraciones. Además presentaron una muy buena estabilidad en esmalte obteniendo mejores coordenadas cromáticas, que el pigmento comercial en las mismas condiciones.

Otra de las potenciales aplicaciones de este pigmento es en el campo de los denominados “cool pigments” o lo que es lo mismo pigmentos que poseen una elevada reflectancia en el infrarrojo cercano [3]. Estos pigmentos son usados con el objetivo de disminuir el calentamiento en el interior de los edificios, provocado por la incidencia de los rayos solares en fachadas y tejados. Las muestras presentaron unos valores de reflectancia óptimos presentando un uso potencial en dicho campo.

Por lo tanto se sintetizó un pigmento de una tonalidad roja en ausencia de iones tóxicos, potencialmente aplicable en el campo de los pigmentos cerámicos, así como en el campo de los materiales aislantes térmicos para fachadas y tejados.

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UN COMPLEJO BIMETÁLICO DE Pd(II) CON ENTORNO DE COORDINACIÓN INUSUAL

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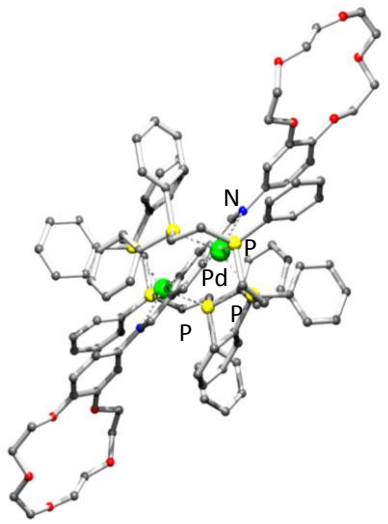
Palabras Clave: *Compuestos ciclometalados, paladio, poliedro de coordinación.*

Es conocido que la naturaleza del ligando puede modificar las preferencias geométricas del átomo del metal en los complejos de coordinación y de esta manera es posible diseñar compuestos con estructura inusual. Entre estos ligandos se encuentran las fosfinas y, en concreto, la trifosfina terciaria $PhP(CH_2CH_2PPh_2)_2$ trifos, que puede forzar un índice de coordinación cinco en complejos de Pd(II), cuya preferencia por la coordinación plano cuadra es conocida. No obstante, determinar el poliedro de coordinación utilizando técnicas espectroscópicas normales, no siempre es sencillo.

En la presente comunicación presentamos la estructura cristalina de un complejo dinuclear de Pd(II) en el cual el poliedro de coordinación de ambos puede describirse como una situación intermedia entre una bipirámide trigonal y una pirámide de base cuadrada.

Dicho complejo se obtiene por reacción de un polímero organometálico funcionalizado con anillos de éter corona y la trifosfina trifos.

La unidad asimétrica del cristal está formada por medio catión complejo y cloruro que actúa como contraión. El catión completo se genera mediante centro de inversión situado en el centro del anillo fenílico metalado. Por lo tanto el entorno de cada átomo de paladio está formado por un átomo de carbono del anillo central, los tres átomos de fósforo del ligando trifos y un átomo de nitrógeno de un grupo imino. El conocido como parámetro τ tiene un valor de 0.42. Dicho parámetro se usa para determinar la trigonalidad de complejos con índice de coordinación 5 y tiene un valor de 1 para una geometría de bipirámide trigonal perfecta y 0 para una pirámide de base cuadrada. El valor registrado en el complejo los sitúa a medio camino entre ambos poliedros. La distancia Pd-N es de 2.567 (5) y es más larga que los 2.23 A descritos para un complejo de Pd(II) pentacoordinado [1] aunque más corto que el valor dado para interacciones débiles Pd-N (en el intervalo de 2.6 a 2.8 A).



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INTERACCIONES π-π ENTRE ANILOS QUELATO ORGANOMETÁLICOS EN COMPLEJOS DE Pd(II) y Pt(II)

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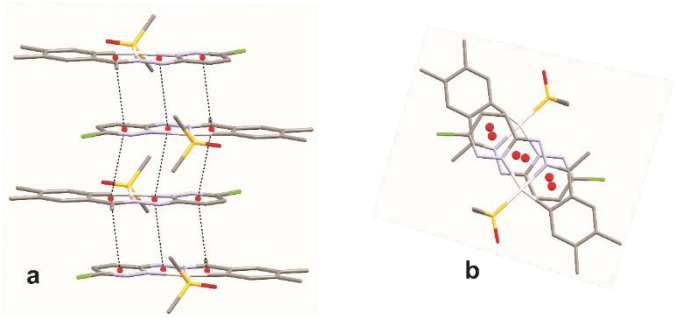
Palabras Clave: *Interacciones intermoleculares, metalociclos, apilamiento π*

Es conocida la importancia de las interacciones intermoleculares a la hora de determinar la forma en que las moléculas se empaquetan en el estado cristalino, lo que a su vez modifica o modula las propiedades de estas especies. Estas ideas han sido objeto de estudio en el campo de "Crystal Engineering" y han tenido aplicaciones en áreas tan diversas como la química farmacéutica o la química supramolecular, por mencionar algunas. Entre las mencionadas cabe destacar las interacciones de tipo π-π y, aunque la vasta mayoría de los estudios se han llevado a cabo sobre sistemas orgánicos, recientemente se ha observado que también pueden presentarse entre anillos quelato, lo que abre nuevas perspectivas al diseño de cristales organometálicos [1].

En la presente comunicación presentamos la estructura cristalina de un complejo organometálico de Pt(II) que presenta una estructura cuasi planar en la cual un total de cuatro anillos, dos anillos quelato, uno organometálico y el otro de coordinación, un anillo fenílico y uno de piridazina se encuentran fusionados en el átomo del metal. En el cristal se observa como las moléculas se encuentran apiladas formado columnas a lo largo del eje cristalográfico *a* con una distancia interplanar de, aproximadamente, 3.55 A. Entre dichas moléculas se observan numerosas interacciones de tipo π-π que implican tanto a los anillos quelato inorgánicos, como a los anillos ciclometalados y a los de piridazina, con distancias entre centroides de 3.6 A. El apilamiento es antiparalelo y se corresponde a una disposición de "slipped stacking" (ver figura anexa).



Muy posiblemente la existencia de la mencionadas interacciones se debe al carácter "pseudo aromático" que presentan este tipo de anillos y que se pone de manifiesto en diversas propiedades estructurales de los mismos [2]

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DEGRADACIÓN ATMOSFÉRICA DE VINIL ÉTERES: REACTIVIDAD CON ÁTOMOS DE CLORO DE BUTIL VINIL ÉTER Y PROPIL VINIL ETER

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Palabras Clave: *éteres vinílicos, constantes de velocidad, mecanismos de reacción, reacciones en fase gas, química atmosférica*

Los compuestos orgánicos volátiles se generan en la atmosfera procedentes de muy variadas fuentes naturales y antropogénicas. En particular, los éteres vinílicos utilizan en fabricación de adhesivos y revestimientos, como disolventes ó como aditivos de los combustibles[1]. El principal proceso de eliminación de estos compuestos en la atmósfera es su reacción con los oxidantes atmosféricos: radicales OH y NO_3, ozono y átomos de cloro. Aunque se dispone de información cinética de las reacciones de vinil éteres con OH, NO3 y ozono[2-4], los datos disponibles de las reacciones con Cl son escasos.

En este trabajo, se han determinado las constantes de velocidad de las reacciones de átomos de cloro con butyl vinil eter y propil vinil eter ($CH_3(CH_2)_3OCH=CH_2$ y $CH_3(CH_2)_2OCH=CH_2$. Los experimentos se realizaron en un reactor de vidrio pirex de 50 litros en atmósfera de N_2 a P atmosférica y T ambiente, y utilizando espectroscopía infrarroja por transformada de Fourier (FTIR) como sistema de detección. Las constantes de velocidad medidas fueron (en unidades moléculas cm^{-3} s^{-1}): 1.15×10^{-9} y 5.87×10^{-10} para butyl vinil eter y propil vinil eter. Estos valores indican una elevada reactividad de estos compuestos con átomos de cloro. A fin de determinar el mecanismo de reacción, se han estudiado los productos generados en la reacción con butil vinil éter usando FTIR y adicionalmente, cromatografía de gases-espectrometría de masas con analizador de tiempo de vuelo (GC-MS/TOF). Los principales productos detectados han sido cloroacetato de butilo, HCOCl y formato de butilo. Se ha propuesto un mecanismo de reacción iniciado por una reacción de adición del cloro a uno de los carbonos del doble enlace. Se han estimado los tiempos de vida troposféricos de estos compuestos concluyendo que la reacción con Cloro no constituye la principal vía de degradación comparando con otros oxidantes como los radicales OH y NO_3 salvo en ambientes donde las concentraciones de cloro alcancen elevados valores.

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S17: *Otros Ámbitos de la Química*

DETERMINACIÓN DE ALQUILFENOLES Y BISFENOL A EN MUESTRAS DE AGUA MEDIANTE EXTRACCIÓN EN FASE SÓLIDA Y CROMATOGRAFÍA LÍQUIDA ACOPLADA A ESPECTROMETRÍA DE MASAS EN TÁNDEM

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Palabras Clave: *alquilfenoles, bisfenol A, extracción en fase sólida, cromatografía líquida, espectrometría de masas*

Los alquilfenoles y el bisfenol A son compuestos fenólicos que se utilizan en una gran variedad de aplicaciones. El bisfenol A es un monómero utilizado en la producción de policarbonatos o resinas epoxi, que a su vez se emplean en una gran variedad de productos plásticos (envases alimentarios, botellas, etc) [1]. Por su parte, alquilfenoles como el 4-tert-octilfenol, 4-n-octilfenol y 4-n-nonilfenol, son los principales productos de degradación de los surfactantes alquilfenoles etoxilados no iónicos, que se utilizan habitualmente en aplicaciones domésticas, industriales y agrícolas, tales como detergentes, papel y celulosa, textiles, pesticidas agrícolas, aceites combustibles y lubricantes, metales y plásticos [2]. El uso generalizado de estos compuestos ha originado que se encuentren ampliamente distribuidos en el medioambiente.

Los alquilfenoles y el bisfenol A pueden actuar como disruptores endocrinos, causando una gran variedad de efectos adversos, y de ahí, que estos contaminantes hayan sido incluidos en la legislación de control medioambiental. La Unión Europea [3] ha establecido límites muy restrictivos para octilfenoles y nonilfenoles en diferentes tipos de aguas superficiales, y ha incluido el bisfenol A dentro de la lista de sustancias a revisar en un futuro, para su posible identificación como sustancia prioritaria.

Se presenta una nueva metodología de análisis para la determinación de estos compuestos en aguas continentales: Se comienza con una extracción en fase sólida, seguido de determinación mediante cromatografía líquida acoplada a espectrometría de masas en tándem. La extracción en fase sólida permite conseguir extracciones muy selectivas con un elevado factor de concentración de la muestra acuosa. La espectrometría de masas en tándem ofrece excelente sensibilidad y gran selectividad. Así, la metodología desarrollada permite dar cumplimiento a las normas de calidad ambiental en el ámbito de la política de aguas.

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S17: *Otros Ámbitos de la Química*

BORON – THE FORGOTTEN ELEMENT? CLUSTERIZATION OF PHYSICAL-CHEMISTRY, MATERIALS SCIENCE, BIOCHEMISTRY AND MATHEMATICS*

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Keywords: *boron, quantum chemistry, molecular architectures, biochemistry, mathematics*

Since the disclosure of borane compounds, used for rocket fuel in the 1950's during the Soviet Union – USA space career, an enormous amount of literature of synthesis of boranes and their derivatives has appeared in the literature [1]. In the last 15 years we have been involved with the determination of the electronic structure of heteroborane derivatives, such as carboranes, as ground states [2] and excited states [3]. The knowledge of the electronic structure of molecular architectures built from polyhedral heteroboranes, through quantum chemical computations, leads to very interesting results, such as the possibility of using chains, rings and three-dimensional structures as molecular magnets [4], the use of borane structures to produce new lasers [5], and the determination of the yet-unknown role of boron, if any, in biology [6]; the {mass\atomic}(%) content of boron in human beings is $\{70\backslash 3\}\times 10^{-6}$!, as compared to {3\1.1} and {18\12} for nitrogen and carbon respectively. Why do we have such tiny amounts of boron as compared to carbon or nitrogen? Why does boron have such rich architectural molecular constructs as compared to nitrogen? As compared to carbon, there is only a difference of one electron! Clusterization of boron compounds – polyhedral (metala)heteroboranes – is due to the need of satisfying (quantum) valencies when combined - namely, a chemical bond - but having less electrons than carbon; hence clusterization occurs, such as in the icosahedral dianion $B_{12}H_{12}^{2-}$. We also use the construction of hypothetically stable borane structures by concatenating pentagonal structures in order to study unsolved problems in mathematics, such as the number of structures that can be built given a number of building units / molecules (self-avoiding walks).

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* Dedicated to Paul von Ragué Schleyer (1930-2014), *in memoriam*

S7: *Otros Ámbitos de la Química*

POLYDIMETHYLSILOXANE (PDMS)-THYMOL/NITROPRUSSIDE DELIVERY COMPOSITE SENSOR FOR RAPID ANALYSIS OF AMMONIUN IN WINES

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Keywords: *Ammonium sensor, wine samples, delivery PDMS composite*

Nitrogen compounds play an important role in the fermentation kinetic and production of aromatic compounds and some undesirable compounds like SH_2. Low ammonium levels during the alcoholic fermentation increase the production of SH_2. Diammonium phosphate is added during the fermentation to avoid a deficit of ammonium. However, high residual ammonium levels in wines favour the microbiological instability [1]. The quantification of ammonium with other nitrogen compounds can be performed using chromatographic methods and previous derivatization. The use of these methods for the ammonium monitoring has drawbacks related to the analysis time, the cost and portability of the analysis system.

In a previous work, a PDMS- $[NH_4]^+$ composite sensor based on the Berthelot reaction was developed to monitoring ammonium in water samples [2,3]. In the present work, this composite sensor was tested to the $[NH_4]^+$ analysis in different types of wines (must, white and sweet wines). Comparable results were obtained from both, solution and de PMDS composite containing the reagents. Matrix effects were evaluated spiking wine samples with 150 and 200 mgL^{-1} ammonium. Obtained recoveries (80 %-90%) found showed that there is not matrix effect in the optimized method. Values of ammonium up to 250 mg L^{-1} were quantified in wine samples. For the ammonium monitoring, the method proposed achieves a good requirements of the portability and cost.

Acknowledgements

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COMPLEJOS DE LOS LANTÁNIDOS DERIVADOS DE PLATAFORMAS MACROCÍCLICAS PARA APLICACIÓN EN IMAGEN MOLECULAR

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Palabras Clave: *Lantánidos, Imagen por Resonancia Magnética, Macrociclos*

Los complejos de los iones trivalentes de los lantánidos presentan gran interés debido a su aplicación como agentes de contraste en Imagen por Resonancia Magnética (IRM). La mayor parte de los agentes de contraste clásicos son complejos de Gd^{3+} con ligandos de tipo poliaminocarboxilato que proporcionan una estabilidad termodinámica elevada y cinéticas de disociación lentas, evitando así la liberación del ion metálico tóxico.[1] En los últimos años ha surgido una nueva clase de agentes de contraste que funcionan mediante el mecanismo de transferencia de saturación por intercambio químico (CEST, de las siglas en inglés de 'Chemical Exchange Saturation Transfer').[2] Los agentes de contraste basados en este método utilizan la señal de RMN de protón del agua que se modula mediante la transferencia de magnetización saturada generada mediante la irradiación a la frecuencia de absorción de protones del agente que intercambian con el medio. El funcionamiento de un agente CEST se ilustra en la Figura 1. En ausencia de saturación (Figura 1, izquierda) los dos conjuntos de protones intercambiables presentan una señal proporcional a sus respectivas magnetizaciones. Cuando se satura la señal de los protones del agente CEST esta señal desaparece mientras que la señal del agua disminuye su intensidad, generando así el contraste (Figura 1, derecha). En la presente contribución se presentarán una serie de ligandos macrocíclicos y sus complejos de los lantánidos, diseñados como agentes CEST. Estos sistemas derivan de la plataforma macrocíclica ciclen, y contienen grupos amida intercambiables.

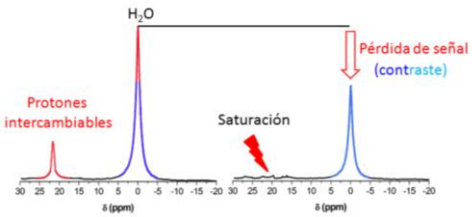

Figura 1. Representación esquemática del funcionamiento de un agente CEST.

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S17: *Otros Ámbitos de la Química*

REARRANGEMENT OF A KREBS-TYPE POLYOXOMETALATE UPON COORDINATION OF N,O-BIS(BIDENTATE) LIGANDS

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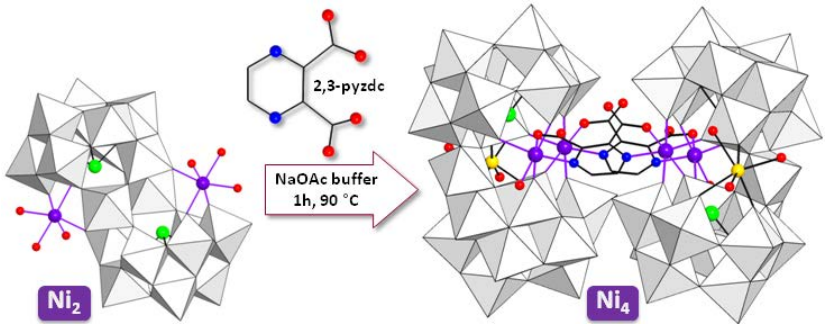
Keywords: *Polyoxometalates, Coordination, Crystal Structure, Solution Stability*

Organic derivatization of polyoxometalates (POMs) is a current hot topic for these anionic clusters composed of oxo-bridged early transition metals. The replacement of labile terminal molecules with organic ligands in 3d-metal substituted POMs is a suitable approach to obtain such type of hybrid derivatives, but still remains largely unexplored. We have recently studied the reactivity toward N,O-chelating ligands of a representative family of 3d-metal substituted POMs, the Krebs-type $[\{M(H_2O)_3\}_2(WO_2)_2(SbW_9O_{33})_2]^{10-}$ anions (M = Mn, Co, Ni, Zn), and found that isolation of hybrid clusters is fully dependent on the specific nature of the ligand [1].

Herein we report the results obtained from analogous studies performed with the N,O-bis(bidentate) bridging ligands pyrazine-2,5- and -2,3-dicarboxylate [2]. While the former is inert, the latter shows selectivity towards the Ni-containing precursor (**Ni_2**). The attack of the ligand promotes a rearrangement of the POM skeleton to lead to the dimeric hybrid species $[\mu\text{-}\{2,3\text{-pyzdc}\}_2\{Ni_2(H_2O)Sb_2W_{20}O_{70}\}_2]^{24-}$ (**Ni_4**, see the Figure below), which is formed by two unprecedented 20-tungsto-2-antimonate(III) clusters linked by two N,O-bis(bidentate) ligands. The dimeric assembly undergoes full dissociation in water that can be partially hindered upon addition of acetone as identified by ESI-mass spectrometry. The magnetic properties of **Ni_4** are dominated by the zero-field splitting of Ni^{II} centers.



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S17: *Otros Ámbitos de la Química*

H_2 GENERATION MECHANISMS IN THE REACTION OF Al CLUSTERS WITH WATER MOLECULES: A THEORETICAL STUDY

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Keywords: *Aluminium clusters, Hydrogen generation, Water molecules.*

The reaction of aluminium clusters with water molecules is a subject of intense research both experimentally and theoretically due to its technological importance as a possible source of H_2. Despite that research work many aspects of the H_2 generation and release mechanisms are unclear.

We have studied from a theoretical point of view the H_2 generating reactions between negative and positively charged Al clusters and water molecules that take place in the flow tube experiments performed by Castleman et al. [1] and Arakawa et al. [2]. We have focussed on $Al_{17}^{(-,+)}$.

We have studied different adsorption positions of the water molecules on the cluster surface as well as the most likely water-splitting and molecular hydrogen eliminations. As a first step, we have taken and geometrically re-optimized the cluster-frame structures using previous theoretical calculations, such as those by Aguado et al. [3].

We have also performed a dynamical analyses based on QCT (quasi-classical trajectories) and RRKM simulations.

We have evaluated the impact of tunneling or catalytic Grotthuss-type mechanisms in the water and H_2-elimination steps by means of transition-state theory.

Our results, which are compared with former work in the case of the anionic system [1,4,5,6], unveil new mechanisms.

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EVALUATION OF THE TEMPLATE ACTIVITY OF Sr(II), Ca(II) AND Mg(II) IN THE SYNTHESIS OF LATERAL MACROBICYCLES DERIVED FROM 4,13-DIAZA-18-CROWN-6: WHAT THE INTERMEDIATES TELL US

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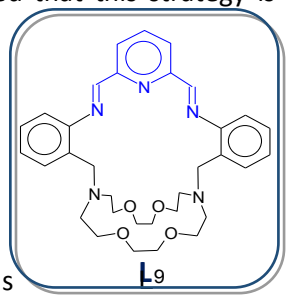
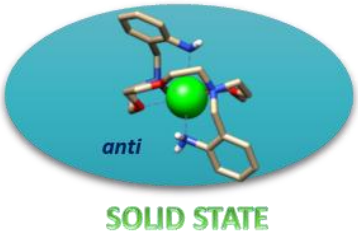
Keywords: *Macrobicycle, Template Synthesis, Alkaline-Earth, Dynamic Equilibrium*

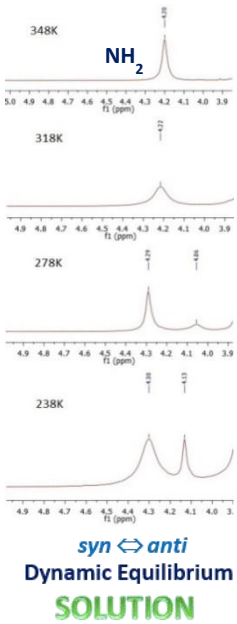
The use of metal template agents is an excellent synthetic strategy in the preparation of those macrocycles that cannot be synthesized by direct reaction from its organic precursors due to the predomination of polymerization side reactions. We have reported that this strategy is necessary in the formation of Schiff-base lateral macrobicycles derived from *N*,*N'*-bis(aminobenzyl)-diazacrowns, where a template capable to force the *syn* conformation of the precursor diamine is required. The Ba(II) ion was found to be a useful template in this case [1]. As a continuation of that work, in this contribution we evaluate the template effectiveness of other alkaline-earth ions (Sr, Ca, Mg) in the formation of the versatile **macrocbicycle L**, which is known to behave as a lead(II) extracting agent [2].



Our present results indicate that both Sr(II) and Ca(II) are effective templates in the synthesis of **L**. The **study of the intermediates** shows that, although in the solid state the three metal ions induce an *anti* conformation of the diamine precursor, a dynamic equilibrium ***anti*** ⇔ ***syn*** occurs in solution for Sr(II) and Ca(II), which explains the effective template behavior of both metal ions. On the contrary, Mg(II) cannot force the required *syn* conformation in solution and lacks of template activity.



A study on the effect that the solvent (acetonitrile *versus* ethanol) as well as the use of microwaves have on the template process has been also carried out.



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A DFT STUDY OF THERMAL AND PHOTOCHEMICAL CYCLIZATION OF 1,2-DI-THIENYLETHENES (DTEs)

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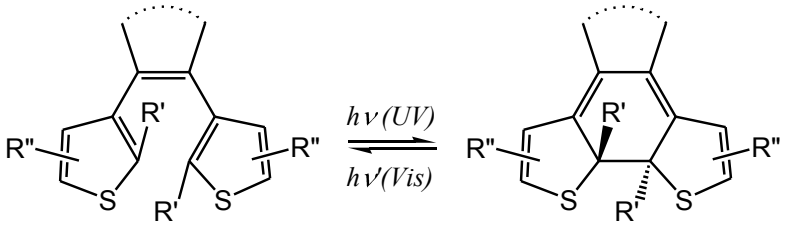
Keywords: *1,2-di-thienylethenes (DTEs), molecular switching, DFT, photocyclization*

Organic photochromic compounds, like 1,2-di-thienylethenes (DTEs), have received increased interest due to their potential applications in optoelectronic molecular devices, such as molecular switches, logic gates, and information storage devices. The molecular switching of DTEs is based on an efficient and reversible ON–OFF control photocyclization: reaction between colorless ring-opened and colored ring-closed isomers by selective irradiation.[1]



Both isomeric forms show marked differences, not only in their absorption spectra, but also in other physical properties (*e.g.* fluorescence intensity, redox potentials, etc.).
This communication describes the computational study, electronic structure calculations, of the thermal and photochemical cyclization between colorless ring-opened and colored ring-closed isomers. All calculations have been performed with the GAUSSIAN-09 program suite. Geometries were fully optimized by using density functional theory (DFT) with the Becke3LYP functional (B3LYP) level with 6-31++G** and 6-311++G** basis sets. Rigid rotor and harmonic oscillator models were used for the calculation of thermodynamic parameters. Solvation was simulated using the density-based solvation model (SMD).

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CHELATION ASSISTANCE AS A TOOL FOR THE SELECTIVE PREPARATION OF MESOIONIC CARBENES

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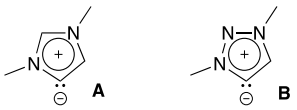
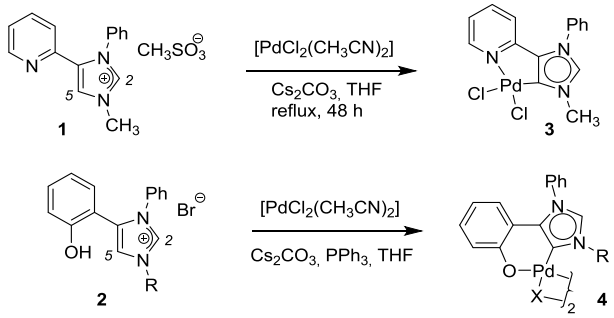
Keywords: *Carbene, mesoionic, palladium.*

Mesoionic carbenes (MICs) are a type of *N*-heterocyclic carbenes (NHCs) that require mesoionic resonance forms to represent their structure (**A** and **B**)[1] and are bound to the transition metal through the carbene carbon.



Imidazol-2-ylidenes are more stable than imidazol-4-ylidenes and classical C(2)-bound NHCs are obtained in most cases. The selectivity in favor of the abnormal coordination seems to be related to steric control, however, in most cases these compounds are obtained as mixtures with the normal NHC complexes. Protection by bonding of an alkyl or aryl group is the most widely used method to prepare this kind of complexes [2].

We speculated that chelation assistance could govern the selectivity in obtaining C(4)- *versus* C(2)-bound NHC complexes without the need for C(2)-protection. This hypothesis was tested by designing the imidazolium salts **1** and **2**. In these molecules both the C(2) and C(5) positions of imidazolium are able to form a carbene but only deprotonation of the C(5)–H can generate a complex stabilized by the chelation effect. MIC–Pd **3** and **4** were the only compounds obtained after treatment with $[PdCl_2(CH_3CN)_2]$ using Cs_2CO_3 as base, despite the low steric bulk of the wingtip group R and the high acidity of C(2)–H [3].



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TIME COURSE OF THE FRACTIONAL MODIFICATION OF THE MONOCYCLIC ENZYME CASCADES, DEFINED IN AN ALTERNATIVE WAY INVOLVING THE TWO FORMS OF THE MODIFIED PROTEIN

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Keywords: *Enzyme, kinetic, monocyclic, cascades, fractional modification*.

This paper presents the time course progress of the fractional modification of a monocyclic enzyme cascade, based on a more complete than usual definition of fractional definition given by Varon *et al*. [1,2], for a steady-state study only, as the quotient of the sum of all forms of the modified protein, *i.e.* the free one and the intermediate complex converter enzyme of the original protein-modified protein, between the initial concentration of the target protein.

From this general equation, obtained under three assumptions necessary to linearise the set of differential equations describing the kinetic of the system, we derive, as particular cases, other simpler expressions, by applying additional simplifying assumptions, which have, therefore, a smaller range of validity. We discuss the relationships between the kinetic parameters and concentrations needed for the fulfillment of both, the necessary and unnecessary, assumptions. The goodness of the analysis was tested by using the simulated time progress curves, corresponding to the whole course reaction, obtained by numerical integration.

Seven arbitrarily chosen examples differing in one or more of the values of the concentrations and/or kinetic parameters have been used to support the results. This contribution is an extension of a previous one concerning only with the steady-state.

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S17: *Otros Ámbitos de la Química*

INTEGRACIÓN DE NANOTUBOS DE CARBONO EN DISPOSITIVOS ELECTROANALÍTICOS COMO HERRAMIENTAS PARA LA CLASIFICACIÓN DE VINOS BLANCOS BASADA EN EL CONTENIDO DE POLIFENOLES ESTIMADO MEDIANTE DETECCIÓN AMPEROMÉTRICA

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Palabras Clave: *Nanotubos de carbono; FIA; Electroforesis capilar; Detección electroquímica; Polifenoles; Vino*

El empleo de técnicas electroanalíticas para el análisis rutinario del contenido de polifenoles en vinos se presenta actualmente como una alternativa interesante a los métodos espectrofotométricos tradicionales. La oxidación electroquímica de los polifenoles a potenciales moderados permite su cuantificación en muestras de interés agroalimentario de forma sencilla, pudiendo simplificar los procesos de tratamiento de muestra. En este sentido, la integración de nanotubos de carbono en la interfase sensora mejora notablemente la respuesta electroquímica de los dispositivos electroanalíticos utilizados para estos fines, siendo especialmente destacable el incremento en la estabilidad de las señales.

En esta comunicación se muestra como la incorporación de películas de nanotubos de carbono en la superficie de electrodos de carbono vítreo permite llevar a cabo la estimación del contenido de polifenoles en muestras de vinos blancos sin más tratamiento que su dilución y/o filtrado, mejorando significativamente la estabilidad, reproducibilidad y sensibilidad de las señales obtenidas respecto al comportamiento observado en electrodos no modificados. Los dispositivos electroanalíticos utilizados se han acoplado a sistemas de análisis por inyección en flujo (FIA) y electroforesis capilar (EC), permitiendo evaluar el contenido de grupos de polifenoles mediante FIA así como la obtención de perfiles electroforéticos mediante EC, estos últimos relacionados con el contenido de polifenoles individuales. Los resultados obtenidos en ambos casos al analizar vinos elaborados con uva *airén* o *verdejo* han mostrado que pueden haber diferencias en el contenido de polifenoles en función del tipo de uva empleada en estos vinos. A partir de las señales obtenidas con estos dispositivos electroanalíticos ha sido posible generar modelos de clasificación con ayuda de técnicas quimiométricas (Análisis de Componentes Principales y Análisis Discriminante), capaces de asignar correctamente en función del tipo de uva más del 70% de las muestras de vino analizadas.

S17: *Otros Ámbitos de la Química*

NACIMIENTO DE UN NUEVO ECOSISTEMA: EVOLUCIÓN DE LA CALIDAD FÍSICO-QUÍMICA Y BIOLÓGICA DEL LAGO DURANTE EL LLENADO DEL HUECO MINERO DE AS PONTES

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Palabras Clave: *indicadores físico-químicos, nutrientes, fitoplancton, Estado Ecológico*

Durante los últimos 7 años, se ha llevado a cabo el estudio del Estado Ecológico del Lago Minero de Endesa, en As Pontes, norte de Galicia (España), correspondiente a la fase de llenado artificial y posterior rebose.

En este estudio, se han evaluado diferentes indicadores de calidad biológica y físico-químico con el fin de determinar el estado ecológico del lago de acuerdo con la DMA (Directiva Marco del Agua), Orden ARM/2656/2008 (IPH) y R.D 60/2011.

La determinación de indicadores biológicos tales como biovolumen fitoplanctónico, biomasa algal, IGA (índice de Catalá), %cianobacterias, y recuento taxonómico en combinación con indicadores físico-químicos tales como perfil de diferentes parámetros en profundidad (pH, k, O_2 disuelto, potencial redox y temperatura), transparencia, nutrientes, han permitido seguir la evolución de la composición y abundancia fitoplanctónica y observar las diferentes sucesiones producidas en este grupo de microorganismos y relacionarlo con la evolución físico-química durante la fase de llenado y posterior rebose del Lago.

Los resultados obtenidos muestran una tendencia del lago a un estado de Oligotrofia, con un bajo contenido en nutrientes y una buena oxigenación en toda la columna de agua (incluso en la zona más profunda de 200 metros). En cuanto a la composición y abundancia fitoplanctónica se observan principalmente los filos *de Bacillariophyta, Cyanophyta, Chlorophyta* y un incremento progresivo de *Streptophyta.* En los últimos años se ha observado un aumento de especies zooplanctónicas como branquiópodos, rotíferos y copépodos, evidenciando un aumento en los eslabones de la cadena trófica. Los elementos indicadores de calidad biológica mostraron una evolución del lago hacia un potencial entre BUENO Y MÁXIMO.

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