# 4<sup>th</sup> Workshop for Young Researchers in Chemistry



May 23<sup>rd</sup>-24<sup>th</sup> Faculty of Chemistry Universitat de València



VNIVERSITAT (À?) Facultat de Química



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# Welcome

Dear colleagues,

The organizing committee kindly welcomes you to the fourth edition of the Workshop for Young Researchers in Chemistry, which is being held in the Faculty of Chemistry of the University of Valencia.

The aim of this workshop is to share the research done by PhD students in the different fields of chemistry. This workshop is thought of as an excellent opportunity for every PhD student in chemistry to practice and give an oral communication in a friendly environment and, even, open new multidisciplinary collaboration lines between the different departments of the Faculty. Although the congress has been designed by and for PhD students, undergraduate or Master's students are also welcome to present their research in the format of a poster presentation. We hope that this workshop is of interest to you, and that you enjoy your time with us.

Organizing committee

# Organizing committee

- Gonzalo Abellán Dumont. Departament de Química Inorgànica
- Inés Adam Cervera. Institut de Ciència dels Materials de la Universitat de València- ICMUV
- Paloma Arjona Mudarra. Departament de Química Analítica
- Jaume Béjar Grimalt. Departament de Química Analítica
- Fernando Déniz Correa. Departament de Química Inorgànica
- Sofía H. Casal García. Departament de Química Inorgànica
- Patricia García Atienza. Departament de Química Analítica
- Alejandro García Juan. Departament de Química Analítica
- Javier Martínez Ponce. Departament de Química Inorgànica
- Miguel Muñoz Bartual. Departament de Química Analítica
- Víctor Navarro Esteve. Departament de Química Analítica
- Cristina Pintado Zaldo. Departament de Química Inorgànica
- Lidia Prieto García. Departament de Química Orgànica

# Coordination

- Prof. Dr. Rafael Ballesteros Garrido. Departament de Química Orgànica
- Prof. Dr. Begoña Milián Medina. Departament de Química Física



# Workshop structure and program

# 23<sup>rd</sup> of May

14.30h	Registration			
15.00h	Opening			
Session 1.	Chair: Gonzalo Abellán Dumont // Patricia García Atienza			
15.30h	OC1	Mercy Arteaga: Cu (II) and Mn (II) micellar systems with superoxide dismutase activity.		
15.45h	OC2	Rita Belén Cevallos Toledo: Upconversion Photoluminescence in a Dye-Ln 3+ Material.		
16.00h	0C3	Hanane El Mansour El Jastimi: Synthesis and Magnetic Characterization of Novel Spin-Crossover Complexes.		
16.15h	OC4	Thais Grancha Marco: From natural amino acids to Metal-Organic Frameworks.		
Session 2.	Chair: Miguel Muñoz Bartual // Paloma Arjona Mudarra			
16.30h	OC5	Pau Congost Escoin: Understanding the interaction between 2D materials and cells.		
16.45h	OC6	Camilo Jaramillo Hernández: Influence of Crystallographic Structure on the OER Performance of Co & Ni-based Layered Hydroxides.		
17.00h	0C7	Nazish Jabeen: Bioderived Functional Hydrogels: Tailoring Lignin for Enhanced Thermoelectric Performance.		
		Alejandro Orellana Silla: Guest-controlled polymorphism and exceptionally marked bi-stability in a spin crossover 3D porous amino-functionalized		
17.15h	0C8	coordination polymer.		
17.30h	Coffee break/Poster session			
Session 3.	Chair: Fernando Déniz Correa			
18.00h	L1	Round table: "Academic career beyond PhD"		



# 24<sup>th</sup> of May

Session 5.	Chair: Víctor Navarro Esteve // Patricia García Atienza				
9.30h	0C9	C9 Michele Forzatti: Semitransparent OLEDs with Ultrathin Light Emitting Layer and extraordinarily thick Perovskite Hole Transport Layer.			
9.45h	OC10	Erika Palazzetti: Design, synthesis and characterization of fluorescent chemosensors for selective recognition of metal cations in solution.			
10.00h	OC11	Luis Fernando Jiménez Hernández: Nanoencapsulation of Alkanes for Glass-Based Thermally Activated Building Systems.			
10.15h	OC12	Pau Peiró Vila: Transferability of global retention models between medicinal plants in liquid chromatography.			
Session 6.	Chair: Jaume Béjar Grimalt // Javier Martínez Ponce				
10.30h	OC13	Jose Huerta Recasens: Microencapsulation of Plant Protection Products in Lignin by Spray Drying.			
10.45h	OC14	Miguel Muñoz Bartual: Development of an easily assembled and affordable auto-sampler for <i>in-situ</i> wastewater sampling.			
11.00h	OC15	Christian Rodríguez Boscà: Imparting structural robustness of metal-organic cages based on oxo-dimolybdenum clusters.			
11.15h	OC16	Paula Rodrigo Martínez: Synthesis and Evaluation of a novel DT-diaphorase-responsive Nanoprobe for Hypoxia Imaging.			
11.30h	Coffee break/Poster session				
Session 7.	Chair: Alejandro García Juan // Jaume Béjar Grimalt				
12.00h	OC17	Pablo Navarro Madramany: Mimicking Superoxide Dismutase: Nanozymes with Remarkable Antioxidant Activity.			
12.15h	OC18	Iván Soriano Díaz: Characterization of triplet excited states in the photophysics of Cyclometallated Ir(III) Complexes.			
12.30h	OC19	Gerardo Gustavo Ripoll Rascheya: Bimetallic palladium-iron metal-organic framework MUV-23.			
12.45h	OC20	Roberto Sáez Hernández: Investigation of the Islamic gold coin collection of the University of Valencia.			
Session 8.	Chair: Sofía H. Casal García // Alejandro García Juan				
13.00h	OC21	Cristina Rodríguez Carrillo: Revolutionizing Sunscreen Formulation: Microwave-Assisted Synthesis of Ti-UVM-7 and Ce-UVM-7 for Sun Protection.			
13.15h	OC22 Sergio Ruíz Gamarra: Broadening the Reticular Chemistry Building Block Archive for Highly Interconnected Frameworks.				
13.30h	OC23	Ana Cristina Puig: De la cosecha desperdiciada a productos de alta calidad. Doctorado Industrial - Persiskin Auto.			
14.00h	Lunch break/Poster session				
Session 9.	Chair: Lidia Prieto García				
16.00h	L2	Round table: "From PhD to Industry"			
18.00h	Closure				



# **Round tables**

#### Rosa Adam Ortíz



# Academic career beyond PhD

Rosa Adam Ortiz graduated in Pharmacy in 2008 from the University of Valencia. In 2013, she obtained her PhD from the same university, funded by an FPI scholarship from the Valencian Government. During this period, she completed a stay at the University of Strasbourg. Following this, she joined as a postdoctoral researcher at the Leibniz Institute for Catalysis with a postdoctoral scholarship from the Ramón Areces Foundation. In 2017, she returned to the Valencian Community as a postdoctoral researcher at the Institute of Chemical Technology (ITQ), and in 2018, she secured funding to start an independent research line

through the Junior Leader Incoming postdoctoral program of the La Caixa Foundation and the SEJI program of the Valencian Government. In 2022, she joined the Department of Organic Chemistry at UV as a Ramón y Cajal researcher.

#### Salvador Cardona Serra



Salvador Cardona completed his PhD at the University of Valencia, focusing on the theoretical-experimental study of molecular magnets based on polyoxometalates. Following this, he received a postdoctoral scholarship with the medium-term goal of developing new materials for molecular spintronic applications at Trinity College Dublin (TCD). He rejoined UV within an ERC-CoG team (DECRESIM) for 13 months until obtaining a "Talent Attraction" scholarship from the campus of International Excellence and a "Juan de la Cierva" scholarship from MINECO. In 2023, he secured a Ramón y Cajal contract and currently

holds a teaching contract as an Assistant Professor in the Department of Physical Chemistry at the University of Valencia.



Adrián Pastor



Adrián Pastor graduated in Chemistry from the University of Córdoba (UCO). He completed his doctoral thesis in 2022 as an FPU contract holder in the FQM-214 group at UCO. During his doctoral studies, he was a Visiting PhD Student at the University of Oxford. Following his doctoral studies, he spent 1 year as a Postdoctoral Researcher at the University of Lisbon. Currently, he continues his postdoc with a Margarita Salas scholarship at the Green Technology Institute (ITQ).

#### David Pérez Guaita



David Pérez Guaita earned his doctoral degree in 2014 from the University of Valencia. In the following years, he has undertaken various positions in different laboratories across Europe and Australia, including 1 and a half years in France, 6 months in Germany, 4 and a half years in Australia, and 2 years in Ireland. His research has focused on the development of vibrational spectroscopic techniques to address a broad range of bioanalytical problems spanning clinical and biological fields. He has ultimately settled at the University of Valencia with a Ramón y Cajal scholarship, where he is establishing himself as an independent researcher.



#### Josep García

### From PhD to Industry



Josep García García, PhD received his doctoral degree in nanoscience and nanotechnology in 2016 at IRB Barcelona. Upon completion, he extended his stay for two years, conducting postdoctoral research at the same center. His work focused on the use of nanoparticles (both metallic and polymeric) for controlled drug release. He then returned to Valencia as a researcher at AIMPLAS for two years, focusing on the use of polymers for human health. Finally, in 2021, he joined the Curapath team, where he currently serves as the R&D Formulation Manager, responsible for producing a wide range of formulations, including lipid-based (LNPs) and polymer-based (PNPs).

#### Antonio Latorre Martínez



PORCELANOSA

Antonio Latorre Martínez, Director of Sustainable Development and Technological Innovation at Porcelanosa Group, holds a PhD in Chemical Sciences with a specialization in organic synthesis from Universitat Jaume I of Castellón. With over 15 years of experience in research and development across various fields, he began his work in 2007 focusing on the design, synthesis, and evaluation of cysteine protease inhibitors as part of drug development in the organic and medicinal chemistry group. He is the author of numerous academic articles, presentations, and communications aimed at knowledge transfer. In 2017, he transitioned to leading the R&D department at Porcelanosa Group, where he focuses on integrating new laboratory processes and methodologies.

During this time, his efforts have centered on enhancing product performance and process innovations. Concurrently, as Director of Sustainable Development and Technological Innovation, he has embarked on the decarbonization process of the ceramic sector, advocating for measures promoting energy efficiency and reconversion. He is actively involved in the transformation of hydrogen as an energy vector for thermally intensive sectors.



#### Andrés Nohales



Andrés Nohales holds a PhD from the University of Valencia in the field of epoxy resins. In 2007, he joined UBE Corporation Europe in the R&D department and has since pursued his career in the development of polycarbonate diols and their applications in high-performance polyurethanes. He has also contributed to the development of other products and processes at UBE and currently serves as the R&D manager for fine chemistry product development and process improvements.

#### Juan Pablo Villarroya



Juan Pablo Villarroya Roig holds a Ph.D. in Pharmacy from the University of Valencia. He presented his doctoral thesis in December 2000, titled "Synthesis and Study of Cyclohexyl-18-Crown-6 Macrocycles Involved in the Complexation of the Sr+2 Cation." He has developed his professional career in the food industry, working in the areas of Food Safety, Quality, R&D, and Operations in various international companies. He currently holds the position of Corporate Director of Food Safety and Quality at Natra, a manufacturer of cocoa-derived products.



# Oral contributions

- **OC1.** Mercy Arteaga. Cu(II) and Mn(II) micellar systems with superoxide dismutase activity.
- **OC2.** Rita Belén Cevallos-Toledo. Upconversion Photoluminescence in a Dye-Ln<sup>3+</sup> Material.
- **OC3.** Hanane El Mansour El Jastimi. Synthesis and Magnetic Characterization of Novel Spin-Crossover Complexes.
- OC4. Thais Grancha. From natural amino acids to Metal-Organic Frameworks.
- **OC5. Pau Congost-Escoin.** Understanding the interaction between 2D materials and cells.
- **OC6.** Camilo Jaramillo-Hernández. Influence of Crystallographic Structure on the OER Performance of Co & Ni-based Layered Hydroxides.
- **OC7. Nazish Jabeen.** Bioderived Functional Hydrogels: Tailoring Lignin for Enhanced Thermoelectric Performance.
- **OC8.** Alejandro Orellana-Silla. Guest-controlled polymorphism and exceptionally marked bistability in a spin crossover 3D porous amino-functionalized coordination polymer.
- **OC9. Michele Forzatti.** Semitransparent OLEDs with Ultrathin Light Emitting Layer and extraordinarily thick Perovskite Hole Transport Layer.
- **OC10.** Erika Palazzetti. Design, synthesis and characterization of fluorescent chemosensors for selective recognition of metal cations in solution.
- **OC11.** Luis Fernando Jiménez-Hernández. Nanoencapsulation of Alkanes for Glass-Based Thermally Activated Building Systems.
- **OC12. Pau Peiró-Vila.** Transferability of global retention models between medicinal plants in liquid chromatography.
- **OC13.** Jose Huerta-Recasens. Microencapsulation of Plant Protection Products in Lignin by Spray Drying.
- **OC14.** Miguel Muñoz-Bartual. Development of an easily-assembled and affordable autosampler for in-situ wastewater sampling.
- **OC15.** Christian Rodríguez. Imparting structural robustness of metal-organic cages based on oxo-dimolybdenum clusters.
- **OC16. Paula Rodrigo.** Synthesis and Evaluation of a novel DT-diaphorase-responsive Nanoprobe for Hyproxia Imaging.
- **OC17. Pablo Madramany.** Mimicking Superoxide Dismutase: Nanozymes with Remarkable Antioxidant Activity.
- **OC18.** Iván Soriano-Díaz. Characterization of triplet excited states in the photophysics of Cyclometallated Ir(III) Complexes.
- OC19. Gerardo Ripoll. Bimetallic palladium-iron metal-organic framework MUV-23.



- **OC20.** Roberto Sáez-Hernández. Investigation of the Islamic gold coin collection of the University of Valencia.
- **OC21. Cristina Rodríguez-Carrillo.** Revolutionizing Sunscreen Formulation: Microwave-Assisted Synthesis of Ti-UVM-7 and Ce-UVM-7 for Sun Protection.
- **OC22.** Sergio Ruiz Gamarra. Broadening the Reticular Chemistry Building Block Archive for Highly Interconnected Frameworks.
- **OC23.** Ana Cristina Puig. De la cosecha desperdiciada a productos de alta calidad. Doctorado Industrial Persiskin Auto.



# Cu(II) and Mn(II) micellar systems with superoxide dismutase activity

#### M. Arteaga<sup>1</sup>, S. Blasco<sup>1</sup>, M.T. Albelda<sup>1</sup>, E. Gracias-España<sup>1\*</sup>.

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Living organisms rely on Superoxide Dismutase (SOD) enzymes to protect themselves from the deleterious effects of the superoxide radical. SODs are a family of enzymes that remove highly reactive superoxide radical anions (O2-) and catalyze their dismutation into the non-radical species dioxygen and hydrogen peroxide.1 In protective humans, alterations in these mechanisms have been related to the pathogenesis of many diseases. However, the therapeutic use of the native enzyme is hampered by, among other things, its high molecular size, low stability, and immunogenicity.<sup>2,3</sup>



Figure 1. MnSOD mechanism and crystal structure of a synthetic mimic for this enzyme.

In this communication, we present the synthesis,

properties, and SOD-like activity for some **scorpiand-like ligands** with **amphiphilic properties**. These ligands form stable pentadentate complexes with electroactive metals such as Cu(II) and Mn(II) as the metal core. Their macrocyclic core is similar to the active center of native MnSOD. Its SOD-like activity has been tested by the McCord-Fridovich test and all of them are capable of SOD-like activity. Hydrophobic pending groups of different lengths modulate the overall hydrophobicity and seem to have an important role in the membrane permeability. The introduction of N-methyl groups also increases the permeability.

#### Acknowledgments

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# Upconversion Photoluminescence in a Dye-Ln<sup>3+</sup> Material

#### <u>R. Cevallos-Toledo<sup>1,\*</sup></u>, D. Bellezza<sup>1</sup>, M. González-Béjar<sup>1\*</sup>, J. Pérez-Prieto<sup>1</sup>

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Dye- lanthanide (Dye-Ln<sup>3+</sup>) materials combine the photophysical properties of organic chromophores (dyes) and the unique properties of rare earths (Ln<sup>3+</sup>) given rise to optical properties such as i) high extinction coefficients, ii) large Stokes shift and iii) high resistance to photobleaching among others. This type of materials were designed to sensitize the emission of lanthanides after absorption of the dye, through the well-known "antenna effect".<sup>[1]</sup>

In contrast, we have recently combined eosin (EOS), a xanthene dye, and ytterbium (Yb) to obtain an EOS-Yb material that presents cooperative sensitization upconversion (UC). The material presents the typical absorption spectrum of EOS, and an emission centered at 600 nm when excited at 980 nm (Figure 1). This emission has a lifetime of 1.76  $\mu$ s in DMSO and 12  $\mu$ s in DMSO*d*<sub>6</sub>. The UC emission presents a lineal response to the concentration and a quadratic response to the laser power density, and it is not affected by oxygen.<sup>[2]</sup>

This novel EOS-Yb material can be easily processed, and it is the first of his kind, which allows for the development of new materials that respond to visible and infrared light.



**Figure 1.** Absorption and emission spectra of EOS-Yb ( $l_{Ex}$ =980nm).

#### Acknowledgments

We thank Conselleria d'Educació, Universitats i Ocupació (CIPROM/2022/57) and to Generalitat Valenciana (GRISOLIA/2019/) for financial support. This study forms part of the Advanced Materials programme (MFA/2022/051) and was supported by MCIN with funding from European Union NextGenerationEU (PRTR-C17.I1) and by GVA.

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## Synthesis and Magnetic Characterization of Novel Spin-Crossover Complexes

Hanane El Mansour El Jastimi<sup>1,\*</sup>, Jana Juráková<sup>1,2</sup>, Miguel Clemente-León<sup>1</sup>, Eugenio Coronado<sup>1</sup>

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This research focuses on the synthesis and magnetic characterization of novel spin-crossover (SCO) compounds based on Fe(II) complexes of new derivatives of the archetypical ligand bis(pyrazol-1-yl)pyridine (1-bpp). In particular, we have functionalized with carboxylic acid and carboxylic alkyl ester the 4-pyrazolyl position of 1-bpp obtaining a family of symmetric and asymmetric ligands. The objective is to design SCO complexes exhibiting interesting behaviors (abrupt spin transitions and Light-Induced Excited Spin-State Trapping (LIESST) effect at relatively high temperatures) or that could be precursors of back-to-back ligands containing two bpp units (in the case of asymmetric ligands) or be deposited on surfaces. A successful example of this strategy was reported by us in the Fe(II) complex of bpp with carboxylic acid groups in the 4-positions of the two pyrazolyl groups (bpCOOH2p). This compound of formula [FeII(bpCOOH2p)2](CIO4)2·3.5Me2CO displayed an abrupt and hysteretic thermal spin transition close to room temperature associated with a crystallographic phase transition and a LIESST effect with an unexpectedly high T(LIESST) of 120 K.<sup>[1]</sup> In this communication, we have prepared a new solvate of the Fe(II) complex of this ligand of formula [FeII(bpCOOH2p)2](CIO4)2·3MeNO2. Structural and magnetic characterization reveals an abrupt an hysteretical spin transition of half of the high-spin centers found at 240 K accompanied by crystallographically symmetry breaking in the 200-220 K temperature range. On the other hand, Fe(II) complexes of asymmetric bpp ligands with a carboxylic acid or carboxylic ethyl ester in one of the two 4-positions of the pyrazolyl rings show in the solid state gradual and incomplete thermal spin transitions and LIESST effect. Finally, magnetic and structural characterization of the Fe(II) complex of 2,6-di[4-(propylcarboxy)pyrazol-1-yl]pyridine suggests a dominant low-spin state. The successful synthesis and characterization of these complexes highlight the potential for controlling spin transition behavior in this type of spin-crossover complexes. Furthermore, the deposition of these complexes onto silver and other surfaces offers opportunities for applications in spintronics and molecular electronics. This research contributes to the understanding of structure-property relationships in SCO complexes and lays the groundwork for the development of advanced functional materials with tailored magnetic properties.



Figure 1. Structural characterization of the three Fe(II) complexes

#### References

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## From natural amino acids to Metal-Organic Frameworks

#### <u>T. Grancha<sup>1,\*</sup></u>, J. Ferrando-Soria<sup>1</sup>, E. Pardo<sup>1</sup>.

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Metal-Organic Frameworks (MOF) are a class of crystalline porous material with a molecular base. They are constructed through coordination bonds between organic ligands and inorganic nodes, exhibiting a wide range of fascinating physical properties that position them as excellent candidates in technological applications of interest for the sustainable economic development of modern societies.

Among all these properties, their high porosity and tunable pore's size and functionality, together with their chemical stability stand out. MOFs possess a porous structure, providing a large surface area and volume, which is advantageous for adsorption and storage of gases and other molecules. In addition, the size of the pores in MOFs can be tailored by adjusting the organic ligands and metal nodes, allowing for selective adsorption of specific molecules.

In our work, we take advantage of our previous expertise on the oxamidate chemistry to modify natural amino acids achieving a vast library of ligands which give rise to a rich family of robust, water-stable MOFs. Their pores, containing open metal sites and the amino acids residues, have demonstrated the capability to capture heavy metals and molecules of organic nature, such as dyes, drugs and pesticides, thus providing great performance on water remediation and catalysis applications. Furthermore, the high crystallinity of these materials has allowed the resolution of MOF structures containing these molecules, providing valuable insights into the interactions that take place and how these molecules accommodate themselves within the pores. All this information paves the way to the design of new structures to face new challenges.



**Figure 1.** (a) Fragment of the structure of MOFs 1–5 emphasizing the common dicopper(II) building block. Perspective views of MOFs 1 (b), 2 (c), 3 (d), 4 (e), and 5 (f) along the *c* axes. Metals and organic ligands are depicted as gray sticks, whereas the amino acid residues are represented with the following color code: -CH<sub>2</sub>OH(1)/-CH(CH<sub>3</sub>)OH(2) (red), -CH<sub>2</sub>CH<sub>2</sub>SCH<sub>3</sub> (3 and 5) (orange), and -CH<sub>2</sub>SCH<sub>3</sub> (4 and 5) (yellow).

#### References

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## Understanding the interaction between 2D materials and cells

#### <u>P. Congost-Escoin<sup>1,\*</sup></u>, M. Alcaraz<sup>1</sup>, V. Oestreicher<sup>1</sup>, M. Lucherelli<sup>1</sup>, Martín Mizrahi<sup>2</sup>, I. Andreu<sup>3,4</sup>, G. Abellán<sup>1</sup>

<sup>1</sup> Instituto de Ciencia Molecular (ICMol), Universitat de València.
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Nanomedicine is the field of medicine that involves the application of nanotechnology for diagnosis, control, prevention, and treatment of diseases. It utilizes nanoscale materials to interact with biological systems at the molecular level, offering precise targeting and enhanced therapeutic effects. In his sense, 2D material arise as promising nanomaterials for their use in biomedical applications. In particular, 2D pnictogens (P, As, Sb and Bi) present an interesting combination of structural flexibility, and tunable properties, with a layer-dependent bandgap, spin-orbit coupling, and high theoretical capacity for electron charging.<sup>[1]</sup> In addition, their chemical reactivity, organic molecules' stabilization and light-conversion properties can be exploited in the field of nanomedicine for drug delivery platforms, biosensors and theranostic agents.<sup>[2]</sup>

Herein we present a comprehensive study of the interaction of this novel 2D pnictogen with cells. We performed a detailed structural and spectroscopic characterization of antimony-based nanomaterials (Sb-nanomaterials) obtained by three different production methodologies (bottomup and top-down routes), investigating the influence of the synthesis on their oxidation state and stability in biological environment. Furthermore, the effects of the Sb-nanomaterials in cells have been investigated by cytotoxic studies and enzymatic assays, revealing the correlation of the cytotoxic effects of the Sb-nanomaterials with their oxidation, shedding light on the toxic mechanisms they exert.<sup>[3]</sup> Finally, we show the next steps in the investigation of the interaction of 2D Pn with cells, complementing the previous studies and allowing qa fully understanding of the complex system between 2D materials and cells.



**Figure 1:** Schematic representation of the experiments conducted in this work. Three different Sb nanomaterials were synthetized following different methodologies and their cytotoxicity, stability and toxic mechanisms were investigated in different cell lines.

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# Influence of Crystallographic Structure on the OER Performance of Co & Ni-based Layered Hydroxides

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At the forefront of hydrogen production methods, water electrolysis emerges as a notably clean approach; however, the oxygen evolution reaction (OER) involved in this process requires high voltages, posing an energetic efficiency challenge.<sup>1</sup> Efforts over the past decade have focused on developing cost-effective electrocatalysts, with earth-abundant materials gaining prominence as non-precious metal OER catalysts.<sup>2</sup> Layered hydroxides (LHs) have proven excellent OER electrocatalysts, offering scalability, affordability, and composition with abundant elements. Despite their electrochemical prowess, fundamental aspects influencing OER, such as the role of LH crystalline structure, coordination environment, and cation distortions, remain understudied.<sup>3</sup>

Here we study different Co & Ni-based LH phases by in-house physicochemical and electrochemical characterizations, followed by XAS measurements in ALBA Synchrotron of the samples previous and after the OER, revealing that the crystallographic structure significantly impacts OER performance. Remarkably, the  $\alpha$ -LH phase, distinct from the layered double hydroxide (LDH), exhibited superior catalytic behaviour for both Co and Ni. This discovery unveils a new chemical signature, paving the way for the rational design of more efficient LH-based electrocatalysts.<sup>4,5</sup>



**Figure 1.** Normalised XANES in Co and Ni edge respectively A) C) and Fourier transform of the extracted κ2-weighted EXAFS oscillations B) D) for LHs samples pre and post-electrochemical performance.

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# Bioderived Functional Hydrogels: Tailoring Lignin for Enhanced Thermoelectric Performance

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Driven by the depletion of fossil fuels and the increasing frequency of climate disasters, the 21<sup>st</sup> century faces an unprecedented energy crisis. This has sparked significant interest from both academia and industry in exploring techniques for converting renewable power sources into electrical energy. Recent research has focused on developing technologies to improve the efficiency of low-grade thermal energy harvesting. In this domain, ionic thermoelectric materials (i-TEs) have garnered significant attention due to their unique properties such as excellent Seebeck coefficients, low thermal conductivity, and high electrical conductivity. A key advantage of i-TEs lies in their ability to generate substantial voltages even under minimal temperature gradients. Unlike conventional thermoelectric materials that rely on electron/holes transport, i-TEs utilize ions as charge carriers, enabling the conversion of heat into electricity. <sup>1</sup>

Extensive research has focused on utilizing hydrogels for developing efficient and eco-friendly i-TE materials. Hydrogels are three-dimensional, highly versatile materials possess tunable mechanical properties and the remarkable ability to hold large amounts of water. This water compatibility allows for the incorporation of ionic solutions, essential for the ionic Seebeck effect and the movement of ions within the material – a key factor in electricity generation from heat. <sup>2</sup> In recent years, lignin presents a promising sustainable alternative for the development of ionic thermoelectric materials. Lignin has a highly branched three-dimensional network structure and functional groups that boast high reactivity. This unique combination makes lignin an ideal candidate for designing high-performance lignin based hydrogels through chemical crosslinking with another synthetic polymer such as PVA. <sup>3</sup>

This study focuses on the production of lignin based hydrogels and their functionalization with amine group. These crosslinked lignin-based hydrogels exhibit lower value of Seebeck coefficient (1.614 mVK<sup>-1</sup>), ionic conductivity (4.04 mScm<sup>-1</sup>) and thermal conductivity (0.22 Wm<sup>-1</sup>. K), that give rise to small value of ionic figure of merit (0.0013). To enhance the performance of i-TE properties, the crosslinked lignin-based hydrogels undergo further functionalization with amine groups. <sup>4</sup> For the amination of lignin-based hydrogel, this research utilizes a green synthesis method composed solely of NaOH-water, eliminating the need for organic solvents. The amination of lignin-based hydrogel with 2-Chloroethylamine hydrochloride (CEH) was greatly affected by the concentration of CEH and the optimized reaction condition. Thus, these functionalized ionic thermoelectric hydrogels result in high negative Seebeck coefficient (-7.873 mVK<sup>-1</sup>), superior ionic conductivity (6.09 mScm<sup>-1</sup>) and thermal conductivity (0.184 Wm<sup>-1</sup>. K) that leads to enhance ionic figure of merit 0.056 as compared to previous hydrogel, making them suitable candidates for various applications such as energy harvesting, waste heat recovery and thermal management systems.

#### Acknowledgments

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# Guest-controlled polymorphism and exceptionally marked bistability in a spin crossover 3D porous amino-functionalized coordination polymer

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Functionalization of spin crossover (SCO) porous coordination polymers (PCPs) with hydrogenbonding active groups is an efficient strategy for the study of multifunctional materials.<sup>[1]</sup> Indeed, the interaction of guests with the host framework may improve the cooperativity of the SCO inducing eventual occurrence of bi-stability. However, comprehensive magneto-structural studies are still needed to understand the role of guests in the enhancement of the SCO properties. Here, we report the 3D Hofmann-type PCP {Fe<sup>II</sup>(dpyan)[Au<sup>I</sup>(CN)<sub>2</sub>]<sub>2</sub>} guest (dpyan = 2,5-di(pyridine-4yl)aniline; guest = ethanol (1·EtOH), methanol (1·MeOH), nitrobenzene (1·NO<sub>2</sub>bz), water/methanol (1·H<sub>2</sub>O·MeOH) where the amino functionalized dovan ligand has been selected to induce host-guest interactions.<sup>[2]</sup> Our X-ray diffraction studies reveal that the packing mode of 1-guest is determined by the trapped guest yielding either orthorhombic (1-NO2bz and 1·H<sub>2</sub>O·MeOH) or monoclinic (1·EtOH and 1·MeOH) phases differing by subtle distortions of the framework. The thermal dependence of the magnetic susceptibility shows that all derivatives present SCO properties modulated by the amount and nature of the encapsulated guest as well as by the crystal phase. The latter is clearly evidenced for the orthorhombic derivatives which, concomitantly with partial desorption of guest, transform into the monoclinic phase whose SCO behaviour is radically different to that of the original orthorhombic structure. As a relevant example, when 1.NO2bz (orthorhombic) converts into 1.077NO2bz (monoclinic), the SCO drastically changes from a non-hysteretic gradual spin transition to a cooperative SCO with a colossal hysteresis 105 K wide as shown in Figure 1. These remarkable SCO properties have been interpreted relying on the obtained structural information.



Figure 1. Evolution of the  $\chi$ T vs. T behaviour of a sample of  $1 \cdot NO_2Bz$  transforming from orthorhombic to monoclinic upon heating in situ within different thermal cycles.

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# Semitransparent OLEDs with Ultrathin Light Emitting Layer and extraordinarily thick Perovskite Hole Transport Layer

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Organic light-emitting diodes (OLEDs) have had a huge gain in popularity by virtue of their simple fabrication process, thin structure and for the possibility to devise transparent devices. However, the production of stable, cheap and efficient devices remains a challenge. Ultrathin nondoped emitting layers have been investigated as a way to simplify fabrication process and lower material consumption, but the consequent reduction in thickness may decrease device stability. Overcoming this issue with thicker transport layers is alluring but tough, as organics have intrinsically low charge-carrier mobilities. On the other hand, metal halide perovskites (MHPs), promising materials in many fields of optoelectronics, have also been used as charge transport materials, where their transparency in the visible region and high hole conductivity make it possible to increase the thickness of the layer to the micrometer-scale without increasing the operation voltage or reducing luminous efficiency.

In light of this, we developed a semitransparent OLED having a thick cesium lead chloride allinorganic perovskite hole transport layer, an ultrathin (<0.1 nm) [Ir(ppy)<sub>2</sub>acac] film as emitting layer and a semitransparent top indium-tin oxide contact deposited on top of a thin metallic layer. The resulting devices have a thickness exceeding 1  $\mu$ m, a combined peak luminance of over 1000 cd m<sup>-2</sup>, a current efficiency of 34 cd/A and a transparency in excess of 60% over the visible spectrum above 480 nm. The hole transporting CsPbCl<sub>3</sub> layer includes two thin (2 nm) CsCl layers at the interfaces, which have been demonstrated to be able to passivate interfacial halide vacancies, improving the photoluminescence and reducing exciton quenching in turn. The nature of the ultrathin layer was investigated by means of contact angle measurement, which confirmed that the molecules forming the LEL are not in the form of a neat layer. The metallic layer could be deposited with little damage to the underlying organic layers but despite its low thickness, essential to guarantee transparency, it still protected towards the final ITO sputtering deposition. The combination of transparent top electrode, thick perovskite HTL and ultrathin LEL, described herein for the first time, entails a reduction in material and fabrication costs and is promising towards future cheap and stable semitransparent OLEDs.



# Design, synthesis and characterization of fluorescent chemosensors for selective recognition of metal cations in solution

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The research of new chemosensors able to selectively bind and signal the presence of specific metal ions in samples of biological and environmental relevance is an always growing field. Metal cations such as  $Mg^{2+}$  and  $Ca^{2+}$  play crucial roles in the human physiology [1-5]. The development of simple and fast systems for the selective detection of metal cations in different matrices is therefore highly desirable and fluorescent chemosensors represent a suitable approach to this task, due to simplicity, reliability, velocity and low-cost. For this reason, a new series of ligands containing the 2-(2-hydroxy-3-naphthyl)-4-methylbenzoxazole (HNBO) fluorophore linked to polyamine scaffolds was synthesized and investigated [6-7]. This fluorophore has been linked to different amine scaffolds obtaining five fluorescent chemosensors (L1-L5, Figure 1). The binding properties of L1-L3 towards Alkali and Alkaline-earth metal ions were investigated in different solvents by UV-Vis absorption, fluorescence emission and NMR spectroscopies. Ligand L3 shows a good selectivity for Mg<sup>2+</sup> in DMSO, so this system was applied to calculate the concentration of magnesium in real samples using solid-state optodes; the quantity of magnesium found with this method is close to the real one. Among the metal ions used in many fields there are also Rare Earth cations (RE), used as probes and labels in chemical and biological applications. For this reason, two strategies were adopted to synthetized ligands for RE metal ions starting from L3: increasing the number of donor atoms (L4-L5, Figure 1) and approaching of polyamines to the acid groups as L6 and L7 (Figure 1) that contain HBO (2-(benzo[d]oxazol-2-yl)-6-methylphenol)) as a fluorophore. The coordination and optic properties towards RE ions have been studied in different conditions founding that L7 shows a good selectivity for RE ions acetonitrile/water solvent mixtures.



Figure 1. (a.) HNBO-based and (b.) HBO-based chemosensors

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# Nanoencapsulation of Alkanes for Glass-Based Thermally Activated Building Systems

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Promising technologies have been recently proposed to exploit heat as a renewable energy source by taking advantage of the latent heat storage capacity of phase transition materials (PCMs). Among others, organic PCMs performing solid–liquid transitions within confined volumes exhibit greater energy density without relevant changes in pressure and volume [1-3]. Encapsulated PCMs of this kind, whose melting temperature ( $T_m$ ) is around the room temperature (i.e. hexadecane), have been extensively studied for thermal regulation, procuring the control of indoor temperatures in buildings [1, 4]. However, their application in the development of modern building materials remains a challenge due to the intrinsic chemical and physical properties of the capsules [3, 4]. In this work, we present different strategies to encapsulate hexadecane within polymer nanocapsules and their study as potential coating fillers in glass-based thermally activated building systems (GTABS).

Miniemulsion-based strategies were studied to prepare the polymer nanocapsules, following either a chemical or a physical method. The general protocol consisted of mixing an organic phase, containing hexadecane along with the desired monomer/polymer, and an aqueous solution of the respective stabilizer. Miniemulsions were obtained by applying a high-shear ultrasound treatment to the mixture for the later formation of capsules under appropriate conditions. First, lignin shells were formed through an emulsion–solvent evaporation technique by dissolving the biopolymer in a volatile organic solvent. Second, polyurethane nanoparticles were obtained via the interfacial polycondensation of an isocyanate and poly(ethylene glycol). Finally, polyaniline and polystyrene capsules were synthesized via free-radical polymerization.

A spheric morphology was confirmed for the polymer nanoparticles by electron microscopy. The incorporation of hexadecane into the preparation formulation resulted in an increase of the hydrodynamic radius measured by dynamic light scattering and in the appearance of two thermal events in the differential scanning calorimetry thermograms (DSC), associated with the phase transitions of the encapsulated hexadecane. The differences in the stored thermal energy between the different systems, calculated from the DSC thermograms, were correlated with the different loads of PCM obtained from the thermogravimetric analysis. The encapsulation efficiency is shown to be related to the physicochemical properties of the different miniemulsion systems, impacting the morphology and the thermal properties of the final materials. Finally, thin films were prepared from hexadecane-polystyrene capsules dispersed in an aqueous solution of a polymer blend by solvent evaporation over glass substrates. The thermoregulation capacity of the coated glasses was assessed by comparing their relative heat conduction when used as a frontier dividing two compartments within a closed temperature chamber under controlled heating conditions. An increase in the thermal conductivity of the polymer films was observed after the incorporation of the nanoencapsulated PCMs during the heating process associated to the melting of the hexadecane suggesting their potential use as functional coatings in GTABS.

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# Transferability of global retention models between medicinal plants in liquid chromatography

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Significant advancements have been made in enhancing the resolution and information accuracy of complex sample analyses, especially in the realm of natural products, through the application of global retention models in Reversed-Phase Liquid Chromatography (RPLC) employing multilinear gradients of organic solvent. These global models, built upon the differentiation of solute retention effects from those originating from the column and solvent, demonstrate predictive capabilities comparable to conventional retention models, all without requirement for standards [1-3]. The implemented gradient facilitates retention modelling even when discernible patterns in peak position are absent, ensuring the consistent elution of compounds with manageable time windows. These methodological innovations significantly improve chromatographic optimisation, accommodating compounds with unknown characteristics and widely varying concentrations, which surpass the constraints of traditional methodologies [4]. While individual models provide finer precision, they often require standards that are typically unavailable for natural product samples. Additionally, creating individual models can be time-consuming due to the need for repetition for additional compounds. Experimental validation highlights the accuracy of resolution forecasts and the long-term stability of results obtained with global models, with minimal variations in peak intensity over time. A carefully designed experimental framework enables the accurate determination of global parameters for column and solvent, ensuring consistency across various plant samples. This study demonstrates the successful transfer of a global retention model from one chromatographic system to another, employing a new column and a sample with comparable natural properties. It also examines the transferability of predictions across diverse plant species. These dual insights highlight both the efficacy of model transfer between instruments and the broader applicability of predictions across botanical varieties.

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# Microencapsulation of Plant Protection Products in Lignin by Spray Drying

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In recent years, the excessive use of fossil fuels and the resulting environmental impact has become a global issue. In addition, the need for innovation in the agricultural sector, driven by the increasing food demand and production, has also had a significant impact on the environment due to the excessive use of plant protection products (PPP's) to enhance plant growth and soil fertility. Therefore, there is a need to create systems capable of reducing this high energy consumption, while minimizing the amount of agrochemicals required. These systems should be resistant to rain and solar radiation, ensuring efficient delivery to plants, long-lasting protection after application, and controllable release. One solution to the efficiency and degradation issues of agrochemicals is the encapsulation of these products using biomass-based materials, such as lignocellulosic polymers.

This work focuses on the encapsulation of a plant-protection compound, difenoconazole, through the formation of micro- and submicrometric capsules of a kraft-type lignin. Encapsulation was carried out by using spray drying. The morphology of the formed particles was determined by scanning electron microscopy (SEM, Figure 1A). The encapsulation was estimated from differential scanning calorimetry (DSC) measurements (thermogram in shown Figure 1B) and the release profiles were studied by ultraviolet–visible spectroscopy. In addition, the degradation with temperature of the different systems was compared by thermogravimetric analysis (TGA). Finally, an efficient encapsulation of diffenoconazole was demonstrated by liquid chromatography coupled to mass spectrometry, confirming the ability of this system to encapsulate PPP's in lignin.



Figure 1. Characterization of the prepared lignin/difenoconazole capsules by SEM (A) and DSC (B).

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# Development of an easily-assembled and affordable autosampler for *in-situ* wastewater sampling

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The problem of drug abuse, involving both illicit and legally prescribed substances, presents a significant concern for our society, with incalculable consequences. The widespread availability and misuse of these substances reflects the importance of understanding consumption patterns and their correlation with public health trends to initiate prevention campaigns and implement effective interventions [1]. In this sense, wastewater monitoring provides objective and anonymous information in almost real-time on licit and illicit drug abuse in a specific population. Nevertheless, wastewater monitoring presents several methodological challenges, and particularly, sample collection, is the most critical step [2]. Designing a sampling strategy to obtain a representative wastewater sample is fundamental for accurately extrapolating the obtained results to the studied community. The collection of spatially and temporally distributed samples is required to ensure the representativeness, and the selection of an appropriate sampling mode and frequency of sampling is a critical factor [3]. Typically, these sampling programs are conducted with high-cost and large-size automatic sampling devices, which additionally present several logistical difficulties. Therefore, there is a need to develop simpler, cheap and more readily available equipment. This study introduces a cost-effective and easily assembled device, utilizing a low cost mini-peristaltic pump with Arduino open hardware and sources, as an alternative for conventional wastewater sampling devices. This system allows for extensive deployment without requiring costly installation or maintenance equipment and is designed to fit into space-restricted installations. The design, component selection, and operational parameters have been assessed to ensure the required functionality. After its development, to demonstrate the effectiveness of the proposed system, wastewater samples were collected at high temporal resolution to obtain representative samples for monitoring illicit and pharmaceutical drugs. Deployment of the developed system was carried out through various sewers located at the University of Valencia's installations on different days throughout the first half of 2024. Following the collection step, a validated analytical method developed by our research group, which combines solid-phase extraction (SPE) and ultra-high liquid chromatography coupled with tandem mass spectrometry determination was applied to the wastewater samples to determine the presence of more than forty licit and illicit substances, to estimate spatiotemporal drug use trends by the university community through wastewater surveillance.

#### Acknowledgments

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# Imparting structural robustness of metal–organic cages based on oxo-dimolybdenum clusters.

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Metal–Organic Cages (MOCs) are a subclass of hybrid com- pounds composed of metal ions or clusters linked by organic ligands forming discrete porous molecular structures. MOCs have shown promising applicability for gas storage,<sup>1</sup> catalysis,<sup>2</sup> molecular separation<sup>3</sup> or biomedicine,<sup>4</sup> among others. Nevertheless, the study of MOCs remains challenging due to their poor thermal and hydrolytic stability that arises from the lack of extended connectivity.<sup>5</sup> Thus, crystals of MOCs often degrade upon activation preventing the structural determination by single crystal X-ray diffraction. This lack of structural data of activated structures hinders precise analysis and understanding of their porosity.

A family of robust and stable molybdenum-based metal–organic cages have been obtained based on the  $[Mo_2O_2(\mu_2-O)_2]^{2+}$  secondary building unit. The resulting cages are decorated with different pyridines, imidazole and tetrazole derivatives that impart structural stability, resulting in the structural elucidation of the activated cage with single-crystal diffraction. The chemical robustness of the cage, denoted MUV-27, is also demonstrated by the post-synthetic modification of the nitrogen containing donors on the surface of the cage, which allows the exchange of the pyridine and imidazole derivatives maintaining the cage structure.



**Figure 1.** (a) Secondary building unit of MUV-27-py containing the  $[Mo_2O_4]^{2+}$  cluster and one DMA<sup>+</sup>(dimethyl ammonium) cation; (b) and (c) orthogonal views of the structure of the octahedral  $[Mo_{12}O_{12}(\mu_2-O)_{12}(BTC)_6(py)_{12}]^{6-}$  cage, MUV-27-py. Color code: Mo = pink, O = red, C = black, N = blue. Hydrogen atoms have been omitted for clarity except those of the DMA<sup>+</sup> cation in (a).

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# Synthesis and Evaluation of a novel DT-diaphorase-responsive Nanoprobe for Hypoxia Imaging

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Cancer remains a significant challenge in modern medicine, despite the advances made in chemotherapy. Hypoxic conditions, characterized by reduced oxygen levels and the overexpression of enzymes such as nitroreductase, DT-diaphorase (DTD) or azoreductase are common in solid tumors. These conditions contribute to poor prognosis and treatment failure, emphasizing the need for tools helping in the evaluation of the hypoxia level [1].

Fluorescence imaging emerges as a sensitive, selective, rapid, and efficient bioanalytical technique for monitoring the state, alterations, and activities of targets in vivo [2]. Of particular interest is DTD, which has garnered attention because of its significantly elevated expression in some malignant tumors, often reaching up to 50-fold higher than those in normal cells [3].

The aim of this work is to develop a hybrid system designed to detect the presence of DTD and release a fluorophore in response. To achieve this goal, we synthesized a novel nanoprobe consisting of an MCM-41 nanoparticle core loaded with a fluorescent molecule and gated with a DTD sensitive molecule, as illustrated in Figure 1.

MCM-41 nanoparticles were synthesized and characterized by several experiments, including Xray powder diffraction and transmission electron microscopy. Following nanoparticle synthesis, rhodamine B, a fluorescent molecule, was efficiently loaded onto the MCM-41. To ensure controlled release of the fluorophore, a gate based on an azo bond was synthesized and anchored to the nanoparticle surface. The release of the fluorophore under hypoxic conditions can be monitored by recording the fluorescence spectra of rhodamine B.



Figure 1. Representation of the MCM-41 gated nanomaterial loaded with Rhodamine B

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# Mimicking Superoxide Dismutase: Nanozymes with Remarkable Antioxidant Activity

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The malfunction of the nervous system associated with several neurodegenerative disorders has been linked to the misregulation of free metal ions and oxidative stress. For example, in Alzheimer's disease, the accumulation of Fe and Cu in beta-amyloid plaques is thought to be responsible for increased oxidative damage in certain areas of the brain. These transition metals promote the aggregation of protein fibrils into peptide aggregates and mediate the production of reactive oxygen species (ROS) through Fenton reactions, with superoxide radicals playing a major role. Ongoing research is focused on the chelation of these redox active transition metals to avoid their participation in the formation of the peptide aggregates, as well as on the reversion of their activity from ROS generation to antioxidant activity. [1]

A family of tetraaza-pyridinophane macrocycles capable of chelating Fe(II) and Cu(II) has been synthesized and characterized. Potentiometric and UV-Vis titrations, along with superoxide dismutase and  $H_2O_2$  removal activity assays, indicate that the synthesised macrocycle can coordinate Cu(II) and Fe(II) at physiological pH, resulting in the formation of complexes with remarkable SOD activity and a significant capacity to scavenge  $H_2O_2$  from solution, respectively. [2]

Boehmite nanoparticles (BNP) were functionalised with the synthesised tetraaza-pyridinophanes and the resulting systems were characterised by NMR, elemental analysis, ICP-MS and DLS. The studies showed the nanoestructured systems had up to 5-fold increased SOD activity, with regard to the non-anchored complexes. This might be attributed to the positive z-potential of the BNP, which would attract the anionic substrates towards their surface. [3]



Figure 1. Family of nanozymes synthesized and studied.

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# Characterization of triplet excited states in the photophysics of Cyclometallated Ir(III) Complexes

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Cyclometallated Ir(III) complexes have been studied in recent years in relation to their use in lightemitting electrochemical cells (LECs).<sup>1</sup> A high emission quantum yield ( $\Phi_{em}$ ) is essential to obtain a good performance of the final LEC device.

In this oral communication, the radiative and non-radiative decay paths will be explored for a series of cyclometallated Ir(III) complexes with the general formula  $[Ir(C^N)_2(N^N)]^+$  using theoretical calculations based on Density Functional Theory (DFT).

The differences in their  $\Phi_{em}$  can be rationalized in some cases as the result of the distinct radiative paths in operation,<sup>2</sup> while in other cases the key variable that determine the global emission efficiency is the accessibility of non-radiative decay paths mediated by metal centered (<sup>3</sup>MC) triplet states.<sup>3</sup>



Figure 1. Chemical structure of  $[Ir(ppy)_2(bpy)]^+$ , the archetype reference complex for  $[Ir(C^N)_2(N^N)]^+$  complexes

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## Bimetallic palladium-iron metal-organic framework MUV-23

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Pd is a widely known catalyst in important reactions such as hydrogenation and coupling reactions (carbon–carbon and carbon–heteroatoms), which exists in the form of homogeneous and heterogenous catalysts. Homogeneous catalysts are characterized by their high activity, selectivity and specificity, but they are difficult to be separated and typically present a limited stability. On the other hand, traditional heterogeneous catalysts are known for they higher stability and easier separation, but present a reduced activity and selectivity due to the absence of good leaving groups and the limited accessibility of their active sites arising from their intrinsic configuration in the form of metal aggregates. This reduced accessibility is typically solved by the introduction of the metal catalyst in porous supports like carbon, silica or alumina.[1]

An attractive approach to combine the advantages of homogeneous and heterogeneous catalysts while minimizing their drawbacks is to immobilize a homogeneous catalyst in a support. [2] In this context, Metal-Organic Frameworks (MOFs) have been extensively studied because of their high porosity and broad range of host-guest interactions, thanks to a virtual infinite possible combination of their building blocks. This versatility has permitted to introduce organometallic palladium complexes as ligands in MOFs, making possible to combine the better accessibility and specific environment of a homogeneous catalyst with the easier separation and in some cases stability of traditional heterogeneous catalyst. [3]

Herein, we present a bimetallic Pd-Fe based MOF MUV-23 (Material from the University of Valencia) synthetized using a bis-3,5-pyridinedicarboxylic acid palladium(II) chloride (H<sub>4</sub>L) as a metaloligand, to introduce the Pd moiety and the well-known [Fe<sub>3</sub>O(CH<sub>3</sub>CO<sub>2</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]ClO<sub>4</sub> trimetallic cluster as iron source (Figure 1). The synthesis and structural characteristics of MUV-23 will be discussed in detail.



**Figure 1.** Scheme of the synthesis and chemical structure of MUV-23. View of the pores of MUV-23 through the c axis, in yellow the 1D channels and in blue the 0D cages.

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# Investigation of the Islamic gold coin collection of the University of Valencia

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The analytical investigation of ancient artifacts allows to obtain valuable information not only about their composition, but also from their origin or state of conservation. In this work, the gold coins collection of the University of Valencia has been investigated in terms of elemental and colorimetric properties.

Given the great historical, cultural and economic value, the analysis of these items must be carried out using non-invasive techniques in order to preserve them to the utmost extent. When it comes to the elemental composition, portable X-ray fluorescence was implemented. The colorimetric investigations were done using an image-based method, after careful tuning and optimization of the procedure to deal with some potential interferences like glaring and dirt sometimes present in the coins.

The image-based method was validated through comparison with a reference device. Applying a characterization process of the camera in order to account for internal and external confounding variables (color enhancement, lighting environment...) allowed to obtain colorimetric descriptors that were statistically comparable to those obtained through the reference device. Mean CIELAB values of the coins were estimated to be L\* =  $76 \pm 3$ , a\* =  $10.9 \pm 1.2$  and b\* = $48.4 \pm 2.6$ .

When it comes to the elemental composition, the investigated coins showed very homogeneous Au content, with values above 90 % in almost all of the samples. However, some remarkable differences and patterns were observed when comparing the coins from Iberian and African mints: coins struck at the early stages of the Almoravid presence in the Iberian peninsula had lower Au contents when compared to those struck in African mints. This result could potentially point to a certain degree of recycling of already-circulating coins which contained lower Au.

All in all, this work describes the elemental composition of Islamic gold coins dating back from the Almoravid period, and presents data that describes some patterns pointing to potential differences depending on the origin and time. Also, a new image-based method to characterize the color of these Cultural Heritage artifacts is presented, and the colorimetric descriptors shown.

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# Revolutionizing Sunscreen Formulation: Microwave-Assisted Synthesis of Ti-UVM-7 and Ce-UVM-7 for Sun Protection

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The synthesis of Ti-UVM-7 and Ce-UVM-7 catalysts using solid-state microwave generators represents a significant advancement in the development of efficient UV absorbing materials for sunscreen applications. Conventional synthesis methods often suffer from prolonged reaction times and lack of control over material properties, hampering the progress of UV protection technologies. In contrast, solid-state microwave generators offer rapid and homogeneous heating, enabling precise modulation of reaction parameters and yielding crystalline and phase-pure catalysts [1].

Through X-ray diffraction (XRD) analysis, we confirm the successful synthesis of Ti-UVM-7 and Ce-UVM-7, transmission electron microscopy (TEM) elucidates uniform particle morphologies, reflecting improved homogeneity achieved through microwave-assisted synthesis.

The UV absorption properties of Ti-UVM-7 and Ce-UVM-7 are thoroughly investigated using UVvisible spectrophotometry. Both materials exhibit pronounced absorption in the UV region, demonstrating their potential as effective UV blockers. Subsequently, their efficacy as UV absorbing materials is evaluated in sunscreen formulations and compared against conventional UV filters [2]. The results indicate that Ti-UVM-7 and Ce-UVM-7 display comparable or superior UV absorption capabilities, underscoring their suitability for incorporation into sunscreens.

	SPF	% metal
1% Ti-UVM-7	$1,24 \pm 0,29$	0,08
5% Ti-UVM-7	$1,62 \pm 0,40$	0,35
10% Ti-UVM-7	$2,41 \pm 0,86$	0,68
2% TiO <sub>2</sub>	$2,\!10\pm0,\!90$	2,00
1% Ce-UVM-7	$1,31 \pm 0,13$	0,12
5% Ce-UVM-7	$2,19 \pm 0,24$	0,62
10% Ce-UVM-7	$6{,}44\pm0{,}30$	1,18
2% CeO <sub>2</sub>	$4,\!00\pm0.69$	2,00

Table 1. Comparison of Sun Protection Factor (SPF) for samples with different amount of material.

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# Broadening the Reticular Chemistry Building Block Archive for Highly Interconnected Frameworks

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Metal organic frameworks (MOFs) are a kind of porous crystalline materials formed by the combination of ions or metals cluster (known as Secondary Building Units or SBU) and organic ligands via strong bonds. Their inherent porosity and robustness as well the different functionalities that can be incorporated into the different building blocks have made these materials potential candidates for extensive applications like gas storage and separation, catalysis, or selective sensing, among others.<sup>1</sup>

Nowadays, advances in the construction of MOFs relies in the control of the connectivity, allowing researchers to design materials with interesting topological profile.<sup>2</sup> Typically, transition metal ions have been widely used in the construction of these materials, however, in modern times the use of rare earth (RE) MOFs have attracted enormous attention due the coordination versatility, allowing to produce diverse structures.<sup>3</sup>

Considering these aspects, a new family of isoreticular TTF based MOF was constructed by the combination of tetrathiafulvalene octabenzoic acid (TTFOC) with different rare earth elements. The reaction of this octatopic ligand with different lanthanoids produce an uncommon topological net where two different class of clusters coexist together.



**Figure 1.** a) 8-connected RE<sub>6</sub> and RE<sub>4</sub> cluster as a cube and the two 5-connected TTFOC linker. b) Single-crystal structure. Colour Scheme: RE cyan; O red; C grey; S yellow. c) Topology of the MOF.

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# Poster contributions

- **P1.** Julio Camargo-Moreno. Temperature Damping Effect of Encapsulated Alkanes on Polymer-Coated Glasses.
- **P2. Iñaki Fernández.** Enantioselective addition of sodium bisulfite to aza-dienes derived from aurone.
- **P3.** Mar Folgado-Grau. Determination of psychopharmaceuticals in wastewater.
- **P4. Valentin Gradisteanu.** Development of embedded machine learning potentials for simulations of enzymatic catalysis.
- **P5.** Judit Hostalet-Romero. Study of the desymmetrization of compounds bearing two phenol groups through an organocatalytic tosylation reaction.
- **P6.** Alberto Llopis-Lacruz. Metal/Lignin/Magnetite Hybrid Nanoparticles as Catalysts for the Degradation of Nitroaromatic Pollutants.
- **P7.** José Luis Monzón-Luque. Trifluoromethylated Compounds Obtained by Near Infra-Red Organic Photocatalysis.



# Temperature Damping Effect of Encapsulated Alkanes on Polymer-Coated Glasses

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The dependance on fossil fuels have accentuated the energy crisis in Europe, where habitational buildings consume about 40% of the energy produced each year [1]. Controlling indoor temperatures is a well-known strategy to reduce the energy consumption which can be easily achieved by integrating phase change materials (PCMs) to building elements such as windows [2]. Encapsulated organic PCMs performing solid-liquid transitions at low temperatures (i.e. short-chain alkanes) are preferred due to the thermodynamic behavior of the system and its potential operation range [3]. Among others, one advantage of the nanoencapsulated PCMs is their practical incorporation in polymer films [4], which can later act as functional coatings for glass-based thermally active building systems due to the isothermal nature of the phase transition [3]. In this study, we present the evaluation of heat conduction across polymer-coated glasses containing either encapsulated hexadecane or octadecane using a closed temperature chamber specifically design for this purpose.

The tested PCMs were encapsulated within polystyrene nanocapsules through free-radical polymerization in miniemulsion for their subsequent dispersion on an aqueous solution of poly(vinyl alcohol) and carboxymethyl cellulose. The films were prepared by a casting-solvent evaporation technique over glass substrates and their temperature regulation capacity was compared against a control group. In a typical experiment, the coated glasses were used as a rigid frontier between two compartments whose temperatures were recorded upon a controlled heating from an infrared bulb placed in one of the compartments, as illustrated in Figure 1A. The temperature difference between both compartments relative to an uncoated glass, shown in Figure 1B–C, demonstrates that the incorporation of PCM into the polymer coatings enhances the temperature damping of the substrate. This behavior was associated to the phase transition upon heating and suggest the viable usage of this materials as functional coatings for the thermal comfort regulation.



**Figure 1.** Technical design of the temperature chamber [A] indicating the measurement spots (T1–T4) and differential temperature analysis of coated glasses containing encapsulated hexadecane [B] and octadecane [C].

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# Enantioselective addition of sodium bisulfite to aza-dienes derived from aurone.

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Organosulfur compounds play a crucial role in organic chemistry. Chiral sulfonic acids and their derivatives, such as sulfonates and sulfonamides, have emerged as highly important pharmacophores in medicinal and pharmaceutical chemistry. They have a wide range of biological activities, including antiviral, antibacterial and antitumor properties, among others <sup>[1]</sup>.

Therefore, finding new catalytic pathways that permit the preparation of chiral sulfur-containing organic molecules is an important objective in current organic chemistry <sup>[2]</sup>.

Adamo and co-workers reported in 2011 the first enantioselective organocatalytic synthesis of chiral sulfonic acids employing sodium bisulfite as nucleophile.<sup>[3]</sup>Following a similar strategy, our group and others have developed a synthetic pathway to chiral taurine derivatives via the addition of sodium bisulfite to nitroalkenes <sup>[4]</sup>.

In this communication, we report a procedure for the enantioselective addition of sodium bisulfite to aza-dienes derived from aurone. This process provides chiral sulfonic acids substituted with a benzofuran ring, serving as precursors for tricyclic sultams.



Figure 2: Enantioselective addition of sodium bisulfite to aza-diene derived from aurone.

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## Determination of psychopharmaceuticals in wastewater

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Nowadays the use of psychopharmaceuticals to combat the effects of different illnesses, as well as everyday discomforts or pains, has become a matter of great social interest. Some of these substances, such as benzodiazepines, are misused without proper medical supervision, leading to dependency [1]. Additionally, there is an environmental problem as water pollution by these medications is harmful to aquatic ecosystems and can affect the biosphere. Therefore, controlling the concentrations of these compounds in wastewater is important. The analysis of wastewater from urban areas offers the advantage of evaluating the overall consumption of psychopharmaceuticals in the population without requiring the permission of specific individuals. However, the main drawback of analyzing this type of sample is the low concentration of analytes, making a pre-concentration process necessary to increase sensitivity. Compared to other sample preparation processes, solid-phase extraction (SPE) allows higher recoveries and lower analysis costs since smaller volume of reagents, solvents, and specific eluents are required [2]. A fast and sensitive reversed-phase liquid chromatography-tandem mass spectrometry (LC-MS/MS) method was developed and validated for the determination of 15 psychopharmaceuticals in wastewater, classified as benzodiazepines and derivatives, antihistamines, and opiate agonists, among others. Wastewater samples were collected from different places in the University of Valencia (Burjassot Campus) and concentrated by SPE using ExtraBond Polymeric ECX cartridges. The proposed method was validated in terms of linearity, limits of detection and quantification, accuracy, precision, extraction efficiency and matrix effect following the guidelines proposed by the European Medicines Agency (EMA). The method limits of quantification ranged from 0.7 to 5.5 ng/L. Seven compounds of those studied were found in the analyzed samples. where doxylamine was the pharmaceutical found in the largest number of samples.

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## Development of embedded machine learning potentials for

## simulations of enzymatic catalysis

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Enzymatic catalysis has been a central focus both in describing biological systems and in advancing methods for quantum chemistry. This work aims to develop a machine learning (ML) potential for application within a ML/MM hybrid model focused on the well-studied chorismate mutase enzyme.<sup>1</sup> The calculations achieve accuracy comparable to DFT/MM level simulations while maintaining the computational cost of a semi-empirical/MM simulation.

The ML model is designed to train on the *in-vacuo* ligand in two distinct environments: within the enzyme and in water, utilizing an active learning methodology. Notably, the ML potential not only distinguishes between reactants and products but is also trained from a broader potential energy surface (PES), enabling the exploration of stationary points for chorismate mutase catalyzed reaction. It is a meaningful advance as it allows the study of complete chemical processes. A significant limitation, however, lies in coupling ML potentials trained solely on the ligand and its interaction with the rest of the enzyme. This work represents the first application of the recently developed EMLE embedding scheme and its corresponding software implementation.<sup>2,3</sup> The embedding will also be done in an active learning principle, for which the embedding is always recalculated from the same conformations as in the ML potential.

The potential for this work lies in its promise to train using more precise electronic structure methods, thereby significantly cutting down computational expenses. This advancement could lead hybrid QM/MM simulations to reach the microsecond scale while retaining accuracies akin to first-principle methods.

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# Study of the desymmetrization of compounds bearing two phenol groups through an organocatalytic tosylation reaction

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The importance of the chirality of organic molecules in different areas, ranging from Biology to Materials Science, is well known.<sup>[1]</sup> Therefore, the development of new methodologies for the enantioselective synthesis of organic compounds constitutes an area of intense research. Among them, catalytic procedures (asymmetric catalysis) are particularly attractive since they allow minimizing chirality consumption and reducing waste production.<sup>[2]</sup> In this context, there are very few examples of the desymmetrization of organic compounds bearing two phenols<sup>[3]</sup> to prepare chiral 1,1-diaryl methanes.<sup>[4]</sup> Therefore, this project aims to study the desymmetrization of compounds with two phenol rings using and organocatalytic tosylation reaction using as the Takemoto's thiourea as catalyst (Scheme 1).



Figure 1. Organocatalytic desymmetrization reaction of bisphenols

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# Metal/Lignin/Magnetite Hybrid Nanoparticles as Catalysts for the Degradation of Nitroaromatic Pollutants

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The reduction and degradation of nitroaromatic pollutants is crucial from both an environmental and an industrial perspective. In particular, 4-aminophenol, formed as the reduction product of 4-nitrophenol, acts as an important industrial precursor in the synthesis of analgesic and antipyretic medications, anticorrosive lubricants, and hair dyeing agents. The catalytic reduction stands as one of the most effective methods to carry out the removal of such nitro pollutants [1].

Nowadays, much attention is being paid to the application of heterogeneous catalysis by using biopolymeric supports for the deposition of different metals. Moreover, magnetic supports are attractive owing to their unique features, such as a simple separation and recoverability by a magnet, a large specific surface area, high magnetic permeability, low cost, small size, and high stability. In this context, lignin is presented as the most abundant natural heterogeneous and three-dimensional amorphous biopolymer on earth after cellulose. Kraft lignin is a highly suitable material for the stabilization of metal nanoparticles because it is abundant, cheap, wood-based, sustainable, and—more importantly—it contains multi-ligating organic functionalities (aromatic, alkenyl, alcoholic, phenolic, carboxylic, carbonyl, and ethereal groups) [2].

In this work, an inverse miniemulsion strategy was used to prepare biopolymeric nanoparticles while synthesizing magnetite in situ. The experimental procedure, partially based on a strategy previously reported by our group [3], consisted of mixing an aqueous phase, containing iron(II) chloride tetrahydrate and iron(III) chloride hexahydrate as precursors of magnetite, and the sulfonated lignin dissolved in water, with an organic phase, containing polyglycerol polyricinoleate (PGPR) dissolved in an appropriate organic solvent. After applying a high-shear ultrasound treatment to the mixture, miniemulsions containing the magnetite precursors and sulfonated lignin in the dispersed phase were obtained. Subsequently, trimethylamine and a diisocyanate were added under an inert atmosphere, the former to promote a basic medium and initiate the formation of magnetite, and the latter to cross-link the lignin chains. As a result, hybrid nanoparticles comprised of magnetite and cross-linked lignin are formed.

The morphology and composition of the materials have been characterized by scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX) and inductively coupled plasma–mass spectrometry (ICP-MS). In addition,

We are currently working on the incorporation of copper on the prepared lignin/Fe<sub>3</sub>O<sub>4</sub> hybrid nanoparticles and investigating their application on the catalytic reduction of 4-nitrophenol by sodium borohydride. Our preliminary results indicate the great catalytic potential of the systems in the degradation of pollutants. In addition, we are also carbonizing the materials to compare the catalytic activity of both carbonized and non-carbonized systems.

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# Trifluoromethylated Compounds Obtained by Near Infra-Red Organic Photocatalysis

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Photochemistry started at the beginning of the 20<sup>th</sup> century and has proven suitable for green reactions.<sup>[1]</sup> Traditionally, UV irradiation has been used to generate radical species capable of undergoing organic reactions. UV and visible light, constitute 5% and 45% of the total solar radiation, respectively. Although most photocatalysts can only be activated by means of UV-vis light irradiation, this limitation hampers the efficiency of photocatalytic systems.<sup>[2]</sup> To overcome this drawback, increasing attention has been diverged to the use of near-infrared (NIR) light. Despite NIR light is less energetic, it represents the 50% of the solar spectrum. In recent years, Os(II) complexes have been efficiently used as NIR-photoredox catalysis, but preparation and handling of the aforementioned catalyst requires the use of a glovebox, and more important, osmium can be an issue in terms of toxicity. In the last years, cyanines have emerged as a greener alternative to replace metallic complexes as photocatalysts in organic transformations.<sup>[3]</sup>

In this study, cyanine-based compounds were employed as NIR photocatalysts in trifluromethylation reactions affording organic molecules containing fluorinated groups, which can be of interest in medicinal chemistry, given the beneficial effects of incorporating fluorinated groups into specific positions.<sup>[4]</sup>



Figure 1. Schematic representation of the near infra-red organic photocatalysis.

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