



JORNADES DOCTORALS

Department of Chemistry

Activities for PhD Students

June 1-3, 2016

Sala d'Actes

Faculty of Sciences and Biosciences

Event Sponsored by:



Welcome to Jornades Doctorals 2016

It is our great pleasure to welcome you to the "Sisena Edició de les Jornades Doctorals" that are organized by the PhD Chemistry Program and the Chemistry Department. This event aims to strengthen the links between the research groups of our Department, with the ultimate goal of promoting interdisciplinary and more ambitious research projects. In addition, it aims to relate the chemical research performed by the PhD students of the UAB Chemistry PhD program, and related programs, with Industrial and Entrepreneurial Opportunities. In this sixth edition, the "Jornades Doctorals-2016" includes an exciting series of conferences by 3rd-4th year UAB-Chemistry PhD students and three lectures by outstanding academic experts in different fields of chemistry:

Luisa De Cola,

Full Professor and AXA chair of Supramolecular and Biomaterial Chemistry, Institut de Science et d'Ingénierie Supramoléculaires, ISIS, University of Strasbourg.

Prof. De Cola has an extensive scientific career. She has held at universities in Italy, The Netherlands, Germany, and France. She has published 280 papers and filed 30 patents. She has received several awards including the Chevalier de la Légion d'Honneur appointed by the President of the Republic of France, François Hollande and the International Prize for Chemistry from the Academia dei Lincei (Tartufari Prize) (2014). Her research interests are: a) luminescent and electro-luminescent materials for optical and electroluminescent devices; b) nanomaterials for imaging diagnostics and therapy.

Luis Liz-Marzán,

Ikerbasque Research Professor and Scientific Director, CIC biomaGUNE.

Prof. Liz-Marzán has more than 20 years of research experience in the University of Vigo, University of Utrecht, Tohoku University, University of Michigan, University of Melbourne, University of Hamburg and Max Planck Institute of Colloids and Interfaces. He is coauthor of more than 350 peer reviewed research papers and co-inventor of 7 patents. He has received several awards, including the medal of the Spanish Royal Society of Chemistry (2014) and Rey Jaime I Award on Basic Research (2015). His research contributions focus on nanoparticle synthesis and assembly, nanoplasmonics, and development of nanoparticle-based sensing and diagnostic tools.

Luisa Torsi,

Full professor of Analytical Chemistry, University of Bari "A. Moro".

She has held a post-doc fellowship at Bell Laboratories Lucent Technologies and has been visiting professor at various French universities. As inventor of a groundbreaking electronic circuit which can be printed on plastic or paper to become a biological sensor, she has won the European Woman Inventor of the Year 2015 award organized by the European Women Inventors & Innovators Network (EUWIIN). She is author of 138 papers, and co-inventor of 6 patents. Her research activity mainly focuses on organic thin film transistors used as ultra-sensitive sensors.

We look forward to your participation in this event.

The Organizing Committee

Organizing, Scientific and Prizes Committee:

- Prof. Mariona Sodupe, PhD Coordinator of the studies in Chemistry and President of the Chemistry PhD Committee (UAB)
- Prof. Félix Busqué, Master Coordinator of the studies in Chemistry and President of the Chemistry Master Committee (UAB)
- Prof. Xavier Sala, Secretary of PhD and Master Studies Committee (UAB)
- Prof. Ramon Alibés, Vocal of PhD and Master Studies Committee (UAB)
- Prof. José Peral, Vocal of PhD and Master Studies Committee (UAB)
- Prof. María Isabel Pivori, Vocal of PhD and Master Studies Committee (UAB)
- Prof. Gregori Ujaque, Professor at the Chemistry Department (UAB)
- Antonio Calvo López, PhD student Department of Chemistry, (UAB)
- Alba Garzón Manjón, PhD Student, Department of Chemistry, (UAB)
- Katia Ghannadzadeh Samper, PhD student Department of Chemistry, (UAB)

Chemistry Department Administrative Support:

Elena Jiménez, Administrative Assistant PhD Studies in Chemistry.

Event Sponsored By:

Estudi de Doctorat en Química – Departament de Química

Grupo HNA

Societat Catalana de Química (SCQ)

Real Sociedad Española de Química (RSEQ) – Secció Catalana de la RSEQ

SCIENTIFIC PROGRAM

June 1

10:00 - 10:15 Opening Ceremony

10:15 - 11:15 Jornades Doctorals Lecture:

Chairman: Prof. Agustí Lledós

“Molecular Thinking for Nanoplasmonics Design”
Prof. Luis. Liz-Marzán

11:15 - 12:00 Coffee Break and Poster Session

12:00 - 13:15 Flash Presentations I

Chairwoman: Prof. Maria Isabel Pividori

12:00 - 12:15 *Fungal metallothioneins: internal architecture of MTs formed by 7-Cys building blocs*, **Selene Gil Moreno** (FP1.1)

12:15 - 12:30 *Design and synthesis of new photo-responsive coordination polymers*, **Jordi Espin Marti** (FP1.2)

12:30 - 12:45 *Understanding the behaviour of multifunctional gold nanoparticles (AuNPs)*, **Asli Raman** (FP1.3)

12:45 - 13:00 *Enhanced photocatalytic activity of gold nanoparticles driven by supramolecular host-guest chemistry*, **Marc Padilla Barriento** (FP1.4)

13:00 - 13:15 *Origin of anti-Markovnikov Regioselectivity in Alkene hydroamination catalyzed by Rhodium complexes*, **Almudena Couce Ríos** (FP1.5)

13:15 - 16:00 Break

16:00 - 17:30 Flash Presentations II

Chairman: Gregori Ujaque

16:00 - 16:15 *Water defluoridation by Hierarchical Alumina Microspheres*, **Sara Gracia Lanas**, (FP1.6)

16:15 - 16:30 *Carboxylated triarylphosphines containing trifluoromethyl groups: synthesis, study of the reaction scope and Applications*, **Daniel Herrera Miranda** (FP1.7)

16:30 - 16:45 *Cu-A β (1-16) Systems Related to Alzheimer's Diseases*, **Andrea Mirats Arce** (FP1.8)

16:45 - 17:00 *Synthetic approach to azaphenalene alkaloids*, **Silvia Alujas Burgos** (FP1.9)

17:00 - 17:15 *Hydrophobic adsolubilization ability of adsorbed surfactant mixtures onto TiO₂ P25*, **Minerva Fernandez Blanco** (FP1.10)

17:15 - 17:30 *Controlled Living Anionic Polymerization of Cyanoacrylates*, **Rubén Saez Fraile** (FP1.11)

June 2

10:00 - 11:00 Jornades Doctorals Lecture

Chairman: Prof. Manel del Valle

“Organic Bio-electronics for future ultra-high sensitive and low-cost sensing applications”
Prof. Luisa Torsi

11:00 - 11:45 Coffee Break and Poster Session

11:45 - 13:00 Flash Presentations III

Chairman: Prof. Ramon Alibés

11:45 - 12:00 *The versatility of voltammetric electronic tongue in environmental monitoring, homeland security and wine industry*, **Andreu Gonzalez Calabuig** (FP2.1)

12:00 - 12:15 *Chiral pH-dependent β -amino acid-based surfactants: synthesis, supramolecular analysis and study as potential new vectors for gene therapy*, **Bernat Pi Boleda** (FP2.2)

12:15 - 12:30 *New Molecularly Imprinted Polymer for Diclofenac Removal from Water*, **Nurlin Abu Samah**, (FP2.3)

12:30 - 12:45 *α 1,4-N-Acetylhexosaminyltransferase EXTL2: The Missing Link for Understanding Glycosidic Bond Biosynthesis with Retention of Configuration*, **Maria Fernanda Mendoza Muñoz** (FP2.4)

12:45 - 13:00 *Metal-Organic Polymers Made of Cyclodextrins*, **Heng Xu** (FP2.5)

13:00 - 16:00 Break

16:00 - 17:30 Flash Presentations IV

Chairman: Xavier Sala

16:00 - 16:15 *Use of neat acetic acid as a solvent for the synthesis of Metal Organic Frameworks based on trimesic acid*, **Marta Sanchez Sala** (FP2.6)

16:15 - 16:30 *Computational Study of the Reaction Mechanism of Human 5-lipoxygenase*, **Patricia Saura Martínez** (FP2.7)

16:30 - 16:45 *Selenium significance in wheat plants: Characterization by XAS and XRF mapping with Synchrotron radiation*, **Maria Angels Subirana Manzanares** (FP2.8)

16:45 - 17:00 *Pd-catalyzed telomerization of 1,3-butadiene with acetic acid: the role of imidazolium acetate ionic liquid and the new trifluoromethylated sulfonated triarylphosphines*, **Joao Marcio Balbino** (FP2.9)

17:00 - 17:15 *Cis/trans Isomerization of a Rull-Complex Bearing the Pentadentate Polypyridylic Ligand bpy2PYMe*, **Marcos Gil Sepulcre** (FP2.10)

17:15 - 17:30 *Integrating NMR and SAXS data with coarse grained simulation to describe IDPs*, **Susana Barrera Vilarmau** (FP2.11)

June 3

10:00 - 11:15 Flash Presentations V

Chairwoman: Prof. Ona Illa

10:00 - 10:15 Wine analyses in centrifugal microfluidic platforms, **Natàlia Sàndez Fernández** (FP3.1)

10:15 - 10:30 Fluorescent markers for amyloid detection: diagnosing Alzheimer's disease, **Francesca Peccati** (FP3.2)

10:30 - 10:45 Anchoring strategies for highly active ruthenium catalysts using functionalized terpyridines, **Rosa Maria Gonzalez Gil** (FP3.3)

10:45 - 11:00 From CoO to Co₃O₄ nanoparticles: towards a new electro- and photochemical water oxidation catalyst, **Jonathan de Tovar Villanueva** (FP3.4)

11:00 - 11:15 New methods in Nuclear Magnetic Resonance (IV), **Nuria Marco Garcia** (FP3.5)

11:15 - 12:00 Coffee Break

12:00 - 13:00 Jornades Doctorals Lecture

Chairman: Prof. Jordi Hernando

"Nanomedicine: dream or reality?"
Prof. Luisa De Cola

13.00 - 13:30 Award and closing ceremony

Jornades Doctorals 2016 distinguished Diploma, along with an iPad, will be given to the two best Poster-Flash Presentations. **Prizes awarded by HNA Group**

Lloc de realització:

- Conferències i flash presentations: Sala d'Actes de la Facultat de Ciències i Biociències
- Exhibició de pòster i coffee break: Hall 1^a pl., davant de la Sala de Graus de la Facultat de Ciències i Biociències

ABSTRACTS

Fungal metallothioneins: internal architecture of MTs formed by 7-Cys building blocks

Selene Gil-Moreno¹, Anna Espart², Paul Iturbe-Espinoza², Weiyu Lin², Sara Calatayud², Sílvia Atrian², Òscar Palacios¹, Mercè Capdevila¹

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² Departament de Genètica, Facultat de Biologia, Universitat de Barcelona, Barcelona, Spain

Abstract

Metallothioneins (MTs) are a superfamily of mostly small and ubiquitous cys-rich proteins present in all eukaryotes and most prokaryotes studied until now. This high cys content allows them the coordination of heavy metal ions through the corresponding metal-thiolate bonds.^[1,2] MTs have been associated to a variety of biological roles, physiological metal homeostasis, toxic heavy metal chelation and also different cell stress responses.

One metallothionein widely studied is *Neurospora crassa* MT, made up of 25 amino acid residues, 7 of which are cysteines.^[3] The characteristic motif (X₂-[CXC]-X₅-[CXC]-X₃-[CXC]-X₂-C-X₃) from NcMT is able to bind 5 Cu ions, and it has been found in a variety of fungal MTs suggesting that they have been formed by evolution and tandem amplification, generating long MTs with blocks which contain this motif.

Examples of this are the *Cryptococcus neoformans* MTs, CnMT1 and CnMT2. These MTs have been identified as essential factors for the infectivity and virulence of this pathogen. Both are unusually long Cu-thioneins with three and five tandem repetitions of 7-Cys motives, respectively, each of them folding into Cu₅-clusters. Through the study of the Zn(II)- and Cu(I)-binding capabilities of several CnMT1 truncated mutants, we show that the 7-Cys segments of CnMT1 fold into Cu₅-species, of additive capacity when joined in tandem. This same basic unit forms Zn₂-cores when coordinating Zn(II). All the Cu-complexes obtained from these truncated mutants practically share the same architectural features, if judging by their almost equivalent CD fingerprints, and they also share their capacity to restore copper tolerance in MT-devoid yeast cells.^[4]

Another example is the *Tremella mesenterica* MT, the longest MT polypeptide reported up to now. It is formed by 6 fragments of 7-Cys, 2 fragments of six Cys and one fragment of three Cys. The perfect alignment of these fragments with the motif previously mentioned, and the analysis of the metal binding abilities of the entire MT lay bare the modular structure and composition of this MT.^[5]

References

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Design and synthesis of new photo-responsive coordination polymers

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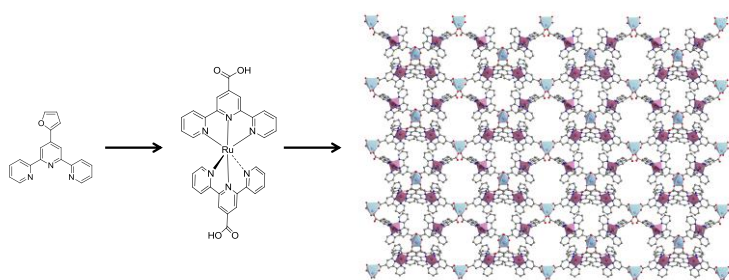
Abstract

Stimuli responsive materials have triggered special attention during the last years, and have been extensively studied due to their potential applications in a wide variety of fields such as biomedicine, sensing, catalysis and electronics among others.¹ The main stimuli applied to these materials are pH, temperature and light. Light is an especially attractive stimulus, allowing spatial and temporal control. The main approach for designing photo-responsive materials consists on introducing an organic ligand or coordination complex that will harvest light and migrate energy to a specific site that will activate, for example, a catalytic center or the conducting layer in dye sensitized solar cells.²

Coordination polymers offer the possibility to combine the functionality of metal ions with the richness of organic chemistry in the same material, and can be structured from 1D chains to 3D frameworks. Because of their exceptional chemical and structural diversity and potential high porosity, coordination polymers have attracted tremendous interest in a wide spectra of applications such as gas storage and separation, carbon dioxide capture, guest dependent luminescence, and catalysis.³

Herein, we present a new family of tailored coordination polymers obtained from the association of organic or metal-organic building blocks, which show light harvesting properties, and a metal cation that will allow the extension of the structure and could promote a desired photocatalytic reaction. Different light absorbing organic motifs have been designed and synthesized with the appropriate functional groups to be expanded with the metal nodes. These ligands can be divided in three subgroups: bis-benzimidazole pyridine, terpyridine and bipyridine-based. Two approaches were considered to obtain the final coordination polymers; on one hand mixing directly the organic ligand with the metal salts, and on the other, preforming an organometallic complex with Ru²⁺ or Ir³⁺ core which can be expanded with other metals.

The organic linkers and complexes were fully characterized, confirming a correct design and synthesis. Different 1D, 2D or 3D coordination polymers were synthesized and their structure solved by single crystal X-Ray diffraction using synchrotron radiation. Their optical properties have been determined and their potential for photocatalytic applications, such as H₂ or O₂ evolution from water, evaluated.



References

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Understanding the behaviour of multifunctional gold nanoparticles (AuNPs)

Asli Raman¹, Carlos Jaime¹, and Victor F. Puntès²

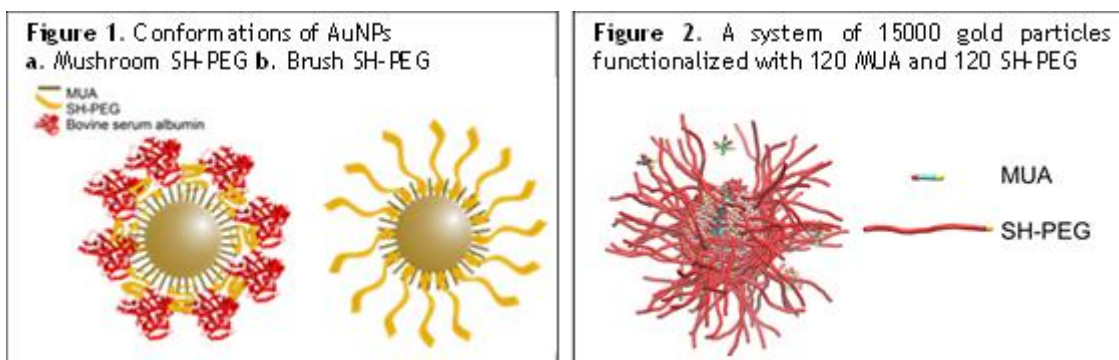
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² Institut Català de Nanociència i Nanotecnologia (ICN2), Barcelona, Spain, Victor.Puntès@icn.cat

Abstract

As gold shows different properties in nanoscale than in bulk form, studies on AuNPs have shown considerable growth over the years. The high surface area-to-volume ratio with excellent biocompatibility using appropriate ligands makes them excellent candidates in wide range of applications such as controlled drug delivery, cancer treatment, biomedical imaging, diagnosis and many others^[1]. It is possible to tune the properties of the AuNPs by grafting a ligand monolayer to the surface such that the physicochemical properties of the surface are controlled by the structure and chemistry of the protecting ligands^[2]. Our aim is to understand the change of the conformation from mushroom to brush in the mixed monolayer, which will allow further engineering of the NP surface.

Dissipative Particle Dynamics (DPD)^[3] method was used to simulate a system containing AuNPs functionalized with 11-Mercaptoundecanoic acid (MUA), thiolated polyethylene glycol (SH-PEG) and bovine serum albumin (BSA). The competition between the MUA and SH-PEG on the surface of the NP is the key point to understand these systems. This study allowed a better understanding on the most widely used mechanisms of AuNPs stabilization in biological media: pegylation and protein corona.



References

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Enhanced photocatalytic activity of gold nanoparticles driven by supramolecular host-guest chemistry

Marc Padilla-Barriento, Francesca Peccati, José Luis Bourdelande, Xavier Solans, Gonzalo Guirado, Mariona Sodupe and Jordi Hernando

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Abstract

Noble metal nanostructures (NMNs) display an intriguing optical behavior which arises from the collective excitation of their surface electrons under irradiation, a process referred to as surface plasmon resonance [1]. Many applications are derived from this phenomenon [2]. Among them, the use of NMNs as photocatalysts is gaining interest nowadays, and plasmon-based photocatalysis has already been demonstrated for some chemical reactions involving reduction, oxidation and dissociation processes [3]. The strong dependence of these processes on the distance from the NMN makes it crucial to ensure maximal approach between the reactant molecules and the photocatalyst. Normally, this is either achieved with the use of naked NMNs [4] or by covalently tethering the reactant molecules to the NMNs surface [5]. In the present communication, we introduce an alternative strategy for this purpose, which relies in the use of NMNs coated with a supramolecular host that brings the reactant molecules close to the nanostructure surface (Fig. 1). As a proof of principle, non-supported gold nanoparticles were prepared and functionalized with a thiolated derivative of β -cyclodextrin, a supramolecular host that forms 1:1 inclusion complexes with a wide variety of organic molecules and have low-to-moderate association constants, thus ensuring continuous renewal of the complexed molecules around the nanoparticles. Then, their catalytic activity to promote the cis-to-trans isomerization of stilbene derivatives using 532-nm visible light was tested. The results obtained validate our supramolecular approach to enhance the photocatalytic efficiency of NMNs, and, in some cases, conversions were achieved for our benchmark reaction that were even higher than upon direct stilbene excitation with UV radiation. Based on computational calculations, such large catalytic activity results from the combined action of photothermal effects and hot charge carrier generation on the surface of the nanoparticles.

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Origin of anti-Markovnikov Regioselectivity in Alkene hydroamination catalyzed by Rhodium complexes

Almudena Couce-Rios, Gregori Ujaque and Agustí Lledós

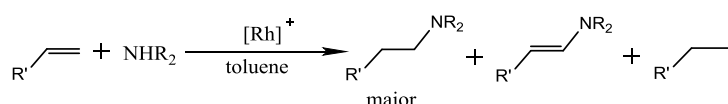
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Abstract

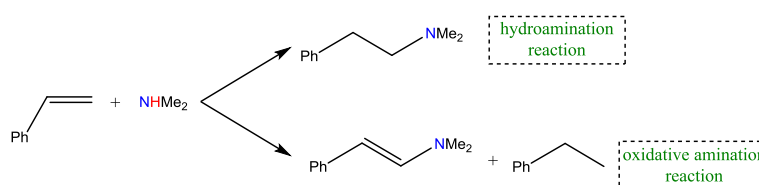
Hydroamination reactions on unsaturated products represent one of the most economical pathways for the synthesis of nitrogen-containing compounds such as amines, imines and enamines. This reaction is thermodynamically accessible but has very high activation energies associated which makes the use of catalysts necessary. Moreover, the anti-Markovnikov hydroamination of olefins catalyzed by transition metals was named as one of the 10 challenges for homogeneous catalysis.^[1]

We studied, through DFT calculations, the reaction mechanism of the anti-Markovnikov hydroamination catalyzed by cationic rhodium complexes using a biphosphine ligand.^[2]



The complete cycle of the two principal proposed mechanisms of hydroamination reaction (amine activation mechanism and alkene activation mechanism)^[3] of styrene were evaluated. We also studied oxidative amination as competing side reaction as well as the formation of the hydrogenated product.

The operating mechanism for the hydroamination reaction will be described by alkene coordination, amine nucleophilic addition, proton transfer through the metal center and reductive elimination steps.



We also studied the origin of regioselectivity for the addition process (Markovnikov vs anti-Markovnikov nucleophilic attack) thus finding an interesting relationship with structural parameters.^[4]

References

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Water defluoridation by Hierarchical Alumina Microspheres

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Abstract

Fluoride (F⁻) in drinking water has a harmful effect on health, as an excessive intake of F⁻ for a long period can result in skeletal fluorosis [1]. Therefore, the concentration in water should not exceed 1.5 mg L⁻¹ [1]. Minerals containing F⁻ are used in several industries, which contribute to F⁻ pollution with concentrations that can reach thousands of mg L⁻¹, much higher than the acceptable level in drinking water. Among the technologies used for F⁻ removal, adsorption is the most viable method due to its flexibility and simplicity of design, ease of operation and low cost.

The application of nanostructured materials with mesoporous nature for water defluoridation have been widely studied in recent years [2], as, due to their high surface area and high loading capacity, they are ideal adsorbents [3]. Among the various adsorbents available, alumina (Al₂O₃) has been recognized as one of the most effective materials for water defluoridation because of the high surface area and porosity, thermal stability and low solubility in a wide pH range [4].

The scope of this work is to prepare new HAM differing for structural/morphological parameters and define the F⁻ adsorption in terms of loading capacity and thermodynamics of the process. HAM have been prepared and characterized by standard methods, while adsorption studies have been performed using a new experimental approach, which combines potentiometry and Isothermal Titration Calorimetry (ITC). While in previous works ΔH_{ads} (enthalpy of adsorption) related to F⁻ adsorption have been calculated by the van't Hoff equation, ITC is applied for the first time in this work for the direct determination of ΔH_{ads} .

Two types of HAM have been obtained and characterized by SEM, TEM, BET, porosimetry, Dynamic Light Scattering and XRD, which reveals that the synthesized materials differ mostly for crystallinity. It has been suggested in the literature that crystallinity has an influence for fluoride adsorption capacity [3,5].

The equilibrium data are well described by Langmuir isotherm while a two-step process describes the adsorption kinetics. The adsorption constant obtained for the amorphous HAM (HAM-A) is one order of magnitude higher than the material with a higher degree of crystallinity (HAM-B), showing that a small change in the synthetic protocol has an important effect on this parameter. The highest defluoridation capacity reaches 26 mmol g⁻¹ after 1 hour of equilibration for HAM-A, revealing that the adsorption is rapid and that the adsorbent has high affinity for F⁻. The ΔH_{ads} values obtained are clearly negative for the different samples investigated.

References

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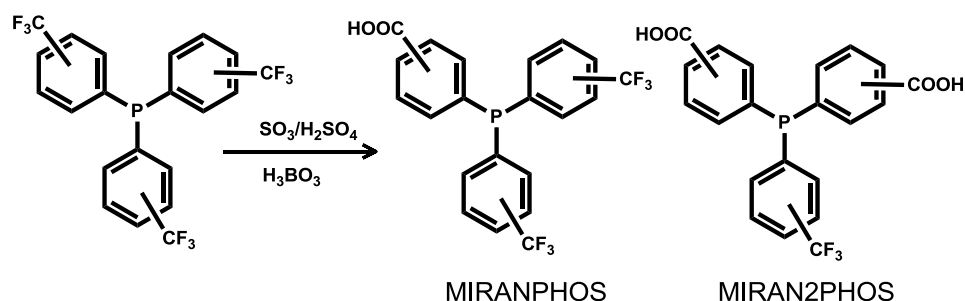
Carboxylated triarylphosphines containing trifluoromethyl groups: synthesis, study of the reaction scope and applications

Daniel Herrera, Joan Carles Bayón

Departament de Química. Universitat Autònoma de Barcelona

Abstract:

Despite the great versatility of carboxylated triarylphosphines, the synthesis of these compounds shows some difficulties.¹ The most common procedure to synthesize triarylphosphines, the reaction between $\text{Ar}_x\text{PCl}_{3-x}$ ($x=0-3$) and a $\text{M}\text{Ar}'$ compound ($\text{M}=\text{Li}$ or MgBr), cannot be applied in this case because of the incompatibility between carboxylic acids and organolithium or Grignard reagents. On the other hand, the hydrolysis of the trifluoromethyl group in aryl derivatives has been known for more than 60 years.² However, no applications of this reaction to the synthesis of phosphines have been previously reported. In our group, we found that trifluoromethyl substituents in triarylphosphines can be converted into carboxylic groups, by using fuming sulfuric acid, in the presence of boric acid:



We report a method to synthesize and purify triarylphosphines containing both carboxylic and trifluoromethyl groups.^{3,4} It has been observed that the rate of the reaction depends on the relative position of the trifluoromethyl group, being easier to hydrolyze when it is located at meta position to P atom than when it is at para or ortho positions. The Miranphos ligands have been used to prepare chelating diphosphines by using a diamine as backbond. Also the Miran2phos ligands have been essayed as ligands in the phase switchable Rh-catalyzed hydroformylation of styrene.⁵

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Cu-A β (1-16) Systems Related to Alzheimer's Diseases

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Abstract

Alzheimer's Disease (AD) is the most common form of neurodegenerative dementia and one of its main hallmarks is the presence of extracellular deposits of amyloid-beta peptide (A β).¹ These deposits show high concentrations of transition metal ions such as Fe³⁺, Cu²⁺ and Zn²⁺, which can induce amyloid aggregation. Moreover, there is evidence that the presence of redox-active Cu²⁺ is associated with the increased oxidative stress present in the brains of AD patients, due to the formation of reactive oxygen species (ROS)⁴ catalyzed by Cu²⁺-A β . Elucidation of the coordination of metal ions to A β is essential to understand their role in the production of ROS. Several coordination spheres for Cu²⁺-A β complexes have been proposed experimentally; however, it is still controversial^{2,3} and highly dependent on the pH. The most popular coordination modes are shown in Figure 1.

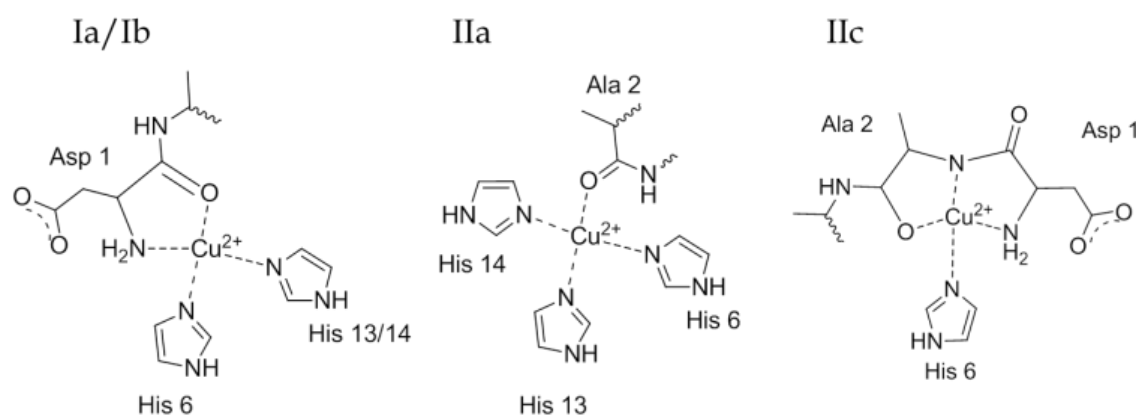


Figure 1. Coordination spheres proposed experimentally for the different Cu²⁺-A β (1-16) complexes from CW-EPR spectroscopy (ref.2).

Here, we present three-dimensional models of Cu²⁺-A β (1-16) complexes that enclose these most plausible coordination spheres. In addition, the standard reduction potential (SRP) values of the Cu²⁺/⁺-A β (1-16) redox pair were calculated. Results show that SRP are strongly dependent on the metal coordination sphere more than on the conformation adopted by the peptide upon metal binding.⁵ In this vein, the oxygen activation is also considered to better understand the production of ROS in the context of AD.⁶

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Synthetic approach to azaphenalene alkaloids

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Abstract

Ladybugs belong to Coccinellidae family. Most of these species eat aphids and mites, which are especially damaging for several kinds of crops. Because of this, coccinellidae insects are very important in the biological control of some agricultural pests. Ladybugs protect themselves against predators by its coloration, especially when they form aggregations. Reflex bleeding is another known method of protection; it consists in an orange fluid secretion, which is toxic due to the presence of some alkaloids with perhydro-9b-azaphenalene structure (Figure 1). Until now, there are only two syntheses of these alkaloids in enantiopure form.^{1,2}

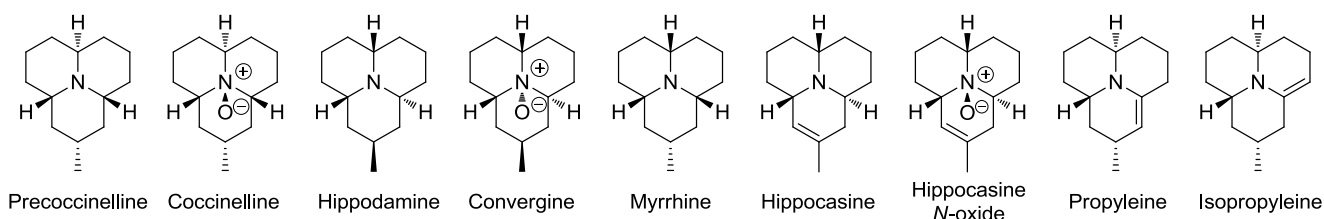


Figure 1: Isolated alkaloids with perhydro-9b-azaphenalene structure.

Our objective is to accomplish the synthesis of azaphenalene alkaloids in enantiopure form. The synthesis has as key steps a palladium catalyzed asymmetric allylic alkylation reaction, two diastereoselective allylic alkylation reactions and two ring closing metathesis reactions.

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Hydrophobic adsolubilization ability of adsorbed surfactant mixtures onto TiO₂ P25

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Abstract

The behavior of binary mixtures of surfactants including anionic surfactant such as alkyl/aryl sulfate and sulfonate derivatives (e.g. SDS, LBS...), cationic surfactant such as alkyl quaternary ammonium bromide (e.g. OTAB, DTAB, CTAB...) and nonionic surfactant onto titanium dioxide P25 surface to form monolayers and bilayers at different pH and at a constant ionic force of 10mM NaCl have been studied. The results show a different behavior from the one found in the literature depending on the chain length[1], a cooperative effect between surfactants with the same polarity[2,3], and between ionic surfactants with the non-ionic surfactants[4,5,6], showing, in this case, a decrease in the expected concentration to form the monolayer and the bilayer on the surface of the P25 nanoparticles. When mixing anionic with cationic surfactant, a double bilayer of surfactants can be created and it can be observed the expected critical concentrations to form the monolayer and the bilayer of both surfactants separately[6]. The presence of a bilayer and combination of bilayers of different surfactants on P25 surface improves the particle suspension stability, and also the adsolubilization of lipophilic substances on its surface as referred in previously reported studies [7–9]. Controlling the stability of suspended particles with these special properties could be a powerful method to eliminate hydrophobic contaminants present in waste waters, and also its use as capsules for controlled release of active substances in the solution media when needed.

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Controlled Living Anionic Polymerization of Cyanoacrylates by Frustrated Lewis Pair Based Initiator

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Abstract:

Cyanoacrylates are a type of monomers that undergo extremely rapid uncontrolled polymerization in the presence of catalytic amounts of nucleophiles and anionic species. Due to this great reactivity they are widely used as instant adhesives, which represents by far their most important commercial use. Best known as “super glues”, cyanoacrylates combine rapid curing and high strength bonding a diverse range of substrates including metals, ceramics, plastics, woods, rubbers, skin and other biologically derived materials.¹

It is well known that the properties of polymers are strongly influenced by its architectural features, and usually their suitability for a particular application is determined by their specific structural and molecular parameters such as molecular weight, molecular weight distribution (MWD), the presence of functional groups and their spatial location.²⁻⁶ Controlled living polymerization techniques allow the synthesis of polymers with tailored properties and architectures, affording industrial processes of interest for the design of high performance polymeric materials and composites for advanced technologies.⁷

This kind of controlled process has not been reported so far for cyanoacrylate monomers due to their mentioned extreme reactivity. Herein we describe for the first time the use of a hydrogenated Frustrated Lewis Pair⁸ as initiator for controlled living anionic polymerization of cyanoacrylates, affording polymers with targeted molecular weight and narrow MWD. The preparation of block copolymers of different cyanoacrylate monomers has also been achieved.

These results open an avenue for the modification of physical and mechanical properties of conventional polycyanoacrylates, and offer a promising window for new applications and products based on cyanoacrylate chemistry.

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The versatility of voltammetric electronic tongue in environmental monitoring, homeland security and wine industry

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Abstract

Over the last years the demand for fast, highly sensitive and selective methods of analysis to meet new challenges in environmental monitoring, food safety and public health has been increasing. However, the difficulty to obtain sensors with appropriate selectivity and sensitivity for a certain analyte, and to solve analytical problems which require the quantification of a certain effect (e.g. toxicity, bitterness, etc.), has led to the concept of electronic tongues (ETs) as a strategy to overcome these difficulties.

The voltammetric ET have several advantages respect the more employed potentiometric versions. Voltammetry has been extensively used in analytical chemistry due to features such as its sensitivity, versatility, simplicity and robustness. Besides, this technique offers a wide range of different possibilities, such as cyclic, stripping and pulse voltammetry. Depending on the technique, different information can be obtained giving voltammetric ETs a plus in versatility for a wide range of applications.

The possibility of modify the electrodes with metal nanoparticles, conductive polymers, organic molecules or enzymes is used to design different arrays of sensors that are going to be used in the different cases of study. Voltammetric ETs have been able to quantify ternary mixtures of Cd(II), Pb(II) and Zn(II) and Cd(II), Pb(II) and Hg(II) at the $\mu\text{g L}^{-1}$ level [1,2]. In homeland security ETs have been applied to discriminate and quantify among nitro-containing and peroxide-based explosive compounds [3]. In the wine field ETs were applied, in contrast with a human sensory panel, as a tool for standardized wine tasting to achieve the discrimination of different wine DOs and the prediction of the global score assigned by the sensory panel [4].

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Chiral pH-dependent β -amino acid-based surfactants: synthesis, supramolecular analysis and study as potential new vectors for gene therapy

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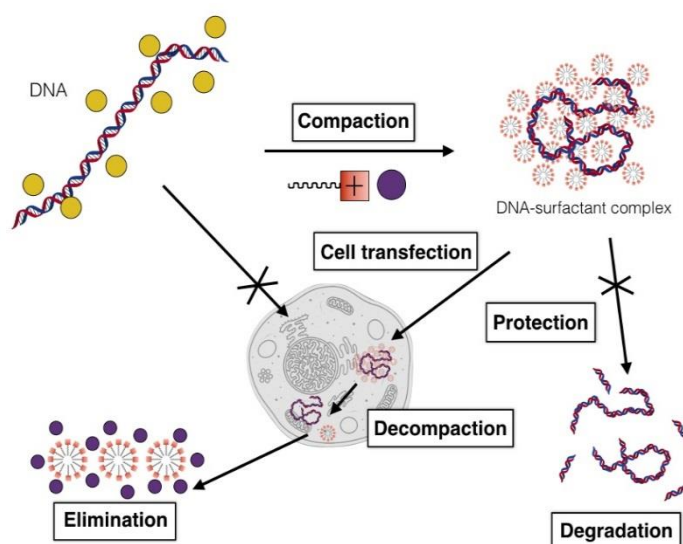
Abstract

Cationic surfactants are being studied as non-viral vectors for gene therapy because of their properties.¹ Amino-acid based surfactants show interesting acid-base behaviour in solution suitable for biological applications.^{2,3} In this work, four new pH-dependent β -amino acid-based surfactants were synthesized. Their physicochemical and supramolecular properties were analysed using different techniques to find out the influence of the stereochemistry and the length of the chain on the surfactant properties such as efficiency, effectiveness, pK_a and the morphology of the aggregates.

A biophysical study was carried out to explore the interaction of these surfactants with DNA. First of all, compaction process was studied using dye exclusion assays and electrophoretic mobility shift assays to determine the efficiency, size and charge of the obtained complexes. Additionally, AFM was used to find out the structure of the complexes. DNA was compacted very efficiently and these surfactants can be compared with commercial surfactants showing an improvement in some cases.

Then, protection of the DNA chain at different surfactant concentrations was analysed using three different DNases. Finally, decompaction of the DNA-surfactant complexes was achieved by modifying the ionic strength of the medium.

Following steps are to develop a biological study to determine the transfection abilities and to check their toxicity.



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New Molecularly Imprinted Polymer for Diclofenac Removal from Water

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Abstract

Since a few decades ago, Environment Persistent Pharmaceutical Pollutants (EPPPs) have been introduced as one type of recalcitrant pollutant sources in water. In this study, the removal of Diclofenac (DCF) has been carried out using Molecularly Imprinted Polymer (MIP), synthesized via bulk polymerization with allylthiourea (AT) as the functional monomer. The DCF detection has been performed by UV spectrophotometer.

From the kinetic study in batch mode, approximately 100% of removal is observed, with an initial concentration of 5 mg L⁻¹ of DCF within three minutes, agitated at 25°C. From the total adsorption study using a cartridge pre-packed with 10 mg of MIP a high adsorption capacity of 160 mg DCF/g MIP was obtained. The Scatchard plot also has been determined showing the profile for the homogenous process of adsorption. The similar result also has been observed by C. M. Dai, et al. [1]. All experiments were carried out in triplicate.

In order to observe the chemical reaction occurred between monomer and template, the pre-polymerization has also been studied by using ¹H NMR. The shift in the signal observed has been identified with the interactions between amine of AT group with carboxylic acid on DCF.

As conclusion, the developed MIP works as a good adsorbent in DCF removal. The molecularly imprinted technology has shown to be a promising technology for the removal of pharmaceuticals from water.

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Computational Study of the Reaction Mechanism of Human 5-lipoxygenase

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Abstract

To date, no experiment has been able to determine if arachidonic acid (AA) is placed head or tail first in human 5-lipoxygenase, the pharmacologically most relevant human lipoxygenase (LOX) isoform.^[1] This head/tail-first orientation is the key to understand the catalytic regioselectivity of these enzymes and to develop isoform-specific inhibitors. In the present study we have first generated a model of the holo form of human Stable-5-LOX by homology modeling calculations that complete the missing regions of the crystallographic structure. Then, protein-ligand dockings and Molecular Dynamics simulations have shown that only the holoenzyme model is a productive form of 5-LOX, in contrast to the apoenzyme structure. Two possible stable orientations of AA have been obtained. A tail-first orientation, with the AA carboxylate end interacting with Lys409, gives structures with C₇ close to the Fe-OH-cofactor, so leading to 5-lipoxygenating catalysis. A head-first orientation, with the AA carboxylate close to Gln363, gives structures in which C₁₀ and C₁₃ are close to the cofactor. Our results show that if the residues of the bottom of the cavity are mutated to bulkier residues, Lys409 no longer can bind AA in a tail-first orientation, whereas the head-first orientation becomes then favored, leading to 15-lipoxygenation and 8-lipoxygenation catalysis, in good agreement with mutagenesis experiments that convert 5-LOX into a 15-lipoxygenating form.^[2] Quantum Mechanics/Molecular Mechanics calculations explain the catalytic mechanism of the hydrogen abstractions and support that our proposed tail-first orientation is consistent with the experimental 5-LOX regio- and stereoselectivity, whereas a head-first orientation will give a 15/11-LOX or 12/8-LOX regioselectivity.

The understanding of how the AA head/tail-first orientation determines the fate of lipoxygenation catalysis can be useful to turn an inflammatory activity into an anti-inflammatory one.

Metal-Organic Polymers Made of Cyclodextrins

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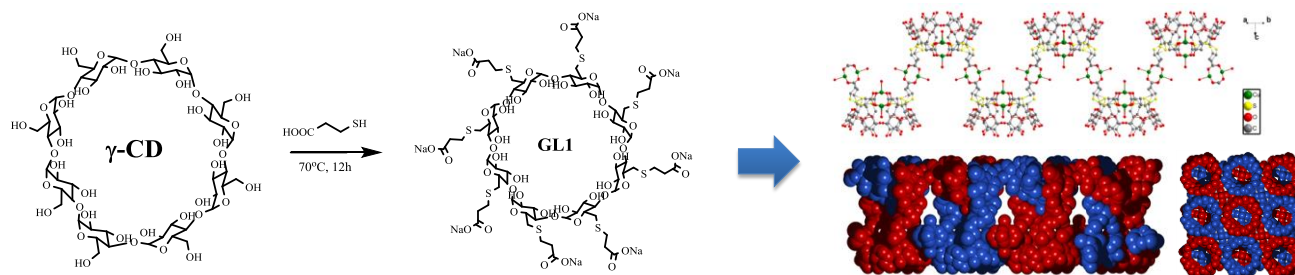
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Abstract

In last two decades, with more than 20,000 structures have been reported, metal-organic frameworks (MOFs) have been one of the most promising materials due to their versatile composition, tunable structures and exceptional porosity properties¹. Recently, many efforts have been dedicated to explore MOFs for drug encapsulation and delivery by taking advantage of their large and functional pores². An excellent approach towards the design of MOFs for biomedical applications is the use of organic linkers that show the capacity to recognize and store drugs by themselves (cyclodextrins for example). With the idea to explore this new approach, the main objective of this thesis is the design, synthesis, characterization and study of a new class of MOFs built up from cyclodextrins (CDs).

To introduce the cyclodextrin molecules to construct rigid and stable MOF architectures, there are mainly three strategies: i) directly using cyclodextrin molecules coordinate with alkali metal ions to form crystals, however, these crystals are usually very sensitive to humidity; ii) functionalize "6-hydroxy" groups of the cyclodextrins which are employed to generate stable structures; iii) some cyclodextrins are easily form rotaxane complexes³ which can be used to construct MOFs.

Herein, we present a new family of CD-MOFs by functionalize the γ -CD with carboxylic acid as the octatopic ligand to construct rigid and stable MOF structures. γ -CD has the big natural cavity ($\sim 7.5 \times 7.9 \text{ \AA}$) suitable for encapsulating many drug molecules. The organic linker (GL1) has been successfully characterized and forms an unprecedented coordination polymer with copper ion. The 2D structure has been solved by single crystal X-Ray diffraction using synchrotron radiation (Scheme 1). Investigation of the properties is undergoing and offer us a promising strategy to construct MOFs for drug delivery.



Scheme 1. Synthetic γ -CD likers and construct coordination polymers.

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Use of neat acetic acid as a solvent for the synthesis of Metal Organic Frameworks based on trimesic acid

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Abstract

Metal-organic frameworks (MOFs) present a huge diversity of structures with tuneable properties and found multiple applications in gas storage and separation, catalysis and as nanostructured materials precursor. [1] Besides searching new materials, nowadays there is also a large interest in the design of new synthetic routes that can be easily translated to the industrial scale, allowing at the same time control on the properties of the prepared materials. In this context, the use of neat acetic acid has been explored for the synthesis of MOFs in this work. Trimesic acid (H_3BTC) was used as the organic linker. This compound originates a large number of MOFs. [2] A metal acetate is used to provide the metallic cation and also the base necessary to deprotonate the H_3BTC ligand. All the synthesis were performed at ambient pressure. Results denote that the metal determines the nature of the material produced. $[Cu_3(BTC)_2]$ was produced from copper acetate. Although the specific surface area of the material obtained by this route was relatively low ($500\text{ m}^2/\text{g}$), the compound presents hierarchical porosity, a feature desirable in several applications. Compounds with similar stoichiometry than HKUST-1 have been described for other first row transition metals using solvothermal synthetic methods. However, the use of acetic acid as a solvent yielded different compounds. $[Mn(HBTC)(HAC)(H_2O)_{0.25}]$ was produced from manganese acetate. The 2D non-porous compound $[Co_6(BTC)_2(Ac)_6(HAc)_3]$ was obtained from cobalt acetate. This compound has a crystalline structure containing hexanuclear cores linked by BTC bridges. $[Co_6(BTC)_2(Ac)_6(HAc)_3]$ was further used as a precursor for the synthesis of nanostructured Co_3O_4 . For the nickel acetate, the synthesis in acetic acid yielded an amorphous material. The study was extended to some heavy metals, thus, allowing the isolation and characterization of some new phases, including $[Pb(HBTC)(HAc)_{0.5}(H_2O)]$, $[Cd(HBTC)(HAc)(H_2O)]$, $[Yb(BTC)(HAc)_{0.5}(H_2O)]$ and $[Bi(BTC)(HAc)]$. For some of them the crystal structure was elucidated.

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α 1,4-N-Acetylhexosaminyltransferase EXTL2: The Missing Link for Understanding Glycosidic Bond Biosynthesis with Retention of Configuration

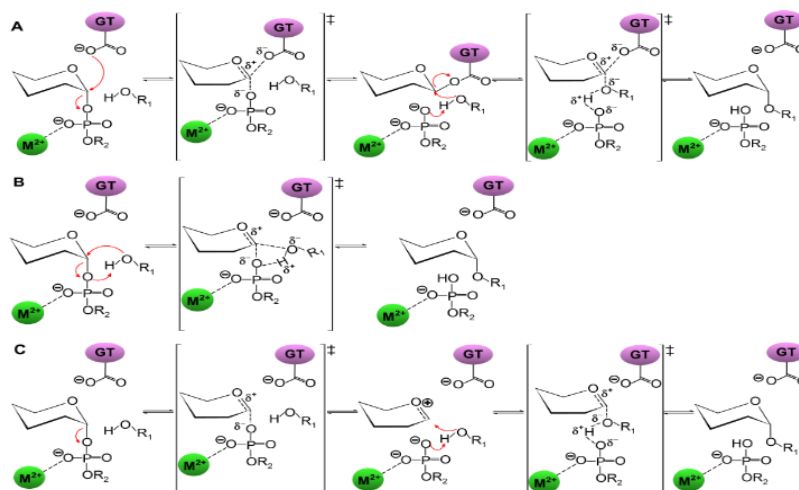
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Abstract

EXTL2 is a Glycosyltransferase (GT) member of the GT64 family which catalyzes the transfer reaction with retention of the configuration of both, the N-acetylgalactosamine (GalNAc) and the N-acetylglucosamine from the respective UDP-sugar to the [glucuronic acid] β 1-3[galactose], a natural common linker of various glycosylaminoglycans.

The mode of action of retaining-GTs is still unclear and two different reaction mechanisms have been suggested to obtain the same product: the Double Displacement mechanism that involves the formation of a Covalent Glycosyl Enzyme (CGE) intermediate employing a nucleophilic residue belonging to the enzyme, ^[1,2] (Figure 1A) and the Front Side Attack mechanism which can occur either by a Single Displacement mechanism with an oxocarbenium ion-like transition state^[3] (TS) (Figure 1B) or via a two-step mechanism with an oxocarbenium ion par (IP) intermediate.^[1,5] (Figure 1C)



Here we present a full QM/MM mechanistic study of EXTL2 with one of its donor substrates, UDP-GalNAc. The intriguing dyad Asp-Arg featured by this enzyme on the nearby region of the anomeric carbon and its effects on the reaction mechanism are analyzed. The implications of this model for the understanding of retaining glycosidic bond formation and the catalytic mechanism of other members of the GT-A family are discussed.^[4]

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Selenium significance in wheat plants: Characterization by XAS and XRF mapping with Synchrotron radiation

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Abstract

Selenium is an essential micronutrient for humans and it has been shown to be antioxidant, anti-tumoral, anti-viral and to contribute in the treatment of cardiovascular diseases. Therefore, appropriate selenium intake can benefit human health, but millions of people worldwide consume it at levels below the body's need for the correct expression of proteins, where Se is found as selenoamino acids. Selenium enters the food-chain through plants but Se-poor soils around the world produce Se-deficient crops, resulting in deficient food for humans,. Soil Se enrichment in edible plants has been proposed as a solution for this problem, and wheat has been chosen as an ideal candidate to contribute to human welfare in the form of functional foods.

The chemical speciation of Selenium in the system is crucial, since the properties of Se in wheat (bioavailability, toxicity, etc.) are strongly dependent on the form in which it is found. Consequently, characterization of the different species present is required in order to assess the potential health benefits as well as its safety. In this context, it is important to gain an understanding of the plant's physiology, and how it affects the mechanism of bioassimilation of Se, and its metabolism, where inorganic species are transformed to selenoaminoacids. It is also critical to determine the distribution of the species in the different plant tissues (roots, stems, leaves, and grain).

The novel element in the proposed research includes a chemical tuning. By controlling the Se species added to the soil by the related redox potential, it is feasible to obtain the desired ratio of selenoamino acids in wheat grain. This enables the possibility to ensure specific selenium bioavailability and to target determined health benefits for the applications of the obtained functional food. At the same time, it is possible to avoid seasonal variability of the mentioned selenoamino acids ratio. Proper characterization is essential. Conventional techniques to analyze chemical speciation, (such as HPLC-ICP-MS) require a pretreatment that may alter the selenium species. On the contrary, Synchrotron-based techniques are non-destructive methods that can provide real insight on speciation and also perform distribution studies in small samples. Synchrotron results serve as a reliable validation technique for HPLC-ICP-MS data. Accordingly, the Se content and speciation in wheat tissues has been measured by direct X-Ray Absorption Spectroscopy (XAS) with Synchrotron Radiation. Furthermore, the location and distribution of several elements through the plant and the grain, including Se and essential nutrients, has been determined by X-Ray Fluorescence mapping (XRF), providing novel significant results on wheat physiology and selenium enrichment.

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Pd-catalyzed telomerization of 1,3-butadiene with acetic acid: the role of imidazolium acetate ionic liquid and the new trifluoromethylated sulfonated triarylphosphines

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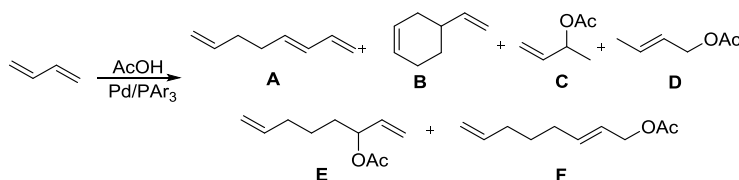
The telomerization of 1,3-dienes is an important atom-efficient transformation, which effectively adds nucleophiles (carboxylic acids, alcohols, water or amines, for example) over two C-C coupled dienes, providing an economically route for the production of C8 bulk chemicals.¹

The reaction was first investigated by Smutny² and Takahashi,³ and since these pioneering reports, a great variety of metals have demonstrated to be actives in catalyzing this reaction, including cobalt, rhodium, nickel and platinum, but Pd-based systems are superiors in activity and selectivity.⁴ These catalytic systems also include promoters, such as phosphines, isonitriles and N-heterocyclic carbenes.⁵

Alkylphosphines, triphenylphosphine and its sulphonated analogues are the most commonly employed ligands.⁶ However, trifluoromethylated arylphosphines, whose π -acceptor capacity increases with the number of trifluoromethyl substituents, have not been essayed in this reaction.

The reaction of 1,3-butadiene with acetic acid yields branched (E) and linear (F) acetoxyoctadienes, as illustrated in Scheme 1. These unsaturated esters can be used as starting materials for the synthesis of many artificial and natural products.⁷ The reaction also leads to the acetoxabutenes (C) and (D), resulting from the catalyzed reaction of the diene and the nucleophile, as well as the butadiene dimers (A) and (B).^{8,9} A conventional scheme of the telomerization of 1,3-butadiene with AcOH employs the catalyst system $[\text{Pd}(\text{OAc})_2]_3/\text{PPh}_3/\text{base}$, eventually leading to very high catalytic activity.¹⁰ The addition of a base in this reaction have a beneficial effect,¹¹ since it leads to the formation of the acetate, increasing the nucleophilicity of AcOH.¹² Sodium or potassium acetate is generally added as the base, but its role could be taken by an imidazolium ionic liquid (IL) containing acetate anions, which could act, besides of as co-catalyst, as solvent and stabilizer for the catalytic system itself.

We report here the telomerization of 1,3-butadiene by $[\text{Pd}(\text{OAc})_2]_3$ in an imidazolium acetate IL, using a variety of new trifluoromethylated and sulfonated triarylphosphines recently disclosed by us.¹³ Under optimized conditions, a high TON of 14600 with 78% of selectivity to the linear telomere was obtained.¹⁴



Scheme 1

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Cis/trans Isomerization of a Ru^{II}-Complex Bearing the Pentadentate Polypyridylic Ligand bpy2PYMe

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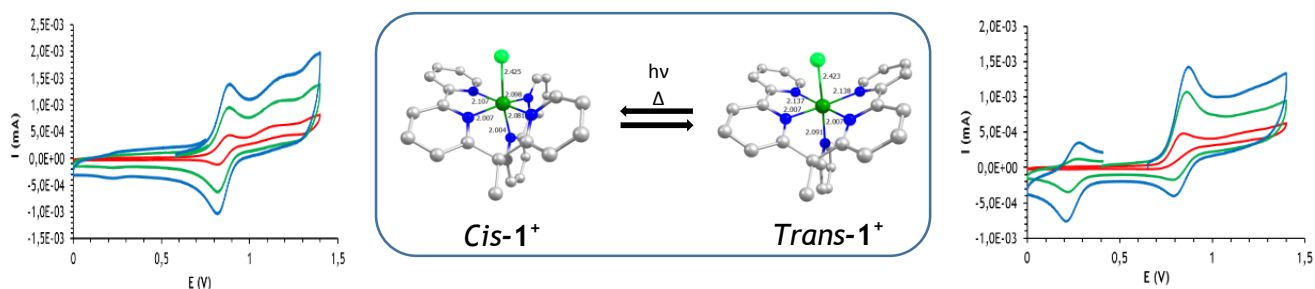
Abstract

Polypyridylic complexes of transition metal ions have been extensively used in catalytic oxidation systems due to their stability and synthetic versatility. From these, Ru(II) complexes are particularly interesting because of the availability of high oxidation states and their robustness.¹

A Ru^{II}-pentadentate polypyridylic complex [Ru^{II}(bpy2PYMe)Cl]⁺ (**1**⁺) and its aqua derivative [Ru^{II}(bpy2PYMe)(H₂O)]²⁺ (**2**²⁺) have been synthesized and characterized. **1**⁺ shows in MeOH the presence of two isomers, cis and trans, which are interconverted under thermal and photochemical conditions. The Ru^{III}/Ru^{II} systems for both the cis-**1**⁺ and trans-**1**⁺ isomers have been studied by computational and electrochemical methods. Under oxidative conditions in DCM, trans-**1**²⁺ generates a [Ru^{III}(bpy2PYMe)Cl₂]⁺ intermediate after the exchange of a pyridylic ligand by a Cl⁻ counterion, which explains the trans/cis isomerization observed when the system is taken back to Ru(II).

Interestingly, the addition of a methyl substituent in one of the bpy ligands leads to the formation of a single cis isomer for both chloro- and aqua-derivatives, [Ru^{II}(bpy(bpyMe)PYMe)Cl]⁺ (**3**⁺) and [Ru^{II}(bpy(bpyMe)PYMe)(H₂O)]²⁺ (**4**²⁺), due to the steric constraints imposed by the new ligand.

Additionally, catalytic epoxidation and water oxidation tests have been performed with these catalysts and will be also presented.



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Integrating NMR and SAXS data with coarse grained simulation to describe IDPs

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Abstract

The intrinsically disordered proteins (IDPs) play key roles in serious diseases such as cancer, diabetes, Parkinson or Alzheimer. However, little is known about their mechanism because studying experimentally these proteins's structure is very complex. These studies should be based on ensembles of structures rather than a single structure as is the case of canonical structured proteins. Such ensembles cannot be univocally determined experimentally. For this, computer simulations are presented as an interesting alternative.

To understand IDPs structural behaviour, it is necessary to sample a large conformational space, and for that, coarse grained methods are highly desirable, but these methods need to be refined with experimental data as NMR or SAXS. Our goal is to provide research groups with a tool that allows them to combine experimental data with relatively fast computational simulations.

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Wine analyses in centrifugal microfluidic platforms

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Abstract

Winery is a widespread industry in our country. In Catalonia, more than 100 million bottles of wine are produced and sold every year [1,2]. In order to ensure good quality of the products, different analyses are carried out during and after wine's production.

Miniaturized analytical instrumentation allows to easily perform these routine analyses, providing advantages like portability, easy automatization, and reduction of reagents consumption and analyses time, among others [3,4]. In this sense, centrifugal microfluidic platforms are of great interest, as they permit to eliminate the external instrumentation which is normally required to pump liquids inside the platforms. Furthermore, they permit the parallelization of different analyses - different parameters, as well as different samples - in a single device [5,6].

Some of the analytical parameters that should be determined in wines involve specific enzymatic reactions in which NADH or NADPH are involved [7]. The concentration of these coenzymes can be stoichiometrically related with the concentration of the analyte in the sample, and it is possible to determine them by absorbance measurements at 340 nm. In this way, different analytes could be quantified in a single centrifugal platform containing different subsystems and using a simple optical detection system at a fixed wavelength.

With this purpose, we have designed a double aliquoting structure for centrifugal microfluidic platforms. In the platform, two separated metering structures -one for making aliquots of equal volumes and one for making aliquots of decreasing volumes- are put together into a single structure where one aliquot of each subsystem ends into one receiving chamber. Each receiving chamber contains a window through which liquid or solid reagents can be added when desired, as chambers can remain unsealed during the whole aliquoting process.

The possibility of performing NADH absorbance measurements on the platform with a home-made miniaturized optical detection system has been demonstrated. Lactic acid enzymatic determination is now being studied off-chip.

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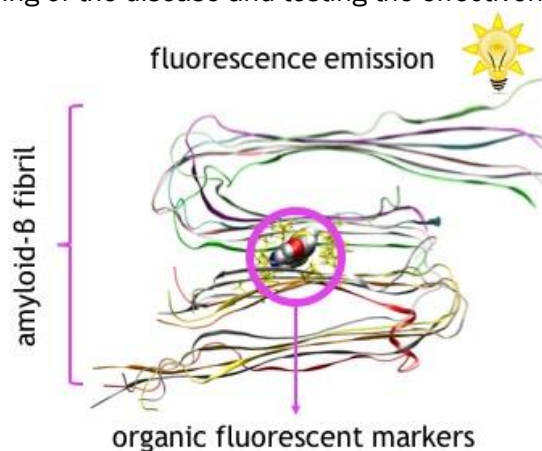
Fluorescent markers for amyloid detection: diagnosing Alzheimer's disease

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Abstract

Alzheimer's disease is one of the most important medical challenges of our time. This neurodegenerative disorder, which normally has its onset after the 65th year of life, is the most common form of dementia, and is affecting an ever-growing number of individuals due to the steady ageing of world population.¹ The main pathological hallmark of Alzheimer's disease is the accumulation and deposition in the brain, as fibrillar aggregates, of the peptide amyloid- β , which is strictly connected to the neurological symptoms. In this regard, a non-invasive and fast detection of amyloid species in the brain of living patients is fundamental for both diagnosing of the disease and testing the effectiveness of drugs.²



Fluorescence imaging is a promising technique for amyloid detection involving the interaction of small organic fluorescent markers with amyloid fibrils. The success of this approach lies in the marked increase in the fluorescence emission of the marker when interacting with amyloid- β fibrils compared to the fluorescence of the free molecule, which is the basis for the imaging contrast of the technique. Despite the large number of markers that have been proposed, little is known about the origin of their fluorescence properties. Our calculations uncovered several different fluorescence enhancement processes, including disaggregation, inhibition of non-radiative decay through spatial constraint, and intersystem crossing. Besides explaining the behavior of existing markers, these results pave the way for the design of new molecules with tailored properties.^{3,4}

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Anchoring strategies for highly active ruthenium catalysts using functionalized terpyridines

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Abstract

In nature, the oxidation of water to dioxygen occurs at the oxygen-evolving complex (OEC) in photosystem II (PSII) and it is driven by sun-light. This reaction provides electrons and protons that are used to convert CO₂ into carbohydrates needed for the sustainability of life forms on earth. Inspired by this, tremendous efforts have been made on artificial photosynthesis systems aiming at light-driven water splitting into molecular dioxygen and dihydrogen.¹ In heterogeneous systems, light-driven water oxidation has been demonstrated in several ways, such as catalytic systems composed of transition-metal photosensitizers and water oxidation catalysts¹ or as semiconductor-based photoelectrodes via the photoinduced electron and hole separation². As the catalyst, ruthenium molecular complexes with ligands containing a terpyridine backbone have been demonstrated to show a great potential for high-performance water splitting due to their relatively easy tunability and high activity.³ Moreover, this kind of systems are also known to have high conversions on the epoxidation of olefins using environmental friendly oxidants, for example hydrogen peroxide⁴. In this work, in order to understand how the electronic nature of the terpyridine backbone affect the catalytic activity, a family of substituted terpyridines with different anchoring moieties, lengths and electronic properties have been synthesized. These new ligands have been used for the heterogenization of highly active ruthenium catalysts, such as [Ru(tda)(py)₂]^{3a}, on semiconductor surfaces and also on conductive carbon surfaces⁵. Finally, these new hybrid materials, can be applied as anodes or photoanodes in catalytic water oxidation or the epoxidation of olefins.

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From Co⁰ to Co₃O₄ nanoparticles: towards a new electro- and photochemical water oxidation catalyst

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Abstract

Nowadays fossil fuels are the main energy source, but due to the increase of the global energy consumption and the fact that they present several drawbacks (ill-distributed, non renewable and highly polluting), it is mandatory to find a new renewable source of energy^[1]. The water splitting reaction, in which both dioxygen and dihydrogen gases are generated, represents an attractive chemical method for renewable energy storage into chemical bonds^[2]. Nevertheless, the oxidation of water into O₂ is a complicated reaction, since four electrons are needed for the formation of an oxygen molecule.³ Furthermore, this oxidative half reaction is thermodynamically uphill and kinetically slow (high overpotentials).

With the aim of improving the kinetics of this half reaction and inspired by nature's photosystem II - responsible of oxygen formation during photosynthesis-, chemists have been developing several electro- and photochemical catalysts^[4] during the last years. From these, heterogeneous catalysts are an attractive alternative, since metal nanoparticles have been identified several times as the real active species in water oxidation when performing this reaction with homogeneous catalysts^[5] (Figure 1). Furthermore, they display high thermodynamic stability and longevity and their introduction into potentially commercial photoelectrochemical cells is feasible from an engineering point of view^[6]. Here, a novel method for the preparation of a Co₃O₄ nanocatalyst for the electro- and photocatalytic oxidation of water is presented. These nanoparticles are obtained by the oxidation of Co⁰ nanoparticles, which were previously prepared through the organometallic approach^[7].

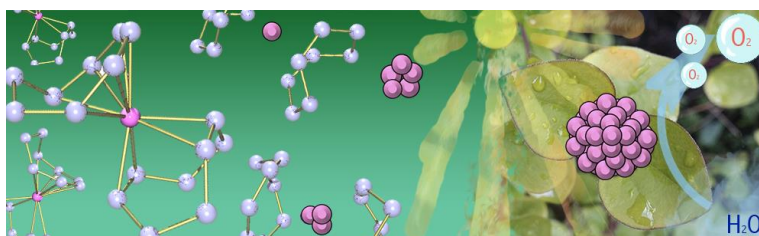


Figure 1. Schematic formation of nanocatalysts for water oxidation reaction

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New methods in Nuclear Magnetic Resonance (IV)

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Abstract

Nuclear Magnetic Resonance is an important tool in the elucidation and characterization of molecular structures and its conformers. To improve the accuracy of this technique we are studying enhancements on different topics.

First of our studies were focused on the achievement of a satisfactory digital and signal resolution in the HSQC spectra by implementing spectral aliasing along F1 dimension and broadband ¹H homodecoupling in the F2 dimension, collapsing the proton multiplets to singlets. [1]. None of these techniques add time to the experiments and the resulting 2D cross-peaks exhibit ultra simplified multiplet patterns from which the efficient measurement of J coupling values is performed in a straightforward manner. The experimental data has been provided for the simultaneous determination of the magnitude and the sign of J(CX) and J(HX) coupling constants from a single cross-peak (X = ¹⁹F, ³¹P or ²H).

We also studied the detection and measuring of long range heteronuclear correlations smaller than 1-2Hz by HSQMBC-COSY and HSQMBC-TOCSY experiments[2]. It is shown that the incorporation of an additional J(HH) transfer step to the basic HSQMBC pulse scheme favours the sensitive observation of traditional missing or very weak correlations and, in addition, extends the detection of a significant number of longer-range connectivities. The experiment is suitable on both protonated and non-protonated carbons under optimum sensitivity conditions.

Currently we keep studying the improvement on the structural characterization of conformers by the use of PMMA gels. Adequate sample preparation and the NMR methodology improvement for the determination of Residual Dipolar Constants in such media is our main research goal, as well as its application demonstration. Also it is being studied the field of NOESY and ROESY experiments [3] and their improvement by applying various new techniques and incorporating new NMR building blocks into the actual experiments.. One of the main research field of application is the issue of enantiodifferentiation and analysis by chiral agents [4].

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Modulating the Absorption Band Maximum in Fluorescent Proteins: A Molecular dynamics and QM/MM TD-DFT description

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Abstract

The development of fluorescent proteins (FPs) has set a milestone in modern bioimaging techniques, since the discovery of the Green Fluorescent Protein (GFP) in the early 1960s. They can be used as noninvasive labels for protein observation in living cells, what has a great impact in molecular biology and biomedical techniques. The first known member of the family, and the most studied one, the GFP, is suboptimal for this use, due to its spectroscopic features. It exhibits two peaks at room temperature, commonly labeled A (395 nm) and B (475 nm), which correspond the neutral and ionized form on the chromophore, respectively. Upon excitation, GFP emits a strong green fluorescence at 508 nm.¹ The reason why these properties are suboptimal is that living mammal tissue is only transparent to electromagnetic radiation between 600 nm (as below there hemoglobin absorbs strongly) and 1000 nm (where water begin to absorb). In this regard, great efforts have been done to develop FPs whose absorption and emission maxima are found in this “transparency window” and, in order to do this, a deep understanding of the factors that may modulate the absorption/emission peaks is needed.

In this regard we want to shed light on the interactions dominating the position of the absorption band and to do so, we have studied two cases, comparing 2 proteins for each one: S65T/H148D-GFP and E222Q/H148D-GFP for the first case, which presents a notable red shift, and mCardinal and mNeptune for the second one which presents an intense band at ~600nm, after performing a mutation that affects the chromophore. By means of the statistical treatment of extensive MD simulations (heading up to 100ns) and using QM/MM TD-DFT calculations, we have been able to reproduce the absorption spectra experimentally reported.^{2,3} Having characterized the excitation taking place, and performing a thorough analysis of the MD simulations, we could rationalize the reasons for the change in the band positions. Given that the excitation has a certain charge transfer character, placing charged residues near the chromophore promoting the electron movement will move the absorption band to the red.

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