



DOCTORAL WORKSHOP

PhD OF CHEMISTRY

May 26th – 27th, 2022

Sala d'Actes

Faculty of Sciences





WELCOME TO THE XI DOCTORAL WORKSHOP OF THE PHD PROGRAM IN CHEMISTRY

May 26th – 27th, 2022

It is our great pleasure to welcome you to the new Edition of the Doctoral Workshop of the PhD programme in Chemistry that is organized by the UAB's Department of Chemistry.

This year's workshop continues its tradition of providing supportive environment for doctoral students to present and discuss their dissertation with peers, members of the program and other experienced researchers, with the aim to strengthen the links and facilitating the exchange of research experiences and new ideas in the fields of entrepreneurship and small business.

During the event, 19 students, mostly on their third year will have an excellent opportunity to share their research. The Doctoral Workshop will also include an exciting series of plenary lectures given by international experts.

All the members of the PhD program in Chemistry and related programs, as well as other members of the research community are more than welcome.

We look forward to your participation in this event.

The Organizing Committee



Organizing, Scientific and Awards Committee:

Prof. Gregori Ujaque, Department of Chemistry, UAB.
Prof. Félix Busqué, Department of Chemistry, UAB.
Prof. Xavier Sala, Department of Chemistry, UAB.
Prof. Daniel MasPOCH, Catalan Institute of Nanoscience and Nanotechnology (ICN2)
Prof. Mireia Baeza, Department of Chemistry, UAB.
Prof. Rosario Núñez, Institute of Materials Science of Barcelona (ICMAB-CSIC)
Kevin Arias Alpizar, PhD Student.
Sohini Sihna, PhD Student.

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Event sponsored by:

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

Dr. Gary A. Molander, Professor
University of Pennsylvania, Department of Chemistry



Professor Gary Molander completed his Ph.D at Purdue University under the direction of Professor Herber Bronw and undertook postdoctoral training with professor Barry Tros tat the University of Wisconsin. He began his acadèmic career at the University of Colorado, Boulder, moving to the University of Pennsylvania in 1999, where he is Hirschmann-Makineni Professor of Chemistry. The central theme of the Molander group's research is the development of new synthetic methods and their application to the synthesis of organic molecules. His reserach group's focus is to expand and improve the Suzuki coupling reaction for organoboron compounds. Robust, air- and water-stable potassium organotrifluoroborates (R-BF₃K), are employed to carry out couplings under relatively mild conditions using non-toxic components. He is author of 461 research ublications with 27,995 citations and H-index of 86 (WOS, May 2022). He won the American Chemical Society Herbert C. Brown Award for Creative Research in Synthetic Methods – 2015.

Info: <http://molandergroup.chem.upenn.edu/profmolander.html>

Dr. Isabel Pastoriza Santos, Associate professor
Universidad de Vigo, Department of Physical Chemistry



Isabel Pastoriza Santos obtanined Ph. D. degree in Chemistry in 2001 from the University of Vigo (Spain). She carried out her postdoctoral research within the group of Prof. Paul Mulvaney (U. de Melbourne) and Prof. N. Kotov (Oklahoma State University). She is currently Assoc. Prof at CINBIO-Department of Physical Chemistry. Since 2012, she is the leader of the Colloid Chemistry Group. Her current interest involves the synthesis, assembly, and surface modification of nanoparticles with unique properties as well as development of (multi)functional nanostructured materials and tools with applicability in nanoplasmonics, (bio)sensing, catalysis and biomedicine. She is author of 167 research ublications with 17,889 citations and H-index of 68 (WOS, May 2022). She won Real Sociedad Española de Química RSEQ award for Research Excellence in 2021.

Info: <https://coloides.webs.uvigo.es/portfolio/isabel-pastoriza-santos/>

SCIENTIFIC PROGRAM

May 26th

09:30–09:45 Welcome and opening

09:45—10:45 Lecture

Chair: Daniel Maspoch

Title: Plasmonic Nanostructures: optical properties, synthesis and sensing applications

Dr. Isabel Pastoriza Santos

10:45—11:45 Poster session

11:45 - 13:00 Session I

Chair: Rosario Núñez

- 11:45-12:00: Development of s-Block metal mediated formation of phospholes: A combined experimental and DFT work. Irina Bozhinovska. 1.1
- 12:00-12:15: Photophysical properties of a series of Zn(II) coordination complexes bearing α -acetamidocinnamic acid and pyridine derivatives. Daniel Ejarque Granados. 1.2
- 12:15-12:30: Hybrid core shell materials for oer by first principles calculations. Dídac Armand Fenoll Silvestre. 1.3
- 12:30-12:45: Role of reduced graphene oxide aerogel support on the CuZnO catalytic activity and enhanced methanol selectivity for the hydrogenation reaction of CO₂. Márta Kubovics. 1.4
- 12:45-13:00: Non-energetic Ethanol Formation via CCH Reaction with Interstellar H₂O Ices. Jessica Perrero. 1.5

13:00—15:00 Break

15:00 - 16:00 Session II

Chair: Mireia Baeza

- 15:00-15:15: Surface Engineered Magnetic Nanoparticles with Metallacarboranes possessing novel Emergent Properties. Jewel Ann Maria Xavier. 2.1
- 15:15-15:30: The production of lipoxins in the 5(S),15(S)-DiHpETE biosynthetic pathway. A combined Molecular Dynamics and QM/MM study. Alejandro Cruz Saez. 2.2
- 15:30-15:45: Fabrication of curcuminoid-based sensors for BF₃ detection and in-situ metal coordination studies. Raquel Gimeno Muñoz. 2.3
- 15:45-16:00: The Energy Dissipation Process of Hydrogenation Reactions of Atomic Nitrogen on Water Ice Surfaces. Stefano Ferrero. 2.4

16:00 - 16:15 Break

16:15- 17:30 Session III

Chair: Gregori Ujaque

- 16:15-16:30: Novel binding site descriptors built upon inverse virtual screening. Arnau Comajuncosa Creus. 3.1
- 16:30-16:45: Electrolyte-Gated Field-Effect Transistors for sensing an Alzheimer's disease biomarker. Sara Ruiz Molina. 3.2

- **16:45-17:00:** Electroreduction of NHC-CO₂ adducts. Agustín Morales Aguilar. 3.3
- **17:00-17:15:** Determination and Adsorption of Trace Levels Tetrachloroplatinate and Cytostatics Cis-diamminedichloroplatinum(II). Dong Han. 3.4
- **17:15-17:30:** Light-controlled CO₂ capture and detection using molecular switches. Arnau Marco Ariza. 3.5

May 27th

09:30—10:30 Lecture

Chair: Adelina Vallribera

Title: Single Electron Processes Enabling Organic Synthesis
Dr. Gary A. Molander

10:30 - 11:30 Session IV

Chair: Xavier Sala

- **10:30-10:45:** Advanced Manufacturing at Pharmaceutical Industry. Desirée Moya Rodríguez. 4.1
- **10:45-11:00:** Studying the catalytic effect of supramolecular hosts in a prins cyclization reaction. Iker Zapiain Gysling. 4.2
- **11:00-11:15:** A novel electronic tongue using electropolymerized molecularly imprinted polymers for the simultaneous determination of active pharmaceutical ingredients. Mingyue Wang. 4.3
- **11:30-11:30:** A Quantum Chemical Study on Formamide Formation Route from Reaction between NH₂ and H₂CO on Interstellar Water Ice Surfaces. Berta Martinez i Bachs. 4.4

11:30—12:30 Poster session

12:30 - 12:30 Award and closing ceremony

Doctoral Workshop 2022 distinguished Diploma, along with a gift, will be given to the two best Poster & Presentation (Gift: tablet).

VENUE:

- ✓ Lectures and PhD students' presentations: Sala d'Actes (Auditorium), C1/-178, Faculty of Sciences, UAB.
- ✓ Poster Exhibition: Hall (in front of Sala d'Actes I), Ground floor, Faculty of Sciences, UAB.



INVITED SPEAKERS' ABSTRACT



Plasmonic Nanostructures: optical properties, synthesis and sensing Applications

Prof. Dr. Isabel Pastoriza Santos

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The novel field of Nanoplasmonics focuses on the manipulation of light using materials with significantly smaller sizes than the radiation wavelength. This is typically achieved using nanostructured metals since they can very efficiently absorb and scatter light due to their ability to support coherent oscillations of free (conduction) electrons. The great development of nanoplasmonics is based on the fine control over the composition and morphology of nanostructured metals. Particularly, wet-chemical methods have the advantage of simplicity and large-scale production, while offering several parameters that could determine the final particle morphology and surface properties, which is essential for further applications. This seminar will provide an overview of the optical properties of metal nanoparticles as well as the synthetic strategies to achieve size and shape control. Besides, I will show recent developments of the FunNanoBio Group in the Nanoplasmonic field with special emphasis on plasmonic nanostructures for (bio)sensing based on surface-enhanced Raman scattering and localized surface plasmon resonance.



Single Electron Processes Enabling Organic Synthesis

Prof. Dr. Gary A. Molander
University of Pennsylvania, Department of Chemistry

Many organic reactions are mechanistically driven by two-electron processes. Although such methods are highly effective for a vast number of transformations, there are still many such conversions that have proven challenging or that suffer from harsh reaction conditions or intolerance of sensitive functional groups.

The limitations of such transformations are often inherent to the mechanism of these processes at the most fundamental level, and thus predispose many of these reactions for failure. Processes transpiring via single electron mechanistic paradigms have promise to resolve some of the aforementioned limitations.

Described will be our efforts to develop a suite of radical precursors generated by photoredox chemistry, and the incorporation of these radicals in diverse carbon-carbon and carbon-heteroatom bond-forming transformations, emphasizing the tolerability of the developed conditions to an unprecedented array of functional groups. The value of generating radicals in a process that is *synchronized and catalytic* will be emphasized. Sequential transformations and multi-component reactions based on radical chemistry will be outlined, both in dual catalyzed processes and in radical/polar crossover processes where a subsequent catalytic transformation is not utilized. Applications of methods developed to biomolecules and DNA Encoded Library synthesis will be presented.

PhD STUDENTS' ABSTRACT

| Ph.D. Student | Abstract title | Order |
|--------------------------------|--|-------|
| Bozhinovska, Irina | Development of s-Block metal mediated formation of phospholes: A combined experimental and DFT work | 1.1 |
| Ejarque Granados, Daniel | Photophysical properties of a series of Zn(II) coordination complexes bearing α -acetamidocinnamic acid and pyridine derivatives | 1.2 |
| Fenoll Silvestre, Dídac Armand | Hybrid core shell materials for oer by first principles calculations | 1.3 |
| Kubovics, Márta | Role of reduced graphene oxide aerogel support on the CuZnO catalytic activity and enhanced methanol selectivity for the hydrogenation reaction of CO ₂ | 1.4 |
| Perrero, Jessica | Non-energetic Ethanol Formation via CCH Reaction with Interstellar H ₂ O Ices | 1.5 |
| Xavier, Jewel Ann Maria | Surface Engineered Magnetic Nanoparticles with Metallacarboranes possessing novel Emergent Properties | 2.1 |
| Cruz Saez, Alejandro | The production of lipoxins in the 5(S),15(S)-DiHpETE biosynthetic pathway. A combined Molecular Dynamics and QM/MM study. | 2.2 |
| Gimeno Muñoz, Raquel | Fabrication of curcuminoid-based sensors for BF ₃ detection and in-situ metal coordination studies | 2.3 |
| Ferrero, Stefano | The Energy Dissipation Process of Hydrogenation Reactions of Atomic Nitrogen on Water Ice Surfaces | 2.4 |
| Comajuncosa Creus, Arnau | Novel binding site descriptors built upon inverse virtual screening | 3.1 |
| Ruiz Molina, Sara | Electrolyte-Gated Field-Effect Transistors for sensing an Alzheimer's disease biomarker | 3.2 |
| Morales Aguilar, Agustín | Electroreduction of NHC-CO ₂ adducts | 3.3 |
| Han, Dong | Determination and Adsorption of Trace Levels Tetrachloroplatinate and Cytostatics Cis-diamminedichloroplatinum(II)) | 3.4 |
| Marco Ariza, Arnau | Light-controlled CO ₂ capture and detection using molecular switches | 3.5 |
| Moya Rodríguez, Desirée | Advanced Manufacturing at Pharmaceutical Industry | 4.1 |
| Zapirain Gysling, Iker | Studying the catalytic effect of supramolecular hosts in a prins cyclization reaction. | 4.2 |
| Wang, Mingyue | A novel electronic tongue using electropolymerized molecularly imprinted polymers for the simultaneous determination of active pharmaceutical ingredients | 4.3 |
| Martinez i Bachs, Berta | A Quantum Chemical Study on Formamide Formation Route from Reaction between NH ₂ and H ₂ CO on Interstellar Water Ice Surfaces. | 4.4 |

Development of s-Block metal mediated formation of phospholes: A combined experimental and DFT work

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Formation of phosphorous-carbon bonds by divergent hydrophosphanylation of alkynes yielding phosphanyl alkenes and 1,2-bis(phosphanyl)alkanes (Figure 1) represents an atom-economic resourceful method.¹

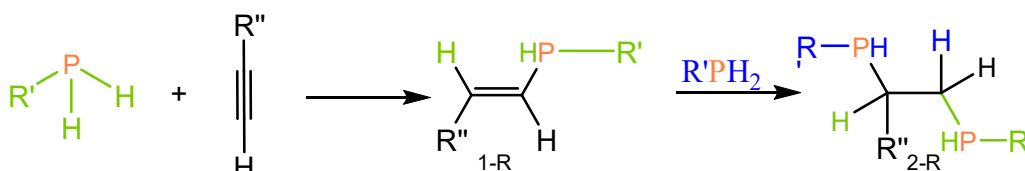


Figure 1: Single and double alkyne hydrophosphanylation, producing alkenylphosphane 1-R and 1,2-bis(phosphanyl)alkane 2-R.

Progression from transition metal catalysts to 1st and 2nd group-base catalyst is highly desirable considering that the later ones are more profitable, environmentally benign and present with higher global accessibility.² Hitherto, coalescence of phosphane oxides under akin reaction conditions has been reported.³ In this vein, we are interested in the synthesis of phospholes by addition of primary phosphanes onto butadiynes promoted by M(HMDS)_x {M= K, Li, Na and Ca; (HMDS=bis(trimethylsilyl)amides, x = 1, 2)} (Figure 2).

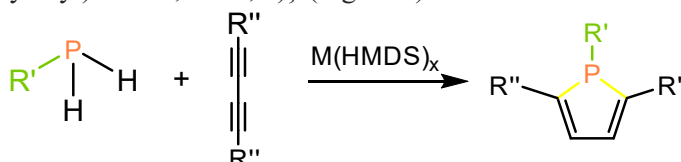


Figure 2: s-Block metal mediated hydrophosphanylation generating phosphole

The influence of the s-block metal on the process will be evaluated along with the reaction's selectivity. DFT calculations (B3LYP-D3) will be employed coextensively to the experimental work to obtain comprehensive insights into the fundamental steps of the reaction mechanism.



- Easily-accessible starting material
- One-step procedure
- S-block catalysis
- Regio and stereo-selectivity
- DFT calculations

References:

- [1]a) O. Kolodiazny, 1998. Tetrahedron: Asymmetry, 9(8), pp.1279-1332. b) N. Tran Huy, L. Ricard and F. Mathey, Comptes Rendus de l'Académie des Sciences - Series IIC - Chemistry, 1998, 1, 53-56.
2)a) R. Réau and P. Dyer, 2008. Phospholes. Comprehensive Heterocyclic Chemistry III, pp.1029-1147.b) D. Seyferth, Organometallics, 2009, 28, 2-33.
3) a) B. Fener, P. Schüler, N. Ueberschaar, P. Bellstedt, H. Görls, S. Kriek and M. Westerhausen, Chemistry – A European Journal, 2020, 26, 7235-7243. b) S. Härling, B. Fener, S. Kriek, H. Görls and M. Westerhausen, Organometallics, 2018, 37, 4380-4386. c) S. Härling, S. Kriek, H. Görls, M. Westerhausen, Inorganic Chemistry, 2018, 56, 9255-9263.

Photophysical properties of a series of Zn(II) coordination complexes bearing α -acetamidocinnamic acid and pyridine derivatives

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The preparation of coordination complexes through self-assembly presents many factors to be considered influencing the structure of the resulting compounds, such as the starting metal salts/precursors, metal-ligand ratio, bulkiness of ligands or solvent, among others. Herein, the reactions between $M(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ ($M = \text{Zn(II)}$, Cd(II)) and α -acetamidocinnamic acid (HACA) have been assayed obtaining two isostructural compounds with formula $[M(\text{ACA})_2(\text{H}_2\text{O})_2]$, whose reactivity towards 4-ppy was assayed yielding two compounds with monomeric ($M = \text{Zn(II)}$) and dimeric ($M = \text{Cd(II)}$) arrangements¹. Furthermore, the reactions of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ with HACA and a range of pyridine derivatives based on their increasing denticity and bulkiness (dPy: py, 3-ppy, 4-ppy, 2,2'-bipy, 1,10-phen, terpy and mptery) were performed, resulting in the formation of one family of Zn(II) complexes with diverse nuclearities (monomeric, trimeric, and polymeric)^{2,3}. Their X-ray crystal structures were elucidated, and the supramolecular synthons responsible of the crystal packing were identified. In addition, the UV-Vis and photoluminescent properties of the complexes were analyzed relating the size of the dPy with the fluorescent efficiencies expressed through the quantum yield (Φ) value. Thus, the use of different dPy ligands permitted to study the equilibrium between the beneficial chelate enhancement effect (CHEF) formed by the bidentate/tridentate dPy ligands and the negative steric crowding effect generated by steric effects around the metal cores (Fig. 1)³.

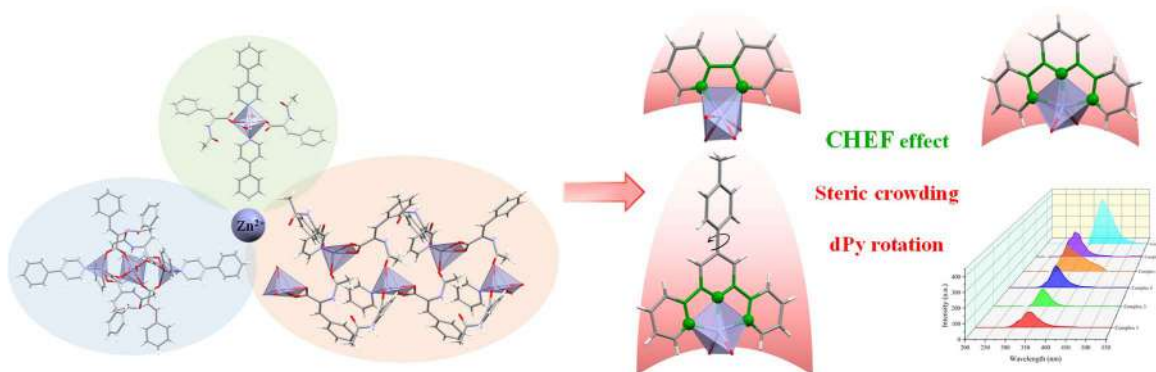


Figure 1. Outline of the diverse nuclearities of the presented Zn(II) compounds and the main structural factors affecting their photophysical properties.

Keywords: Zn(II) complexes, pyridine derivatives, chelate enhancement effect, steric crowding, photophysical properties

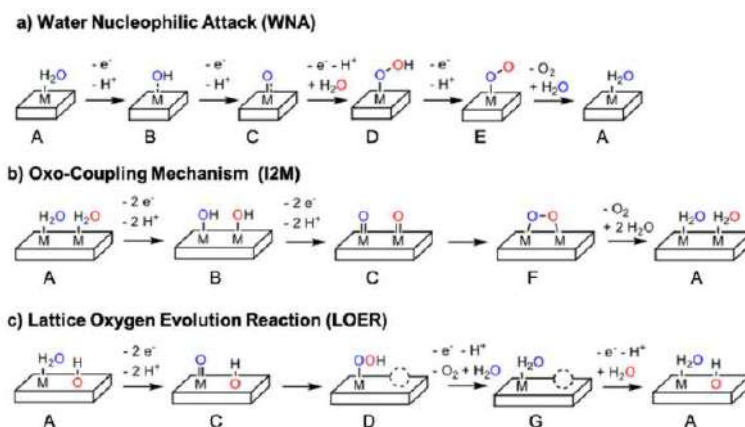
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- 2 D. Ejarque, T. Calvet, M. Font-Bardia and J. Pons, *Molecules*, 2020, **25**, 3615.
- 3 D. Ejarque, T. Calvet, M. Font-Bardia and J. Pons, *CrystEngComm*, 2021, **23**, 6199–6213.

Hybrid Core Shell Materials for Oer by First Principles Calculations

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Extensive research is currently focused on H₂ production and storage as a means to develop a sustainable, clean energy source. [1] Water undergoes electrochemical splitting through the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER), with the former being widely considered to be the rate-determining half reaction. [1,2] Many different catalysts have been developed for the OER, with IrO₂ providing great efficiency in acidic media owing to its remarkable stability (essential property in harsh acidic media) and activity. Yet reaction upscaling remains limited by the costly iridium. [3] Thus current research naturally develops into mainly two different directions. On the one hand, reducing the kinetic overpotential may enhance the process' overall efficiency. On the other hand, advanced nanofabrication could provide an effective means to minimize metal loading on the catalyst without compromising its activity. [4] Hybrid core shell nanoparticles happen to conveniently merge both strategies: not only can their catalytic properties be tuned finely, but their composition may also be changed to perfectly suit the required noble metal ratio at the catalytic sites whilst minimizing its content elsewhere. [4]



Scheme 1. Proposed reaction mechanisms for the oxygen evolution reaction. [5]

In this contribution we will show our work on the catalytic activity for the oxygen evolution reaction of three hybrid core shell surface models: RuO₂@IrO₂; Ir@IrO₂ and IrNi@IrO₂. For that, for each material, we will discuss by means of DFT periodic calculations the feasibility of the three most frequently described OER mechanisms, namely, the water nucleophilic attack (WNA), the oxo-coupling mechanism (I2M) and the lattice oxygen evolution reaction (LOER) (Scheme 1) [5]. Moreover, we will also analyze how the shell-to-core ratio influences the catalytic performance and report the most efficient systems, which ultimately will allow us to propose new potentially active materials.

Keywords: DFT, hybrid materials, oxygen evolution reaction

References:

- [1] L. Hammarström, S. Hammes-Schiffer Acc. Chem. Res. 2009, 42, 12, 1859–1860
- [2] X. Sala et al. Acc. Chem. Res. 2014, 47, 504–516.
- [3] D. Lebedev et al. ACS Cent. Sci. 2020, 6, 1189–1198
- [4] H.N. Nong et al. Nat. Catal. 2018, 1, 841–851.
- [5] D. González et al. J. Catal. 2021, 396, 192–201.

Role of reduced graphene oxide aerogel support on the CuZnO catalytic activity and enhanced methanol selectivity for the hydrogenation reaction of CO₂

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The rapid rising of CO₂ concentration in the atmosphere is one of the hot topics of recent years, as we are already experiencing the preliminary indications of the imponderable climatic negative consequences. For this reason turning CO₂ to value-added chemicals, such as methanol is a subject of great interest, and it is most frequently attempted by metal-based heterogeneous catalytic systems. Traditional catalysts still suffer from cost limitations, short lifetime or low selectivity. Many of these drawbacks can be improved by the careful selection of catalytic support.

In this work a novel CuZnO multicomponent catalyst, involving reduced graphene oxide (rGO) as a support, was synthesized to be applied in the catalytic hydrogenation of CO₂ to methanol. The composite was prepared in a 3D aerogel form using supercritical CO₂ for the structuration and H₂ treatment for reduction. Extensive characterization was performed on the aerogel in the as-synthesized form and after the catalytic reaction, as well. Electron microscopy to visualize the meso/macroporous morphology, elemental mapping to depict the homogenous distribution of CuZnO nanoparticles deposited on the rGO flakes are some of these applied techniques.

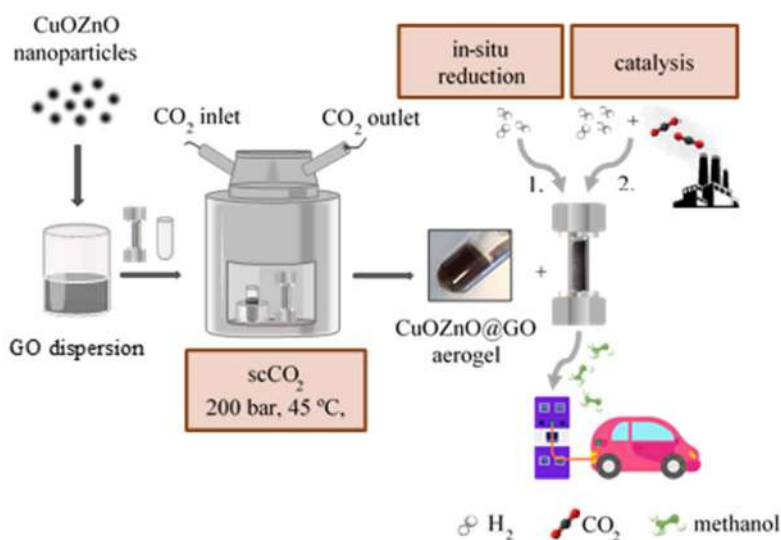


Illustration of the 3D CuZnO@rGO aerogel preparation and utilization in catalytic CO₂ hydrogenation.

The catalytic activity of the unsupported nanoparticles and the rGO aerogel supported catalysts were contrasted. Outstanding methanol selectivity and remarkable increase for the CuZnO@rGO composite was observed, and this behavior was ascribed to a different interaction established between the Cu⁰ and ZnO nanoparticles used as synthesized or deposited on rGO, which was analyzed based on X-ray photoelectron spectroscopy and catalytic tests.

Keywords: CO₂ heterogeneous catalysis, reduced graphene oxide support, supercritical CO₂

Non-energetic Ethanol Formation via CCH Reaction with Interstellar H₂O Ices

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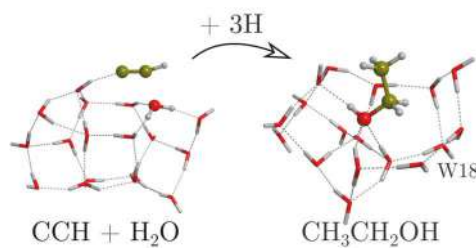
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The presence of molecules in the extreme physical conditions of the interstellar medium was considered impossible, until in 1937 the first diatomic species were observed. Since then, more than 250 gaseous species were identified and, in the coldest environments¹, the presence of dust grains made of silicates and carbonaceous material covered in water-dominated ice mantles was discovered². Ethanol (CH₃CH₂OH) is a relatively common molecule, often found in star-forming regions. Recent studies suggest that it could be a parent molecule of several so-called interstellar complex organic molecules (iCOMs), that are the building blocks of the molecules responsible for the origin of life, and are thought to be inherited through the different stages of the evolution of a planetary system³. However, the formation route of this species remains under debate. In the present work, we study the formation of ethanol through the reaction of CCH with one H₂O molecule belonging to the ice mantles of dust grains as a test case to investigate the viability of chemical reactions based on a “radical + ice component” scheme as an alternative mechanism for the synthesis of iCOMs, beyond the usual radical–radical coupling^{4,5}. This has been done by means of DFT calculations adopting two clusters of 18 and 33 water molecules as ice models. Results indicate that CH₃CH₂OH can potentially be formed by this proposed reaction mechanism. The reaction of CCH with H₂O on the water ice clusters can be barrierless, leading to the formation of vinyl alcohol precursors (H₂CCOH and CHCHOH). Subsequent hydrogenation of vinyl alcohol yielding ethanol is the only step presenting a low activation energy barrier.



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Keywords: interstellar medium, astrochemistry, DFT, iCOMs, grains.

Surface Engineered Magnetic Nanoparticles with Metallacarboranes possessing novel Emergent Properties

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Cobaltabis(dicarbollide), $[3,3'\text{Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ (COSAN), is a representative example of θ -shaped metallacarboranes with the metal ion sandwiched between the two carborane units. These boron clusters are interesting due to their diverse properties such as non-localized negative charge and 3D-aromaticity¹, ability to form hydrogen, $\text{C}_c\text{-H}\cdots\text{O}$ and dihydrogen, $\text{C}_c\text{-H}\cdots\text{B-H}$, bonds², water solubility and derivatization capacity similar to organic compounds. On the other hand, a major thrust of research has been carried out on super-paramagnetic iron oxide nanoparticles (SPIONs) owing to their properties of high surface-to-volume ratio, ease of surface functionalization and magnetic character³. This work discusses the potential possibilities and advantages of integrating the metallacarborane on MNPs from the perspective of two different applications: photoredox catalysis and bio-sensing devices (**Fig. 1**). The work would discuss in detail the synthetic procedures and the different techniques such as TEM, zeta potential and SQUID used for characterizing the as-formed systems. The strong dihydrogen interaction of COSAN with amine groups, $\text{N-H}\cdots\text{H-B}$, have been exploited to decorate the amine functionalized MNPs with the metallacarborane. While, silica-coated MNPs functionalized with amine groups and decorated with COSAN have been employed as the heterogenous photoredox catalyst for the oxidation of alcohols⁴, 'naked' MNPs functionalized with amine groups have been used as pre-concentrators in sensing devices. The work would explore the need to modify and adapt the system under study to suit the applications.

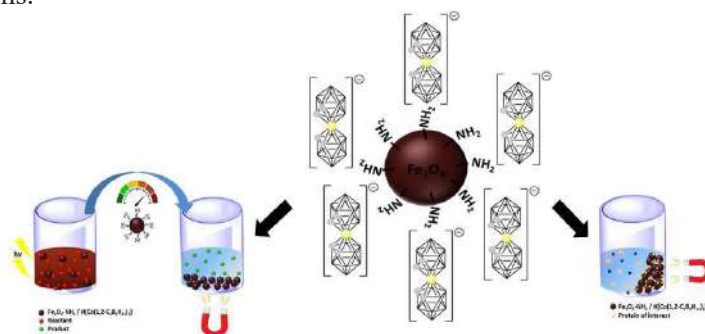


Figure 1. Schematic representation of metallacarborane decorated amine functionalized MNPs employed in photoredox catalysis and bio-sensing.

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Keywords: Metallacarboranes, Magnetic nanoparticles, Photoredox catalysis, Bio-sensing.

The production of lipoxins in the 5(S),15(S)-DiHpETE biosynthetic pathway. A combined Molecular Dynamics and QM/MM study.

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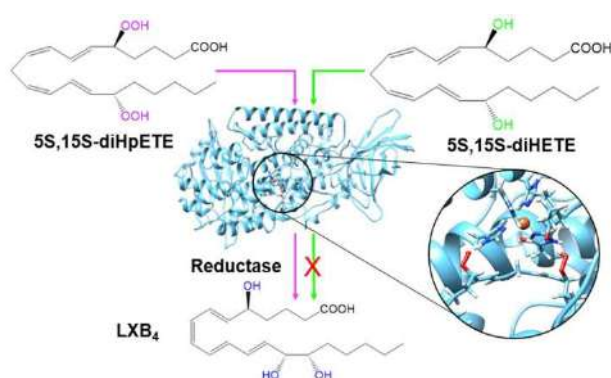
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Chronic inflammation is now widely recognized to play important roles in many commonly occurring diseases, including COVID-19. The resolution response to this chronic inflammation is an active process governed by specialized pro-resolving mediators (SPMs) like the lipid mediators known as lipoxins. The biosynthesis of lipoxins is catalyzed by several lipoxygenases (LOXs) from arachidonic acid. However, the molecular details of the mechanisms involved are not well known yet. In this work, we have combined molecular dynamics (MD) simulations and quantum mechanics/molecular mechanics (QM/MM) calculations to analyze how reticulocyte 15-LOX-1 catalyzes the production of lipoxins from 5(S),15(S)-diHpETE. Our results indicate that the dehydration mechanism from 5(S),15(S)-diHpETE, via the formation of an epoxide, presents huge energy barriers even though it was one of the two a priori synthetic proposals. This result is compatible with the fact that no epoxide has been directly detected as an intermediate in the catalytic formation of lipoxins from 5(S),15(S)-diHpETE. Conversely, the oxygenation of 5(S),15(S)-diHpETE at C₁₄ is feasible because there is an open channel connecting the protein surface with this carbon atom, and the energy barrier for oxygen addition through this channel is small. The analysis of the following steps of this mechanism, leading to the corresponding hydroperoxide at the 15-LOX-1 active site, indicates that the oxygenation mechanism will lead to the formation of lipoxin B₄ after the final action of a reductase. In contrast, our calculations are in agreement with experiments that lipoxin A₄ cannot derive from 5(S),15(S)-diHpETE by either of the two proposed mechanisms and that 5(S),15(S)-diHETE is not an intermediate of lipoxin biosynthesis catalyzed by 15-LOX-1.[1]

Figure/Scheme:



Keywords: Inflammation, 15-LOX-1, Arachidonic acid, Lipoxins.

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Fabrication of curcuminoid-based sensors for BF₃ detection and in-situ metal coordination studies

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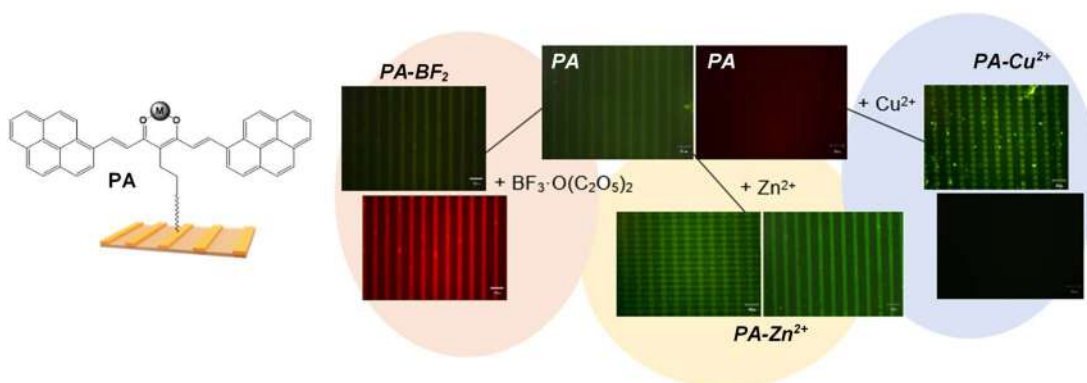
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Boron trifluoride (BF₃) is a highly reactive gas with significant catalytic activity and is therefore involved in a wide variety of reactions in industry. However, it also causes serious environmental and health problems due to its corrosive properties and high toxicity, largely due to the production of HF as a by-product during its degradation in contact with water present in ambient humidity. ^[1]

In order to fabricate a BF₃ sensor with easy handling and fast measurement time, we designed a new system based on fluorescence changes as a detection mechanism. For this purpose, the organised immobilisation of the curcuminoid (CCMoid) PA was studied using the microcontact printing technique ^[2] (μCP) on previously functionalised surfaces. ^[3] This process allowed the observation of line patterns due to PA emission in the green region by fluorescence microscopy. After 1 or 2 minutes in contact with BF₃, the coordination of the β-diketone group of the PA with the BF₂ groups modifies the fluorescence from the visible to the near IR, emitting in the red region. This process has been shown to be very sensitive and selective towards other boron compounds.

In addition, detailed study of PA-functionalised surfaces with metals has also shown different types of responses. Depending on the chemical species coordinated with the PA, an increase in emission intensity was demonstrated when reacting with diamagnetic metals such as Zn²⁺ or a loss of emission when reacting with paramagnetic metals such as Cu²⁺. Therefore, the different fluorescence changes of the PA-functionalised surface have enabled the development of CCMoid-based sensors for metals and metalloids.



Keywords: Curcuminoid, BF₃ gas, sensors, functionalization, microcontact printing.

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The Energy Dissipation Process of Hydrogenation Reactions of Atomic Nitrogen on Water Ice Surfaces

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In the colder (10-20K) regions of interstellar medium, the icy surfaces of interstellar grains serve as solid state supports for chemical reactions.[1] Among the plausible roles of these surfaces, that of third body is advocated, in which the formation energy of surface reactions can be dissipated among the grain causing the stabilization of the product.[2] This energy dissipation process is poorly understood at the atomic scale and it can have a tremendous impact on astrochemical surface processes like chemical desorption and diffusion.[3][4] In this work, we studied the formation of NH₃ via successive H-addition to atomic nitrogen on crystalline and amorphous ice surfaces. We first characterized the potential energy surfaces of the hydrogenation reactions and of possible competitive processes (i.e., H abstractions) using static quantum chemical calculations. Subsequently, the partitioning of the nascent energy released by the hydrogenation reactions between the newly formed species and the surface has been elucidated by means of *ab initio* molecular dynamics (AIMD) simulations. Results indicate that the H-additions on N are largely favorable reactions at 10 K, being barrierless and exhibiting large negative reaction energies, as opposed to the competitive H-abstractions, which are either endothermic or present high activation energies. AIMD simulations show that such favorable nascent energies are, in large part, quickly absorbed by the ice surfaces and their dissipation can be accelerated by mechanisms which involve an H exchange between the surface and the newly formed species.

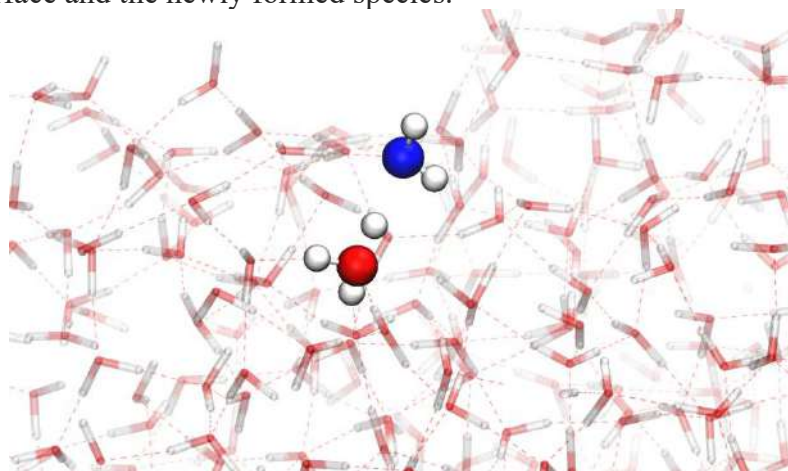


Figure 1: H₃O(+) NH₂(-) complex formation on an amorphous ice surface

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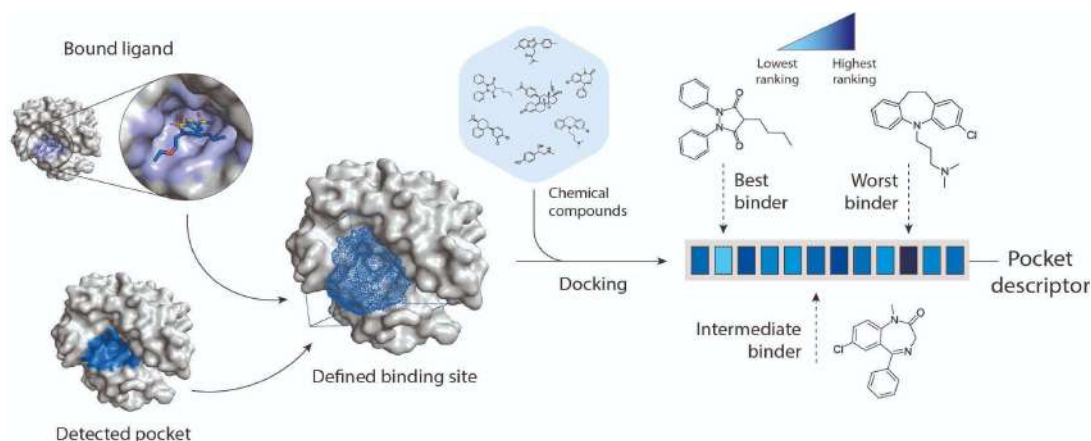
Novel binding site descriptors built upon inverse virtual screening

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Pocket descriptors embed relevant features of protein binding sites in the shape of numerical vectors¹. Unlike small molecule fingerprints, strategies to derive binding site descriptors are scarce and usually exhibit limited applicability. We herein present PocketVec, a novel strategy to derive comprehensible binding site descriptors based on the assumption that similar pockets bind similar ligands. By first docking an ordered set of molecules against the protein binding site of interest, we then store the corresponding molecular rankings into a numerical vector to finally build the pocket descriptor, which ends up representing the behavior of the binding site against the set of docked compounds. In this way, we are able to provide a unique, meaningful and handy descriptor for each binding site, in a similar way molecular fingerprints do for small molecules. We then benchmark PocketVec descriptors in several pocket similarity exercises² showing remarkable great performances when addressing the sensitivity to the binding site flexibility and sensibility and also when detecting similar pockets in unrelated proteins derived from published literature. Finally, we combine PocketVec descriptors with molecular signatures^{3,4} in order to predict protein-ligand interactions from a proteome-wide perspective and we prove that the use of PocketVec descriptors provides a significant enrichment in such predictions.



Keywords: Cheminformatics, Structure-based Drug Discovery, Binding site descriptors

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Electrolyte-Gated Field-Effect Transistors for sensing an Alzheimer's disease biomarker

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Electrolyte-Gated Organic Field Effect Transistors (EGOFETs) have been investigated recently as a useful means for biological sensing. Their working principle is based on converting a chemical event into a readable electrical signal. These devices can be prepared at low cost and on flexible substrates and present high sensitivity and specificity. [1][2] In this work, we report the study of Amyloid-beta(1-40) ($A\beta_{1-40}$) peptide aggregation kinetics using a label-free EGOFET immunosensor. $A\beta_{1-40}$ is a peptide present in the brain of the Alzheimer's disease (AD) patients. It tends to aggregate in oligomers, that are believed as major toxic effects in this pathology. Thus, they are considered as promising biomarkers for its diagnosis and therapy. [3]. The sensing element of EGOFETs resides at the Au gate-electrolyte interface. One strategy of Au surface engineering with antibodies has been developed. The validation of this protocol has been carried out using electrochemistry, employing Cyclic Voltammetry (C.V.) and Electrochemical Impedance Spectroscopy (E.I.S.) as characterization techniques. In the same way, the aggregation process has been characterized by EGOFET transfer characteristics, using PBS 1X as electrolyte. The results show that the maximum oligomer species are found after 2 hours of incubation in both electrochemical and EGOFET characterization. The final purpose is to combine the EGOFET with a microfluidic system paving the way towards the fabrication of simple and cost-effective devices that allows continuous measurements and more efficient diagnosis.

Keywords: Organic electronics, Electrolyte-gated organic field-effect transistors, amyloid-beta peptide, biosensors.

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Electroreduction of NHC-CO₂ adducts

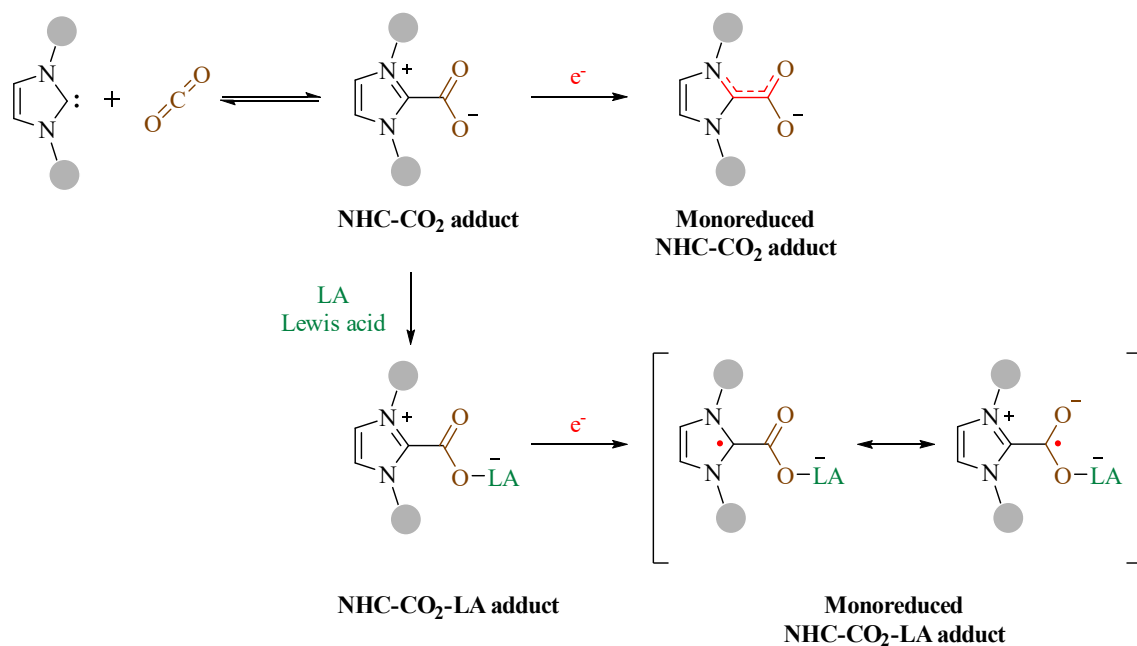
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The single electron reduction of free CO₂ to the corresponding radical anion is energetically demanding as it requires very low potentials to occur.^[1] N-Heterocyclic Carbenes (NHC) are known to react with polar bonds including CO₂ yielding NHC-CO₂ adducts.^[2] Hitherto, the one-electron reduction of these species is rather scarce in the literature.^[3,4] In this contribution, we present a combined experimental-theoretical study questioning the impact of different NHCs species in CO₂ monoelectronic reduction. Ultimately, we also examined the localisation of the spin density in the monoreduced NHC-CO₂ product and the influence of the addition of Lewis acids on this localisation.



Keywords: Electroreduction, CO₂ activation, N-Heterocyclic Carbenes, Lewis Acids, Spin density.

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Determination and Adsorption of Trace Levels Tetrachloroplatinate and Cytostatics Cis-diamminedichloroplatinum(II)

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Platinum-based anticancer drugs are a group of cytostatic agents that promote targeted cancer cell death by interfering with DNA division. They have been often found at low total platinum concentrations from tens of ppt to a few hundred ppb in hospital wastewater, municipal wastewater, and even surface water bodies, due to frequent use and eventually inevitable discharge [1,2]. The occurrence of platinum-based cytostatic drugs in aquatic ecosystems is often ignored and has been poorly characterized, although it has been demonstrated that these drug residues show recalcitrance to conventional wastewater treatment technologies and present serious adverse effects on exposed humans and aquatic organisms [3].

Hence, in the present study, an accurate spectrophotometric methodology has been developed, based on the complexation of either tetrachloroplatinate (PtCl_4^{2-} , used as a model) or cis-diamminedichloroplatinum (cisplatin) with o-phenylenediamine (OPDA) with a stoichiometric ratio of 1(Pt):2(OPDA). After the complex $[\text{Pt}(\text{C}_6\text{H}_4\text{N}_2\text{H}_2)_2]$ formed was extracted and concentrated by methyl isobutyl ketone (MIBK), it presented a strong absorbance signal at 705 nm with long-term stability. The method demonstrated good linearity over the range from 2.5 to 50 $\mu\text{g L}^{-1}$, with a high molar absorption coefficient. Furthermore, three commercial adsorbents cysteine-functionalized silica gel (Si-Cys), 3-(diethylenetriamino) propyl-functionalized silica gel (Si-DETA), and MetalZorb®Sponge (Sponge) were used to evaluate the removal of low concentrations of PtCl_4^{2-} and cisplatin. The influence of different factors including pH, contact time, initial concentration, and solution temperature were investigated.

This study suggests a method for precisely determining Pt(II) by a simple UV-vis method in aqueous samples at the part per billion (ppb) level, and provides a potential strategy for rapid and effective treatment of water contaminated with platinum-based anticancer drugs.

Keywords: platinum-based cytostatic drug; cisplatin; complexation-extraction; spectrophotometry; adsorption.

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Light-controlled CO₂ capture and detection using molecular switches

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In the last years, carbon dioxide concentration in the atmosphere is reaching alarmingly high levels, which human activity is the main responsible for.¹ Power stations account for most of the CO₂ emissions, which can be reduced by means of carbon dioxide capture technologies (CCS).² However, traditional CCS techniques such as amine scrubbing require a high energy consumption in order to recover the CO₂ absorbing materials.² To reduce this toll, more sustainable CCS technologies have to be developed, such as those based on photorecyclable absorbent materials.³ In this work we explore a new strategy to obtain light-controlled CO₂ capture that relies on the use of photoinduced molecular switches, whose interaction with carbon dioxide changes on photoisomerization between their two states. In particular, attention has been focused on spiropyran switches,⁴ which photoisomerize between (i) an inert spiranic state (Spir), and (ii) a merocyanine isomer (MC) that presents phenolate groups capable of interacting with CO₂. To explore this concept, light-controlled carbon dioxide capture has been tested for several spiropyran analogues through acid-base reaction of the phenolates with carbonic acid in aqueous media (Figure 1). The molecular switches with the most promising results have also been introduced in solid materials based on hydrogels to produce a material capable of capturing CO₂ and releasing it upon irradiation. Additionally, these materials possess photochromic and acidochromic properties that can be used as a colorimetric CO₂ detector, which will have interesting applications.

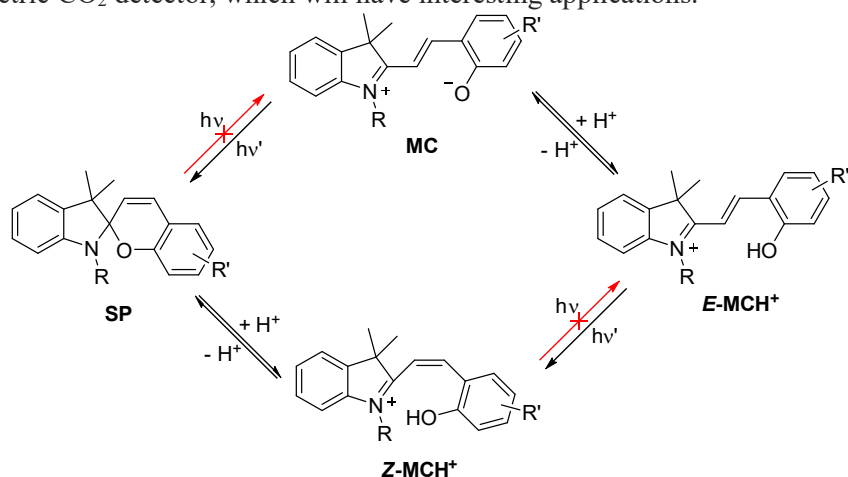


Figure 2: Different species of spiropyran that appear upon interaction with CO₂.

Keywords: Spiropyran, molecular switches, photochromism, CO₂ capture, hydrogels.

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Advanced Manufacturing at Pharmaceutical Industry

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During last years, the regulatory agencies encourage pharmaceutical laboratories to move forward to an advanced manufacturing. The objective is to improve the product quality, the efficiency, flexibility and the agility of the regulation manufacturing processes and reduce the drug shortage problems and costs^{1,2}. The advanced manufacturing include three fields: Continuous Manufacturing (CM), Quality by Design (QbD) and Process Analytical Technology (PAT).

In this work there are presented some of the industrial experiences of different solutions based on PAT advanced manufacturing applied to the pharmaceutical production processes. The application of PAT approach can serve as a control strategy that replaces traditional quality controls. There are included: starting material identification with NIR methods, process control of critical quality attributes (CQAs) for different unit operations and cleaning verification using Total Organic Carbon (TOC) (Figure 1).

- Inspection of incoming starting materials (SM) is essential to verify the correct quality specifications for the received material. A spectroscopic identification by NIR using sub-cascading spectral library was developed including 234 SM. Moreover, in order to guaranty the constant utility of the methodology, a backup NIR equipment is available and the transferability between them must be evidenced. A specific study was development based on a risk assessment approach and exploratory data analysis based on Principal Component Analysis.
- The assessment of CQAs is relevant for the control strategy of drug product manufacturing. Non-destructive nor invasive NIR methods were developed based on a sub-cascading spectral library and Partial Least Square regression for a solid dosage product.
- Cross-contamination between pharmaceutical products is proved by cleaning verification. Non-specific methodology is developed to verify the cleanliness for a specific active pharmaceutical ingredient based on TOC.



Figure 3. Continuous improvement based on PAT advanced manufacturing.

Keywords: Advanced Manufacturing, PAT, CQA, Spectroscopy, Chemometrics.

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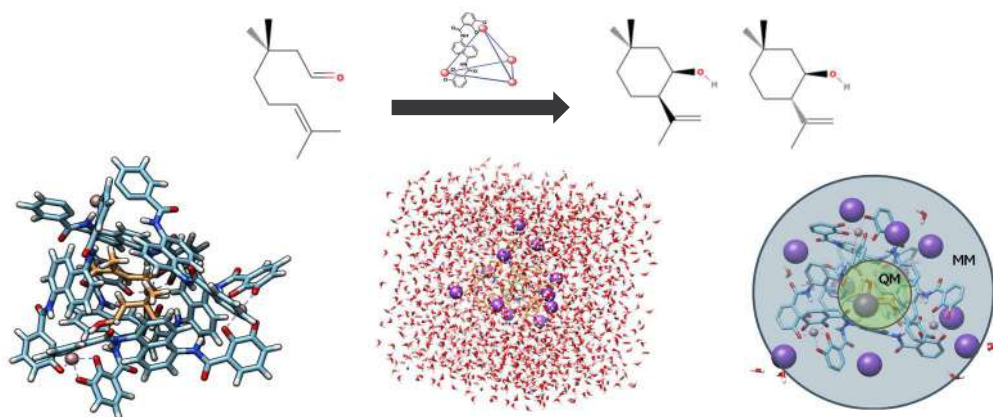
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Studying the catalytic effect of supramolecular hosts in a prins cyclization reaction.

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In recent years, studies on synthetic host mediated catalysis have driven into a better understanding of supramolecular interactions and the effect of chemical microenvironments.¹ [Ga₄L₆]¹²⁻ tetrahedron metallocage synthesized by Raymond's group² have proven to be a powerful catalyst for a variety of reactions. In this communication, the working progress on the intramolecular Prins cyclization of a terpene-like compound will be presented. Unravelling the detailed mechanism under the effect of the cage was pursued by comparing computational calculations with experimental data (Scheme 1).^{2,3}



Scheme 1. Schematic representation of the process and the models computationally employed.

The workflow includes a first DFT approach of both proposed² catalyzed and uncatalyzed reactions in solution, followed by MD and QM/MM calculations considering the reaction inside of the metallocage (Scheme 1).^{4,5} A summary of the most important conclusions will be presented.

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A novel electronic tongue using electropolymerized molecularly imprinted polymers for the simultaneous determination of active pharmaceutical ingredients

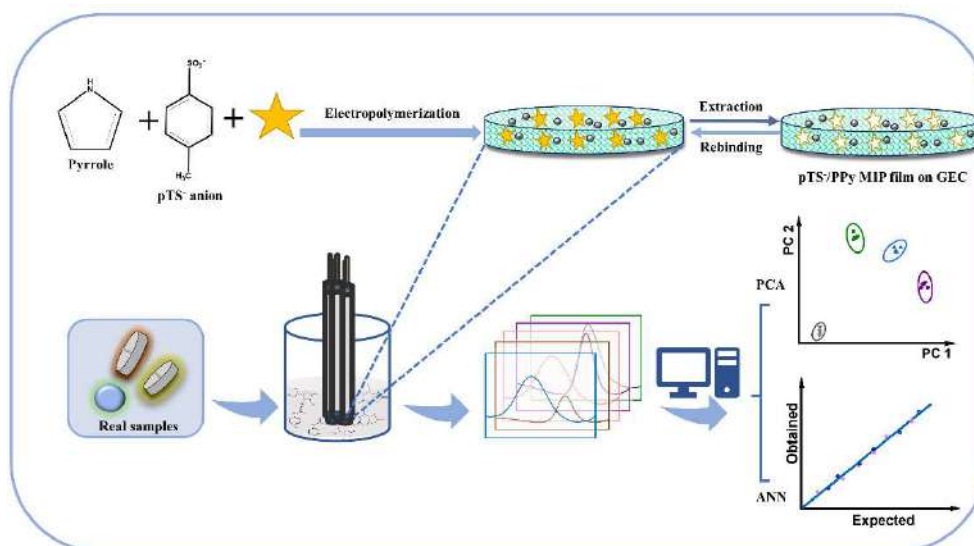
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The ever-increasing use of pharmaceutical drugs against diseases and the more sophisticated methods for detecting key metabolite biomarkers that allow the diagnosis of pathologies contributed to the greatly improved life quality and the extended life expectancy of human being. Thus, drug analysis is vital for pharmaceutical industry and clinical investigation.

In this work, the simultaneous determination of the mixtures of the three active pharmaceutical ingredients (APIs) in pharmaceutical samples including paracetamol, ascorbic acid and uric acid was achieved through MIP-based electronic tongues (ETs), which combines chemometrics with MIP-based electrochemical sensors. MIP-based sensors for the different compounds were prepared by in situ electropolymerization of pyrrole in the presence of *p*-toluenesulfonate anion (*p*TS⁻) that acted as functional doping ion of the polypyrrole (PPy) MIP backbone. Morphological characterization of the MIPs was done by scanning electron microscopy (SEM), while functionalization of the electrodes was monitored electrochemically. Under the optimized measuring conditions, the developed sensors showed a good performance, with good linearity at the μM level ($R^2 > 0.992$, limits of detection between 1 and 24 μM) as well as good repeatability (intra- and inter-day RSD values between 3 and 6% over 30 consecutive measurements). Finally, the quantification of the individual substances in different commercial drugs was achieved by an artificial neural networks (ANNs) model, showing satisfactory agreement between expected and obtained values ($R^2 > 0.987$).



Scheme: Preparation of *p*TS⁻/PPy MIPs by electropolymerization and the incorporation of the fabricated MIP-based sensors into the ET sensor array that applied to the analysis of APIs in pharmaceutical samples.

Keywords: Molecularly imprinted polymers; electronic tongues; electrochemical sensors; artificial neural networks; pharmaceutical analysis

A Quantum Chemical Study on Formamide Formation Route from Reaction between NH_2 and H_2CO on Interstellar Water Ice Surfaces.

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Interstellar formamide is a molecule of significant relevance because belongs to the group of interstellar complex organic molecules (iCOMs), which are representative compounds of the dawn of organic chemistry [1]. Moreover, formamide also plays an important role in prebiotic chemistry, not only because it contains carbon, oxygen, hydrogen and nitrogen (the four most important atoms from a biological point of view), but also because it is the simplest species containing the amide bond, the bond that joins amino acids forming peptides [2]. Due to its importance, alongside that has been detected in several star forming regions, different formation routes have been considered, both considering gas-phase reactions and processes on ice surfaces of dust grains [2]-[4]. In this contribution, the formation route of formamide starting from NH_2 and H_2CO , a synthetic route proposed to occur in the gas-phase [3], has been studied on water ice surface models in the crystalline and amorphous structural states adopting a periodic approach. Potential energy surfaces have been obtained by optimizing the stationary points at the HF-3c level followed by single point energy calculations at DFT. Results indicate important differences with respect to the gas-phase synthesis due to surface effects.

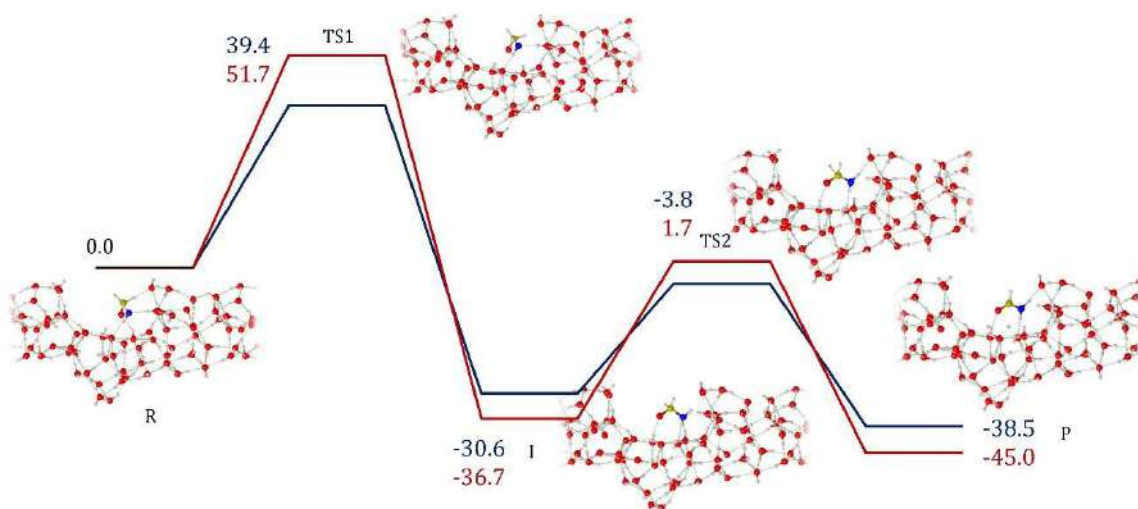


Figure 4: Potential energy surface and the corresponding stationary points of the $\text{NH}_2 + \text{H}_2\text{CO} \rightarrow \text{NH}_2\text{CHO} + \text{H}$ reaction on the amorphous slab model. ZPE corrected relative energy values in blue correspond to those computed at B3LYP-D3(BJ) and in red to those at M06-2X-D3, in kJ/mol. Atom color legend: red, O; blue, N; green, C white, H.

Keywords: astrochemistry, interstellar medium, DFT, iCOMs, grains

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