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BOOK OF ABSTRACTS

Tarragona, 5-7 February, 2025

2nd Meeting of **Inorganic and Organometallic Chemistry** of the Catalan Chemical Society

RQIO 2025

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Scientific Program

Wednesday, February 5		**Thursday, February 6**		**Friday, February 7**	
		Session III	Chair: Albert Figuerola **Sponsored by Inorg. Chem.**	**Session VII**	Chair: Núria Aliaga-Alcalde **Sponsored by Adv. Catal.**
		9:00-9:45	Plenary 2 **Eva Rentschler**	9:00-9:45	Plenary 4 **Alicia Forment**
		9:45-10:00	Oral Communication 9 *Yulia Nelyubina*	9:45-10:00	Oral Communication 22 *Mircea Dincă*
		10:00-10:15	Oral Communication 10 *Rosa Diego*	10:00-10:15	Oral Communication 23 *Leví Arrieche-Hernández*
		10:15-10:30	Oral Communication 11 *Silvia Gómez-Coca*	10:15-10:30	Oral Communication 24 *Pilar Fernández-Seriñán*
		10:30-11:10	Flash 1 – 8	10:30-11:10	Flash 20 – 26 + Joves SCQ
		11:10-11:35	Coffee Break *Poster Session*	11:10-11:35	Coffee Break *Poster Session*
		Session IV	Chair: Rosario Núñez	**Session VIII**	Chair: Mónica H. Pérez-Temprano **Sponsored by AstraZeneca**
		11:35-11:50	Oral Communication 12 *Clara Viñas*	11:35-11:50	Oral Communication 25 *Valentin Novikov*
		11:50-12:05	Oral Communication 13 *Andrea Álvarez-Núñez*	11:50-12:05	Oral Communication 26 *Núria Aliaga-Alcalde*
		12:05-12:20	Oral Communication 14 *Araceli de Aquino*	12:05-12:20	Oral Communication 27 *Jose Muñoz*
		12:20-12:45	Flash 9 – 13	12:20-12:35	Oral Communication 28 *Roc Matheu*
		12:45-13:00	Oral Communication 15 *Arántzazu González-Campo*	12:35-13:20	Plenary 5 **Cathleen Crudden**
		13:00-13:15	Oral Communication 16 *Carles Fuertes-Espinosa*		
		13:15-13:30	Group Picture	13:20-13:40	Closing Ceremony and Awards
14:00-15:30	Registrations	13:30-16:00	Lunch		
15:30-15:45	Welcome and Opening				
Session I	Chair: Oscar Pàmies **Sponsored by AstraZeneca**	**Session V**	Chair: Miquel Costas **Sponsored by Organometallics**		
15:45-16:30	Plenary 1 **Per-Ola Norrby**	16:00-16:45	Plenary 3 **Alicia Casitas**		
16:30-16:45	Oral Communication 1 *Maria Besora*	16:45-17:00	Oral Communication 17 *Yisong Wen*		
16:45-17:00	Oral Communication 2 *Albert Solé-Daura*	17:00-17:30	Flash 14 – 19		
17:00-17:15	Oral Communication 3 *Filippo Scarchilli*	17:30-18:00	Coffee Break *Poster Session*		
17:15-17:30	Oral Communication 4 *Carla Alamillo Ferrer*	**Session VI**	Chair: Xavi Ribas		
Session II	Chair: Carles Bo	18:00-18:15	Oral Communication 18 *Arnald Grabulosa*		
17:30-17:45	Oral Communication 5 *Albert Poater*	18:15-18:30	Oral Communication 19 *Mireia Pujol*		
17:45-18:00	Oral Communication 6 *Isabel Guerrero*	18:30-18:45	Oral Communication 20 *Ricardo Castarlenas*		
18:00-18:15	Oral Communication 7 *Joaquín Soriano-López*	18:45-19:00	Oral Communication 21 *Javier Ordóñez-Hernández*		
18:15-18:30	Oral Communication 8 *Bahareh Khezri*				
18:30-20:30	**Welcome Gathering**	20:45	**Conference Dinner** *Hotel Imperial Tarraco* *Sala Forum*		

Table of contents

Plenaries

PL1

Predicting Reaction Selectivity

P.-O. Norrby[1]

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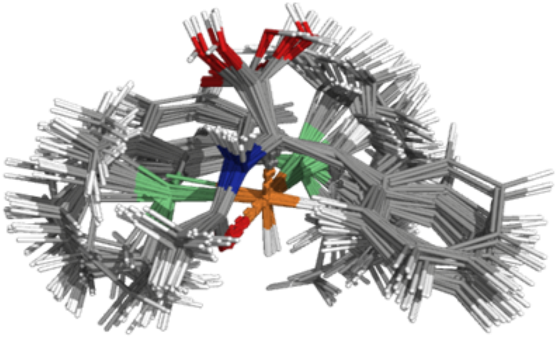
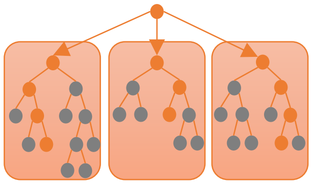
Detailed knowledge of reaction mechanisms will allow prediction of the reaction selectivity, usually by DFT methods. However, such methods are too slow to allow a full exploration of all possible reaction paths for conformationally complex molecules. We explore more efficient and more accurate methods, based on rapid molecular mechanics methods tuned to work for transition states. Our in-house method Q2MM[1] allows prediction of stereoselectivity by screening thousands of transition states for each reaction, as illustrated to the right for asymmetric hydrogenation. More recent examples will be covered in the talk.





For regioselectivity predictions, where classical force fields are invalid, we instead explore different ways of combining quantum chemical calculations with limited experimental data in machine learning approaches to derive selectivity models[2]. A range of such approaches will be illustrated.

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PL2

Metallacrown Complexes: Host-Guest interaction paving the way for Molecular Magnets

E. Rentschler[1], D. Laible[1], A. Hagenow[1], T. Fischer[1], H.-J. Elmers[2], S. Lach[3], C. Ziegler[3]

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[2] *Institute of Physics, Mainz University, Staudingerweg 7, 55099 Mainz, Germany,*
[3] *Department of Physics, RPTU Erwin-Schrödinger Straße, 67663 Kaiserslautern, Germany*

Metallacrown complexes (MCs) have been extensively studied in recent years for their coordination ability with hydroxamic acid and derivatives, especially with first-row transition metal ions. Taking advantage of host-guest chemistry, the atomic arrangement in MCs can be adjusted, allowing tunable magnetic exchange between metal ions within the ring structure[1,2]. By implementing metal ions that can make a significant contribution with high single-ion anisotropy, these systems exhibit SMM behavior and thus promise future applications in data storage, quantum computing, and molecular electronics as discussed in physics, chemistry, and materials science[3,4].

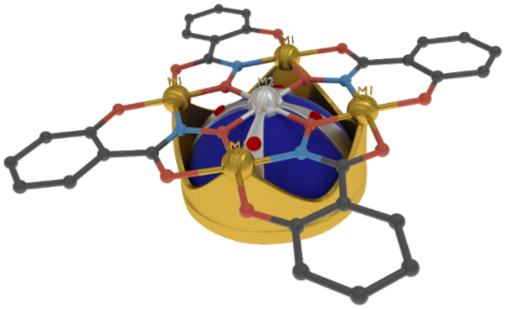

Figure: artistic representation of a metallacrown

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An organometallic perspective to first-row transition metal catalysis

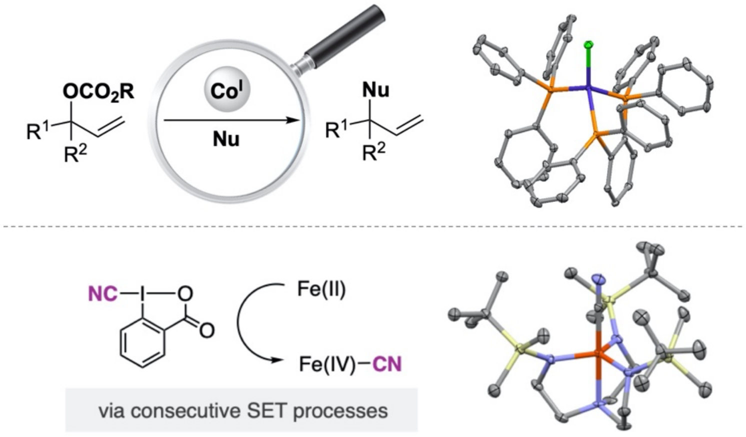
A. Casitas[1]

[1] Philipps-Universität Marburg, Fachbereich Chemie, Hans-Meerwein-Str. 4, 35032 Marburg. casitasm@chemie.uni-marburg.de

Catalysis plays a pivotal role in the development of environmentally friendly and efficient chemical processes towards the synthesis of high-value chemicals from abundant and renewable feedstocks. On the quest of more sustainable synthesis, our research group focuses on the discovery and development of organic reactions catalyzed by middle and late first-row metals (Mn, Fe, Co, Ni).

Transition-metal catalyzed nucleophilic allylic substitutions are well-established methods for the construction of carbon-carbon and carbon-heteroatom bonds in organic synthesis. In this communication, I will present our work in regioselective cobalt(I)-catalyzed nucleophilic allylic substitution reactions. This project aims at finding complementary reactivity to the well-stablished methods that involve precious metals, while providing an in-depth mechanistic understanding.[1]

In the second part of the talk, I will introduce fundamental insights into the reactivity of organoiron species in high oxidation state, which may ultimately find application in catalysis towards organic synthesis. Thus, synthetic strategies to prepare Fe(III) and Fe(IV) cyanide complexes using hypervalent iodine reagents will be disclosed.[2] Finally, I will present our ongoing work on the synthesis of highly reactive organometallic Fe(III) and Fe(IV) complexes and their involvement in carbon-carbon bond-forming reactions.[3]



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Transition metal chalcogenides 2D materials: A playground for chemistry

A. Forment-Aliaga[1]

[1] Instituto de Ciencia Molecular-Universitat de València. C/ Catedrático José Beltrán, 2, Paterna, Valencia, 46980 Spain.
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Two-dimensional materials (2Dms) are a family of nanomaterials composed of ultrathin layers only a few atoms thick. They exhibit unique electronic, optical, and mechanical properties due to electron confinement in two dimensions and their exceptionally high surface area. The development of new functionalities in 2Dms can be achieved through chemical modification with various molecules. To this end, we have been working on the functionalization of 2D transition metal chalcogenides (TMCs) using molecular systems such as Prussian blue analogues, polyoxometalates, and spincrossover compounds.[1-3] These modifications have enabled the introduction of additional functionalities, enhancing the suitability of these nanomaterials for energy and optoelectrònic applications. More recently, we have explored innovative strategies for asymmetric functionalization of 2Dms, leading to the creation of Janus 2Dms, which possess distinct chemical properties on their opposite faces.[4]

However, characterizing symmetric and asymmetric functionalized systems poses difficult challenges due to the limited detection sensitivity of spectroscopic methods like Raman, IR, and XPS. These techniques also lack spatial resolution and struggle to provide information about coating homogeneity. In contrast, Scanning Probe Microscopy (SPM) offers nanoscale analysis with excellent lateral resolution. Beyond topographical studies, SPM is a powerful tool for probing additional properties, such as mechanical characteristics. Our work has demonstrated that SPM adhesion mapping of bare and molecularly functionalized 2Dms enables precise examination of surface chemical properties.[5] These findings underscore the potential of simple adhesion SPM techniques to investigate the chemical nature of 2Dms, offering valuable insights for the broader scientific community engaged in this field.

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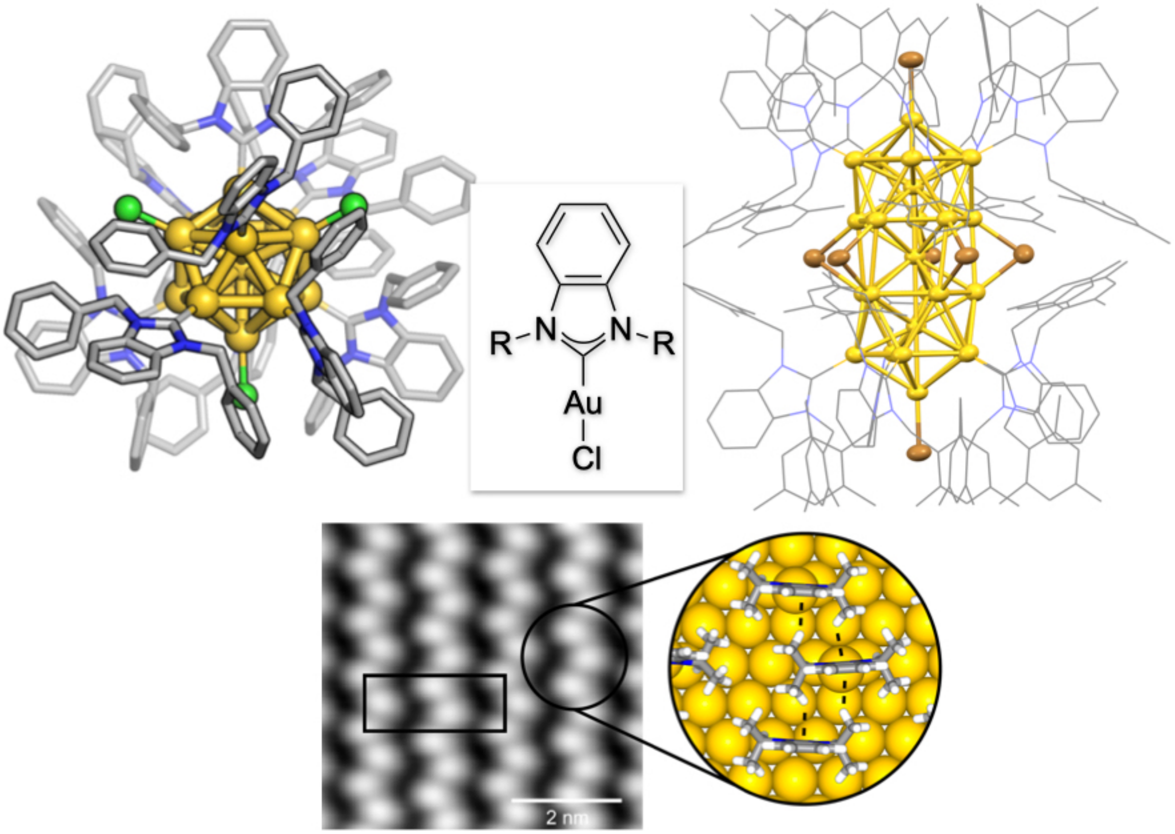
The power of organometallics: From catalysts to self-assembled monolayers to atomically precise nanoclusters

C. Crudden[1]

[1] *Department of Chemistry, Queen's University, Chernoff Hall, 90 Bader Lane, Kingston, ON K7L 3N6. cruddenc@chem.queensu.ca*

The use of N-heterocyclic carbenes to modify homogeneous metal catalysts is widespread since the high metal–NHC bond strength renders high oxidative and chemical stability to the resulting metal complexes. The use of NHCs to modify metal surfaces has received considerably less attention. We will describe the modification of planar metallic surfaces with NHCs and illustrate their power vs. typical thiolate-based SAMs. The nature of the surface overlayer is strongly dependent on the nature of the NHC.

Similarly, NHCs are useful new ligands for the stabilization of metal clusters, with the structure of the cluster being strongly influenced by the nature of the NHC. The use of NHC-stabilized clusters in biological studies and in catalysis will be presented.



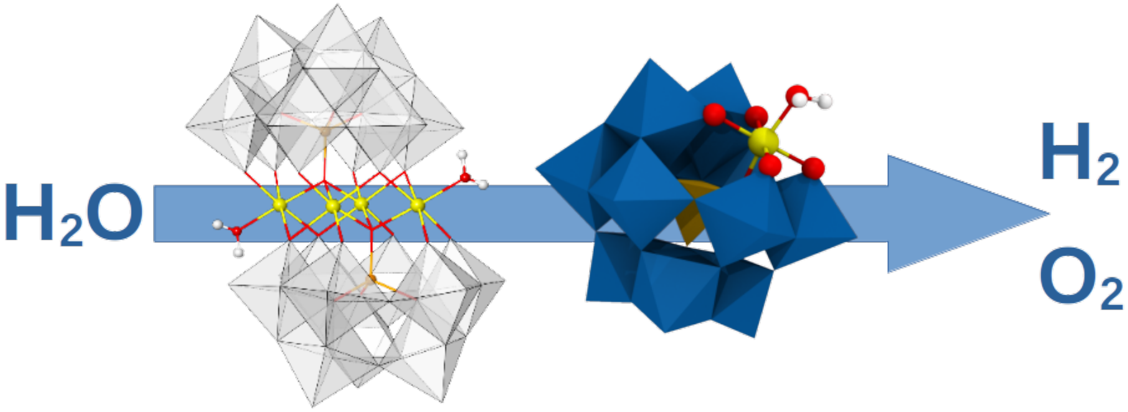
Oral Communications

In Depth Study of the Polyoxometalate Catalyzed Water Oxidation: Electrochemical, Chemical and Statistical Approaches

M. Villares[1], M. Segado-Centellas[1], J. Carbó[1], M. Besora[1]

[1] *Department of Physical and Inorganic Chemistry, Faculty of Chemistry, Universitat Rovira i Virgili. C/ Marcel·lí Domingo, 1 43007 Tarragona. maria.besora@urv.cat*

Water splitting is a promising strategy to transition from fossil to solar fuels. However, water oxidation has associated high overpotentials. To address this challenge, many researchers have focused on developing improved water oxidation catalysts (WOCs). Polyoxometalates (POMs) have emerged as interesting WOCs as they are a special type of molecular catalysts: they are metal oxide fragments with controlled and discrete structure.[1] There is special interest on developing WOCs based on earth-abundant metals, which offer ecological, social, and economic benefits. Computational chemistry is a powerful tool for analyzing catalytic systems in detail, postulating or rejecting reaction mechanisms, increasing the knowledge of active species, and designing improved catalysts. The results and conclusions of computational and statistical studies on polyoxometallate catalytic systems will be discussed.



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Computational Insights into Photocatalytic CO_2 Reduction by Polyoxometalate-Based Complexes and Materials

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The photocatalytic reduction of CO_2 represents a powerful strategy for producing value-added products, leveraging CO_2 as an abundant and inexpensive carbon feedstock and solar light as a clean, renewable energy source. Gaining atomistic insights into the reaction mechanisms governing these processes is essential for the rational design of next-generation catalysts with enhanced efficiency.

This talk will cover recent computational advances in understanding photocatalytic CO_2 reduction processes promoted by polyoxometalates (POMs), a family of discrete metal-oxide clusters, and POM-based host-guest porous materials, primarily Metal-Organic Frameworks (MOFs). Our findings reveal the dual role of POMs as electron reservoirs: serving as redox-active ligands for catalytically active metal centers[1-3] and enhancing the photocatalytic performance of MOFs.[4,5] When immobilized within the pores of porous matrices, POMs actively participate in photoinduced electron transfer processes, either preventing the decomposition of external photosensitizers or extending the lifetime of photogenerated holes in photoactive materials through effective charge separation. Overall, these examples showcase how computational methods can contribute to understanding complex reaction mechanisms and establishing clear design principles for optimizing photocatalytic systems, particularly when closely integrated with experimental research.

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Highly Selective C(sp³)–H Bond Oxygenation at Remote Methylenic Sites Enabled by Polarity Enhancement

F. Scarchilli[1], S. Sisti[2], M. Galeotti[1], M. Costas[1,*], M. Bietti[2,*]

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Procedures for selective functionalization of non-activated C(*sp*^{3})–H bonds represent one of the most investigated approaches to develop new synthetic methodology.[1] In particular, the development of procedures for site-selective oxidation of cycloalkyl structural motifs is of great importance as it can provide straightforward access to functionalized analogues without resorting to lengthy *de novo* syntheses.[2] Herein, we report a detailed study on the C(*sp*^{3})−H bond oxygenation reactions with H_2O_2 catalyzed by the [Mn(OTf)$_2$(^{TIPS}mcp)] complex at methylenic sites of 1-EWG-cycloalkyl substrates.[3] Oxidations in MeCN were compared to the corresponding ones in the strong hydrogen bond donating (HBD) solvents 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and nonafluoro tert-butyl alcohol (NFTBA). Formation of the products deriving from oxygenation at the most remote methylenic sites was observed, with yields and the site-selectivities for oxygenation at the most remote over the next methylenic sites that significantly increased going from MeCN to HFIP and NFTBA (**Figure 1A**). The behaviour is rationalized on the basis of a polarity enhancement effect *via* synergistic electronic deactivation of proximal methylenic sites imparted by the EWG coupled to solvent HB. This concept of polarity enhancement has also been recently applied to a new class of substrates bearing different reactive sites (such as double bonds and allylic positions), providing equally excellent values of remote C(*sp*^{3})-H oxidation. (**Figure 1B**). The results obtained through this study will be presented.

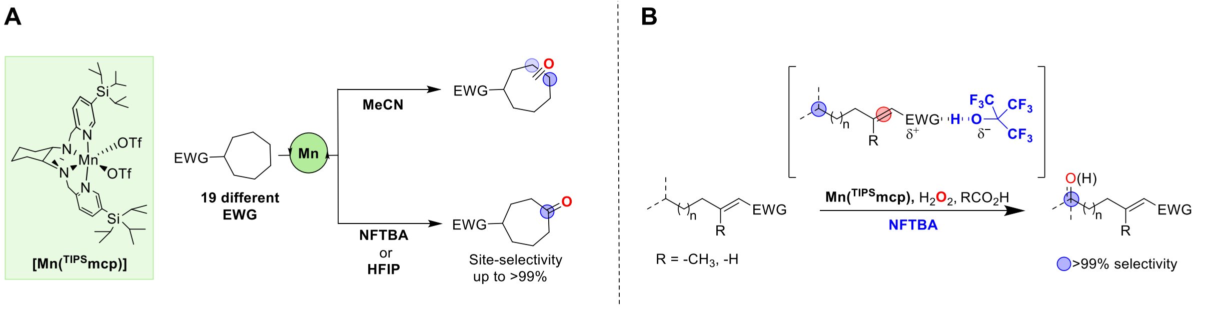

Figure 1A. Site-selectivities for oxygenation of remote methylenes of 1-EWG-cyclcloalkyl substrates. **Figure 1B.** Site-selectivities for substrates with multiple reactive sites.

References

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From Reactants to Products: The Role of NMR in Reaction Progress Analysis

C. Alamillo Ferrer[1], J. Burés[1]

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Nuclear magnetic resonance (NMR) spectroscopy has the potential to serve as a widely applied reaction monitoring tool. As a non-destructive technique, NMR spectroscopy provides an efficient and continuous monitoring of a reaction without disturbing its progress. By providing real-time data on the chemical environment of the nuclei, typically ^{1}H and ^{13}C, this technique allows to unveil changes in reactants, the detection of intermediates and the formation products, making it a powerful tool to follow reaction kinetics and understand the mechanisms of chemical processes.

This presentation will provide experimental evidence how monitoring reactions using NMR can provide mechanistic information, like measuring orders of reaction, estimating the percentage of activated/deactivated catalyst during the reaction, and discerning between catalyst deactivation from product deactivation. [1] Rate-determining step in a catalytic cycle can also be measured by running Singleton experiments, by employing quantitative ^{13}C NMR spectroscopy to measure isotopic ratios.[2] Reactions where fast and continuous transfer of reaction mixture from a reaction vessel into a flow tube it is also possible using InsightMR Flow Tube, with temperature control from the vessel to the probe.[2]

References

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[2] Unpublish results.

Late-Stage Functionalization of Pharmaceuticals by C–C Cross-Coupling Enabled by Wingtip Flexible N-Heterocyclic Carbenes

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The synthesis of complex molecules by palladium-catalyzed cross-coupling has been pivotal in all stages of drug discovery research. However, this approach has been generally restricted to classical aryl halide electrophiles, requiring the use of a limited pool of precursors. Herein, we report the first highly chemoselective approach to the cross-coupling of bench-stable C–O electrophiles in which abundant phenols can be systematically used as electrophilic cross-coupling partners. By using this approach, we have achieved late-stage functionalization of >20 pharmaceuticals covering various architectures and drug targets. Wingtip flexible N-heterocyclic carbenes as ancillary ligands enable to address major challenges of this mode of catalysis, such as fast oxidative addition to prevent hydrolysis of C–O electrophiles and facile reductive elimination to establish the C–C bond forming step in complex settings. This reactivity can be applied to sequential cross-coupling using the same class of bench-stable Pd(II) precursors[1,2]. The design of wingtip flexible N-heterocyclic carbene ligands will enable the cross-coupling of a broad range of electrophiles for the development of important medicines. DFT calculations unveil not only the reaction mechanism but also give hints to address unsolved concerns of cross-coupling reactions that here will be also summarized.

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OC6

Sustainable Photoredox Catalysis with Metallabis(dicarbollides): From Small Alkenes to Unsaturated Fatty Acids

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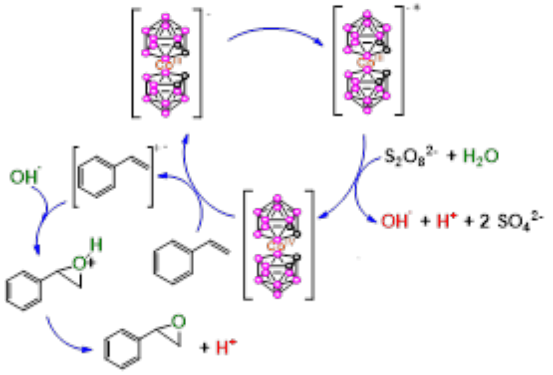
Over the past decades, numerous homogeneous catalysts have been developed for use in photoredox oxidation reactions.[1] We have demonstrated that the cobalt bis(dicarbollide) θ-shaped complex, Na[3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$] (Na[1]) (see Figure), serves as a green and efficient photosensitizer/catalyst for the photooxidation of alcohols,[2] as well as the epoxidation and hydroxylation of alkenes in aqueous media.[3] This process occurs under short reaction times, with low catalyst loading, and operates via single-electron transfer (SET) mechanisms.

The remarkable efficiency of Na[1] arises from its unique properties, including its lack of photoluminescence upon irradiation,[4] water solubility,[5] surfactant behavior,[6] molecular compactness, and the strong oxidizing power of the $Co^{4+}/^{3+}$ redox couple.[7] Preliminary tests using methyl oleate as a substrate and Na[1] as a catalyst showed excellent selectivity for the epoxidation of C=C double bonds.[3]

Building on these results, we developed a proof-of-concept project for the photooxidation of unsaturated fatty acids derived from animal fat, aiming to valorize animal fat waste and promote a circular economy. The system's efficiency in oxidizing unsaturated fatty acids, both as pure acids and in vegetable oils rich in monounsaturated bonds, relies on precise pH and reaction time control to achieve selective epoxidation followed by dihydroxylation. Prolonged reaction times result in bond cleavage, yielding smaller acid and diacid molecules.

Using greener oxidants like molecular oxygen further enabled selective production of desired products. Similar conditions applied to the oxidation of unsaturated fatty acids from animal fat residues yielded comparable results, with the progression from epoxides to dihydroxylated as added-value products, as well as additional compounds, reflecting the heterogeneity of the initial substrates in these complex mixtures.



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OC7

Polyoxometalate-Layered Double Hydroxide Nanocomposites as Water Oxidation Electrocatalysts

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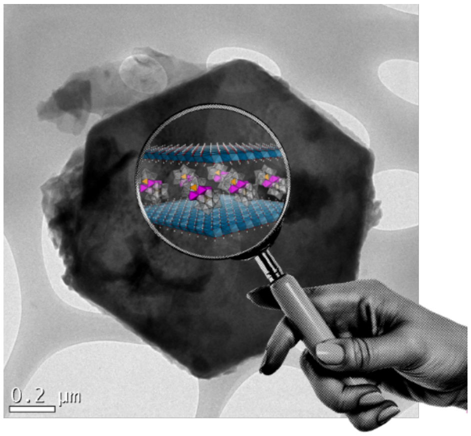
Polyoxometalates (POMs) have been thoroughly studied as oxygen evolution reaction (OER) materials, whereby structure/activity relationships have provided knowledge to rationally design POMs with increased catalytic capabilities.[1] Heterogenization of POMs is a promising strategy to increase their OER activity and to overcome stability issues seen under homogeneous conditions.[2] A common heterogenization approach is the deposition of POMs over the positively charged surface of bulk materials via electrostatic interactions. 2D materials offer an appealing platform to obtain hybrid nanocomposites with monodisperse POMs over the 2D surface. In this respect, layered double hydroxides (LDHs), formed by positively charged brucite-type inorganic layers stacked together with interlayer anions forming sandwich structures, are 2D materials with applications in different energy-related areas.[3] POMs, as polyanionic species, are excellent candidates to be combined with LDHs to obtain hybrid POM/LDH nanocomposites. These nanocomposites have been typically employed as catalysts for fine organic synthesis.[4] However, only a few examples of their use as OER materials are reported in the literature, in which the fate of the POM counterpart under working conditions has not been properly established.[5] Here, I will present our most recent results on the OER activity and stability of hybrid POM/LDH nanocomposites.



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Synergistic Composite Materials for Electrochemical CO_2 Reduction and Hydrogen Generation

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In the quest to resolve the twin challenges of energy sustainability and environmental protection, the development of advanced materials for sustainable energy conversion and storage stands as a critical imperative. These materials are essential not just for academic exploration, but as foundational elements that will power future technological advancements. They enable efficient energy generation, storage, and utilization, all within the framework of environmental conservation.

Our research focuses on enhancing the performance of electrocatalysts through strategic structural and compositional modifications to increase their surface area, activity, and selectivity for specific chemical transformations. Notable achievements include optimizing electrocatalyst morphology to attain over 95% Faradaic efficiency for formic acid production[1]. Additionally, our work has pioneered the use of copper catalysts for the synthesis of C_4 products, setting a new benchmark in the field of electrocatalysis[2].

We address key challenges in catalyst selectivity, stability, and activity by developing multifunctional nanomaterials with tailored active sites. These innovations are characterized by their unique physical and chemical properties that significantly enhance catalytic performance[3, 4]. Central to our approach is the detailed exploration of energy conversion mechanisms, which guides the design of superior catalysts. Our current projects focus on creating biomass-derived carbon materials and MXene-based hybrids[5] for applications in water splitting and CO_2 reduction.

By integrating polyoxometalates (POMs) with MXenes to create novel electrocatalysts, we have observed promising results in hydrogen generation and electrochemical CO_2 reduction. Cobalt and tungsten-based POMs have shown exceptional efficacy, particularly Cobalt-based POMs, which exhibit low overpotentials. For CO_2 reduction, Copper-based POMs have successfully facilitated the production of C_2 products.

This body of work not only advances the field of material science but also paves the way for a future where energy systems are both sustainable and environmentally integrated, aligning with our broader goals of fostering a greener energy landscape.

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In situ NMR search for switchable magnetic compounds

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Spin-crossover (SCO) complexes are exploited in data storage, switching and (bio)sensing applications, e.g., as thermometers and pH-dependent probes for magnetic resonance imaging (MRI). The current method of choice to identify them is the Evans technique of NMR spectroscopy, which requires isolation and purification of each prospective candidate, making the search for new SCO compounds a tedious process. An alternative is following NMR chemical shifts with temperature (or other stimuli), which only needs a correct assignment of a few signals of the studied compound in the NMR spectra[1]. Although admixtures or side products (even paramagnetic) thereby become a non-issue, they are still actively avoided, as is the common wisdom in synthetic chemistry.

We, however, argue that this approach can significantly speed up the search for new SCO compounds if applied to several metal complexes at once produced by simple mixing of different ligands with a metal salt or by 'one-pot' synthetic pathways[2] that include pre- and post-modifications by reversible (de)protonation in an NMR tube. When tested on a series of homo- and heteroleptic complexes of terpyridines and 2,6-bis(pyrazol-3-yl)pyridines[3], functionalized by pH-sensitive groups, it helped us to discover new SCO compounds and ways to control their spin state even for those of them for which it was previously deemed impossible.

A simple ('visual') analysis of NMR spectra collected from mixtures of different compounds and products of their *in situ* modifications without their isolation thus emerges as a powerful tool for a rapid search for new switches, thermometers and pH-dependent probes for MRI boosted by wide possibilities for chemical modifications in heteroleptic complexes.

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Square-Lattice to Square-Complex: Radical-Pyrazine Architectures

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In-situ redox coordination chemistry between non-innocent pyrazine ligand and reducing Cr^{II} ions leads to the formation of the layered conductive magnet $CrCl_2(pyrazine)_2$ under solvothermal conditions.[1] However, using solution-based methods opens up the possibility of modulating the metal-ligand self-assembly differently into other desired structures. In this work, the use of N,N-dimethylacetamide (DMA) as solvent plays a crucial role in directing the dimensionality of the system from two-dimensional (2D) square-lattice networks to an isolated zero-dimensional (0D) square complex. The resulting molecular system, $[Cr_4(pyz)_4(DMA)_{16}]^{8+}$, features strong antiferromagnetic coupling between the Cr^{III} ions and radical pyrazine.[2] It serves as an excellent model for the expanding family of higher-dimensional metal-pyrazine frameworks.[3,4] Furthermore, it holds potential as a molecular building block towards the synthesis of higher crystalline magnetic materials.

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OC11

RQIO 2025

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The Encapsulation of Ferrocenium in an Organic Hosts Enhances Spin Relaxation

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Magnetic molecules, and in particular Single Molecule Magnets (SMM), are interesting candidates for technological devices related with molecular spintronics, quantum computing and quantum sensing[1]. The behavior of these molecules is mainly determined by the intrinsic magnetic anisotropy of the molecule itself and the different mechanisms that allow the spin to relax and lose its coherence. The former can be qualitatively predicted by some models based on the coordination geometry of a paramagnetic center[2]. While the latter is a topic of considerable interest in the field.

In order to gain further insight into the diverse spin relaxation processes and their susceptibility to external influences, we have encapsulated a molecule previously studied by us in the solid state and frozen solution, namely the ferrocenium cation,[3] within two distinct organic hosts. The molecule was encapsulated in α-cyclodextrin (α-CD) and cucurbit[7]uril (CB7), as illustrated in Figure 1, and it was also magnetically diluted with cobaltocenium. The results demonstrated an enhancement in the magnetic properties, likely due to the isolation of the SMM, reducing the dipolar interactions, and the more rigid environment around the molecule.

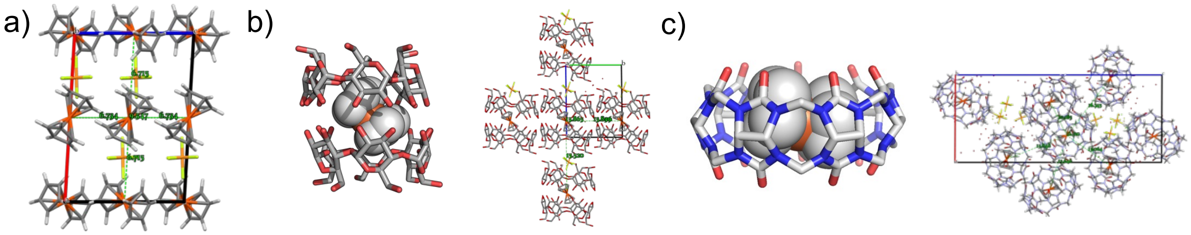

Figure 1. Views of the crystal structure of (a) $[FeCp_2]PF_6$, and encapsulated in (b) α-CD (1:2) and (c) CB7 (1:1). Iron, oxygen and carbon are shown in orange, red and grey respectively and hydrogens have been omitted for clarity.

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Revolutionizing Nanomedicine: How Tiny Amphiphilic Molecules are Transforming Drug Delivery and Therapy

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Aromatic compounds that play important roles in biochemistry found numerous applications from drug delivery to nanotechnology or biological markers. We met a major achievement demonstrating experimentally/theoretically that icosahedral boron clusters display global aromaticity.[1] Based on the relationship between stability-aromaticity, we have opened new applications of boron clusters as key components in the field of biological chemistry.

The research has been focused on the development of purely inorganic *nano*-vesicles/micelles as vehicles of cancer drugs or as anticancer drugs that, exhibiting desirable *in vitro* antitumor activities, offer the possibility of multimodal-action, may result in significant clinical benefits for resistant cancers treatment.[2-4] The interaction of metallabis(dicarbollides) with biomolecules (proteins, *ds*-DNA) as well as their translocation through bilayer membranes were experimentally studied.[2,3,5-8] Molecular dynamic simulations were employed to investigate the translocation mechanism of metallabis(dicarbollide) nano-anions across membranes, which is the result of a flip-flop translocation mechanism with the formation of a transient, elongated structure inside the membrane.[9] Biodistribution studies of metallabis(dicarbollides) in cancer cells and *in vivo* will be reported.[3-8] Finally, but not least, taking advantage of their outstanding chemical and biological properties and their retention in tumors we explored the suitability of this small molecules for multimodal (BNCT, PBFT, gamma radiation, X ray, Mössbauer) cancer therapy.[2,4,8]

Parallel to their use as anticancer agents, boron clusters have been found to be very good scaffolds for diagnostic and therapeutic labelling, opening the door to a wide range of biomedical applications.[10-11]

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OC13

Exploring the intramolecular chemistry of iron(V)-oxo-carboxylato species

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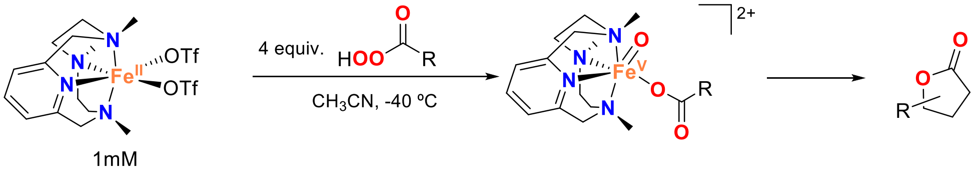
The development of iron(V)-oxo synthetic models that can mimic the reactivity of the iron-oxygenases that are found in nature is an important challenge. Their characterization though, has been hampered due to their high reactivity. It is important to highlight that iron(V)-oxo-carboxylato species have been postulated as the key compounds in the catalytic oxidation of carboxylic acids that leads to the formation of γ-lactones[1].

In this work, the intramolecular reactivity of an iron(V)-oxo-carboxylato species, $[Fe^{V}(O)(OC(O)R)(PyNMe_3)]^{2+}$, reported in the QBIS-CAT research group has been studied[2]. It has been observed that both the accumulation of the iron(V)-oxo-carboxylato compound and the formation of the corresponding γ-lactone are affected by the strength of the γ-C-H bond. Moreover, it could be observed that the iron(V)-oxo-carboxylato species is directly related to the formation of the corresponding γ-lactones by following the formation of the lactone along the formation and the decay of the high-valent species. Also, through intra and intermolecular reactivity competition studies, it has been confirmed that the iron(V)-oxo-carboxylato species is directly related to the formation of the γ-lactones. Finally, mechanistic studies are being carried out to gain more insight into the mechanism for the formation of the γ-lactones.



Generation of $[Fe^{V}(O)(OC(O)R)(PyNMe_3)]^{2+}$ species by reaction of $[Fe^{II}(PyNMe_3)(OTf)_2]$ with different peracids at -40 ºC in acetonitrile followed by the γ-lactone formation.

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Exploring Anion-Dependent Photophysical Properties of Ag(I) and Au(I) Pillarplexes

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The study of supramolecular host compounds has led to the discovery of a fascinating family of complexes known as pillarplexes[1]. These unique compounds have been prepared by coordinating cyclophane ligands with linearity binding metals such as Ag(I) or Au(I). These supramolecular complexes exhibit three remarkable properties: a selective pore for linear guests, adjustable solubility by exchange of its anion, and photoluminescence properties[2,3].

In this work, we present the study of four different pillarplexes, with Ag(I) or Au(I), and with different anions. These pillarplexes have been prepared and subsequently subjected to aggregation-induced emission (AIE) experiments. Two solvents have been used, allowing us to explore the effect of solvent environment on their photophysical properties.

Dynamic Light Scaterring (DLS) and NMR spectroscopy have been used to investigate the conformation of these aggregates in solution, aiming to provide insights into the aggregation behaviour and potential applications of pillarplexes in materials science.

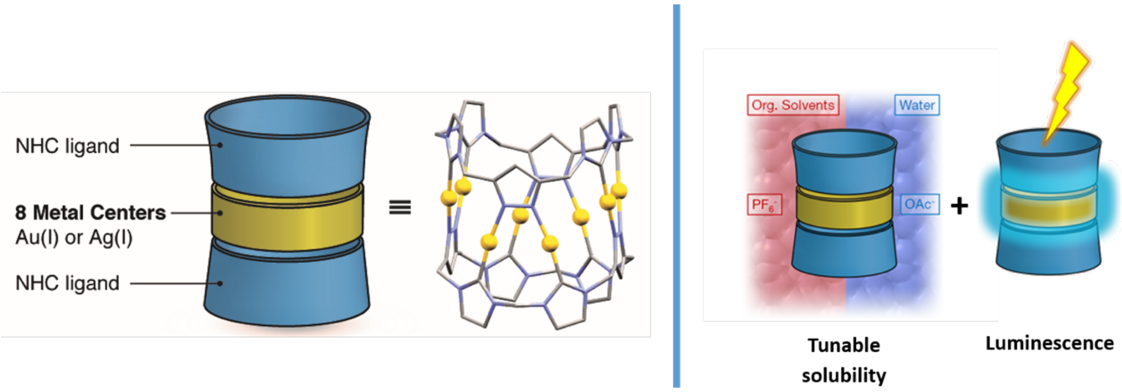

Figure 1. General structure of the pillarplex and representation of their main properties.

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Curminoid-based active surfaces towards the preparation of sensors

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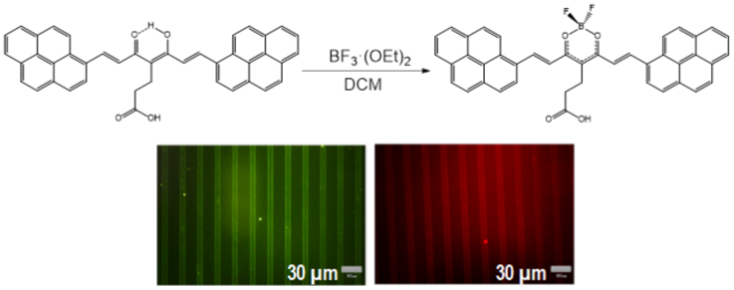
The development of new metal detection devices is a subject of growing interest in the scientific community. Many heavy metals are found in chemical or biological species that collaborate in essential processes, and control of their presence and amount is crucial. Their monitoring is necessary to provide insight in their toxicity, their effects on the environment, the development of diseases due to the excess or deficiency of these metals and/or the study of new drugs based on inorganic chemistry. Regarding this matter, the design of fluorophores, for metal fluorometric detection, that can be switched on or off or exhibit a shift in their emission upon reaction with the analyte is a straightforward approach highly desired. Advances in molecular design have involved the preparation of multifunctional molecular materials, including the synthesis of bifunctional probes or heterogeneous sensors[1]. Here, knowing the great chemical versatility of Curcuminoids (CCMoids), new fluorescent CCMoids and their immobilization on surfaces has been explored. CCMoids are derivatives of curcu-min exhibiting conjugated features, and fluo-rescent behavior with the possibility of coordinating both metals and metalloids, affecting this, the electronic/fluorescent performance.[2] Therefore, the shifts in the fluorescence of the surfaces, depending on the metal or metalloid coordinated, together with the possibility of the metal released upon coordination have been analyzed, obtaining an increase, decrease or even a switch of the surface fluorescence depending on the metal/metalloid under study, Figure 1.[3]



Acknowledgments

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Light-Driven Molecular Motors within Confined Spaces

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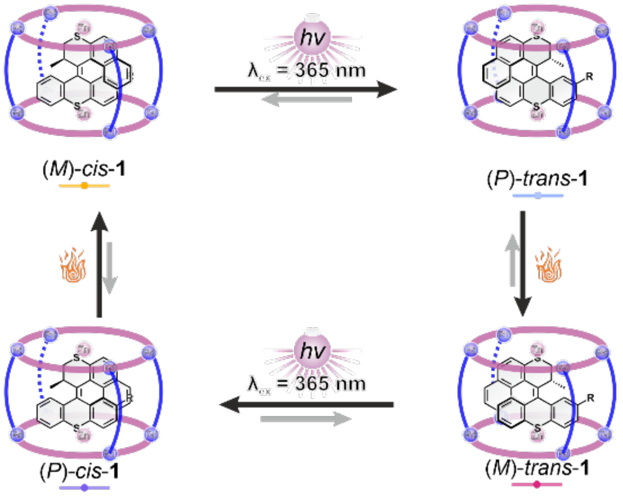
Light-driven molecular motors have gained attention as powerful platforms for enabling stimuli-responsive motion at the molecular level.[1] By incorporating these motors into porous structures, it becomes possible to create advanced dynamic materials that respond to light.[2] These materials offer unique properties, allowing for precise control of molecular motion within their surrounding space and pore volume.

In this context, we detail the synthesis of a coordination cage and the incorporation of a light-driven molecular motor into its internal cavity. We study structural and dynamic properties of the molecular motor in the confined space of the cage and compared with its performance in bulk solution. We finally probe the motor dynamics occurring in the presence of the cage, revealing differences on the kinetics of the thermal helix inversion reactions. The analysis of these new host-guest adducts, allows us to gain design criteria to attain the synthesis of coordination cages that allow a more precise control over the dynamics of light-driven motorized materials.



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OC17

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Cyclometallated Iridium Catalysts for the Asymmetric Hydrogenation of Imines

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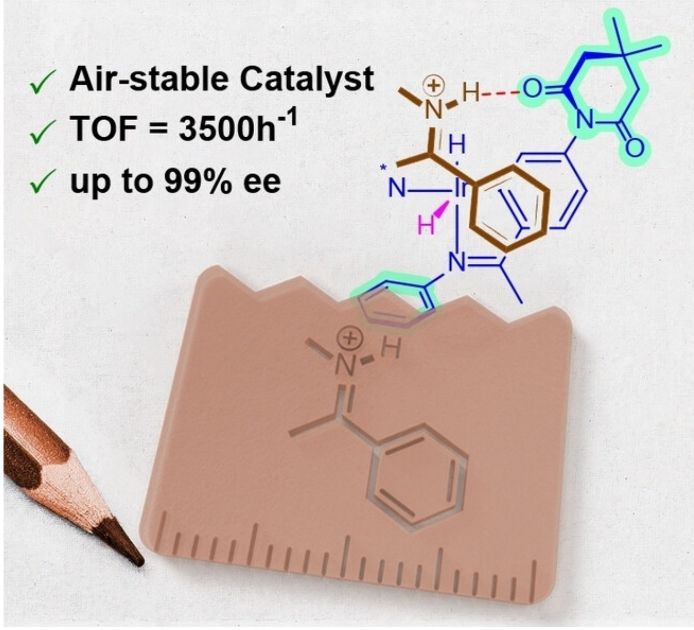

A combined computational and experimental approach allowed us to develop overall the most selective catalyst for the direct hydrogenation of *N*-methyl, *N*-alkyl and *N*-aryl imines described to date. Iridium catalysts with a cyclometallated cyclic imide group provide selectivity of up to 99% enantiomeric excess. Computational studies show that the selectivity results from the combined effect of H-bonding of the imide C=O with the substrate iminium ion and a stabilizing π–π interaction with the cyclometallated ligand. The cyclometallated ligand thus exhibits a unique mode of action, serving as a template for the H-bond directed approach of the substrate which results in enhanced selectivity. The catalyst has been synthesized and isolated as a crystalline air-stable solid. X-ray analysis confirmed the structure of the catalyst and the correct position of the imide C=O groups to engage in an H-bond with the substrate. ^{19}F NMR real-time monitoring showed the hydrogenation of *N*-methyl imines is very fast, with a TOF of approx. 3500 h^{-1}.

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Cyclometallated Pyrenylphosphanes Half-Sandwich Complexes: a Promising New Motif in Antitumoral Drug Design

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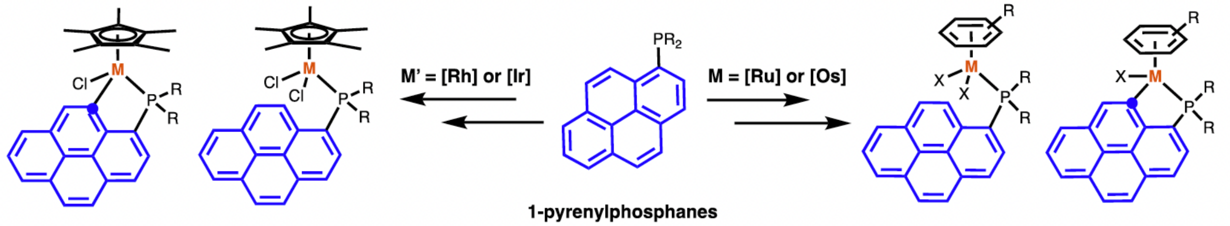
The serendipitous discovery of the chemotherapeutic properties of cisplatin inaugurated the entire field of metallodrugs. Today, more than 50 years later, it is still a burgeoning area that is researching new coordination and organometallic compounds to avoid the undesirable side effects and resistance that plague platinum-based drugs[1]. One of the most promising metals is ruthenium and for this reason some time ago we started a project to study the potential of ruthenium(II) piano-stool complexes with monophosphanes as antitumoral agents. We found that complexes with 1-pyrenylphosphanes were very cytotoxic and since them we have been studying them in depth[2-4].



In this contribution we will give an overview of this chemistry, showing the high tendency of 1-pyrenylphosphanes to cyclometallate and that the resulting species are responsible for the antitumoral activity. For the ruthenium(II) complexes, the influence of the phosphane substituents, the halide and the kinetics of the cyclometallation on the cytotoxicity will be discussed[4]. In addition, our recent extension of this chemistry to osmium(II)[5] and very promising new results with rhodium(III) and iridium(III) will also be disclosed.

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OC19

Stereoselective Control on Cu Activation of β,β-Diboryl Acrylates for Allylic Coupling Protocols with Concomitant Lactonization Reactions

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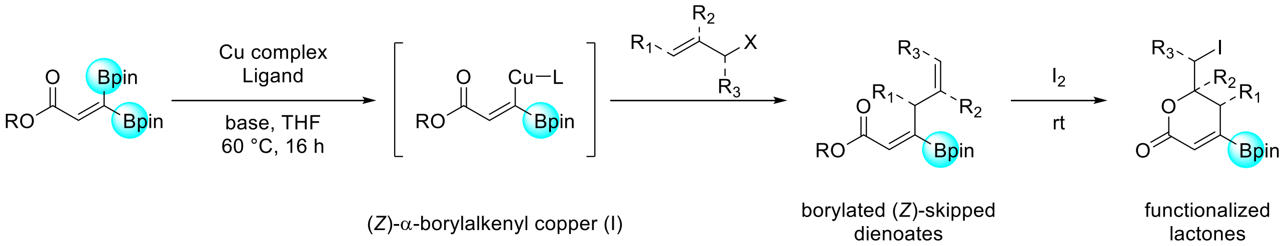
Gem-diborylalkenes have emerged as efficient reagents for selective cross-coupling reactions.[1] Since the two geminal boryl substituents of the *gem*-diborylalkenes can be differentiated and transformed in a stepwise manner, palladium-complexes have shown stereoselective cross-coupling with aryl iodides to generate (*E*)-alkenylboronates as single isomers.[2] In contrast, we have recently discovered a copper-catalyzed approach that enables the selective formation of (*Z*)-alkenylboronates from gem-diborylalkenes with allyl halides.[3] Building upon this knowledge, we describe here the stereoselective C-B activation strategy for β,β-diboryl acrylates, leading to the formation of diverse borylated (*Z*)-skipped dienoates which can be further functionalized via iodo-lactonization sequence for the preparation of borylated lactone cores, that can be used in drug discovery.[4]



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Ligand-Controlled Chemoselectivity between Dimerization and (2+2+1) Cyclotrimerization of Alkynes Catalyzed by Rh-NHC-BHetA Architectures

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The concept of Metal-Ligand Cooperation (MLC) has emerged as an essential piece in organometallic-mediated bond cleavage and formation. The synergistic effect arising from MLC generally triggers an enhancement of catalytic activity and provides a better control of selectivity. In other way, alkynes are valuable starting materials for a myriad of organic transformations, however it is challenging to control their chemo- regio- and stereoselectivity.[1] In this context, we have disclosed that Rh-NHC complexes bearing a 1,3-bis-heteroatomic-acidato (*BHetA*) ligand efficiently catalyze the specific dimerization of terminal alkynes towards Markonikov-type head to tail enynes.[2] The proposed mechanism involves a cooperative *Ligand Assisted Proton Shuttle* (LAPS) process, in which a ligand acts as a transporter of a proton from one substrate to another, coupled with fast reductive elimination of the newly generated metal-organic fragments. Interestingly, the substitution of the labile ligand cyclooctene for a more robust one such as CO inhibits proton transfer processes, thus directing the reaction towards the formation of pentafulvenes (Figure 1). Herein, we will present the relevant factors that governs the LAPS processes and the shift of the reaction path to the chemoselective formation of (2+2+1) cyclotrimerization products.

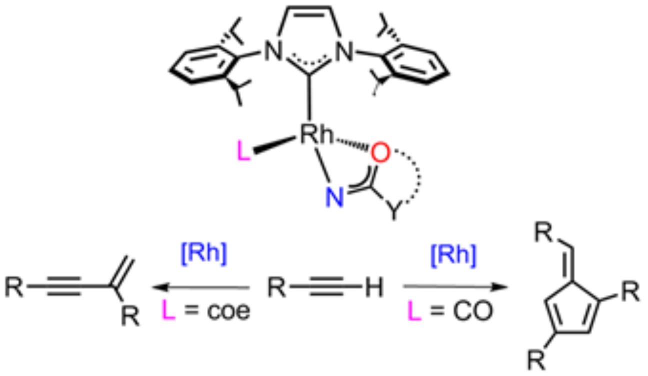

Figure 1. Ligand effects over chemoselectivity of terminal alkynes.

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Biocompatible Boron Cluster-Based Photoluminescent Dyes as Effective Antimicrobial Photosensitizers

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The **increasing resistance of microorganisms**, including bacteria, viruses, and fungi, to antimicrobials and antiseptics is critical in modern medicine and biology. The European Centre for Disease Prevention and Control (ECDC) highlights that healthcare-associated infections, predominantly caused by multidrug-resistant (MDR) bacteria, remain a significant public health threat. This underscores the urgent need **to explore alternative therapeutic strategies that operate via entirely different mechanisms**[1]. One promising approach is **antimicrobial photodynamic therapy (aPDT), using biocompatible photosensitizers (PSs)** to combat infections effectively[2]. The aPDT leverages PS that can be activated by visible light to produce reactive oxygen species (ROS) that induce oxidative damage, causing irreversible destruction of microbial cells. Unlike traditional antimicrobial agents, the major advantage of aPDT lies in its low likelihood of inducing microbial resistance[3]. Despite its growing clinical recognition for treating cancer and infectious diseases, **a largely untapped application of aPDT is the swift, potent, and sustained inactivation of microorganisms and viruses on various surfaces in sanitary instruments and medical devices**. BODIPY and porphyrin compounds stand out among the most promising PS candidates for aPDT thanks to their high biocompatibility, strong light absorption, excellent photostability, fluorescence emission, and efficient generation of singlet oxygen ($^1O_2$)[4]. However, their propensity to aggregate via π-π stacking interactions can quench their excited states, reducing their ROS-generating capacity. To overcome this challenge, we have synthesized and characterized two families of **efficient** biocompatible photosensitizers by linking **3D icosahedral boron clusters (BCs)**[5] that have already demonstrated antimicrobial activity [6] to BODIPY dyes. The photophysical properties, lifetimes, and $^1O_2$ production efficiency have been analyzed, demonstrating their capacity as **promising PSs for aPDT against different gram-positive and gram-negative bacteria**. Ongoing research focuses on exploring their antimicrobial potential, with these findings paving the way for designing even more efficient PSs.

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Catalysis with metal-organic frameworks: opportunities in commodity chemicals

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Metal-organic frameworks (MOFs) are often discussed as privileged catalysts for various heterogeneous catalytic transformations. However, MOFs are unlikely to replace traditional sòlid catalysts in processes where the latter excel. Instead, MOFs can fill a gap where other heterogeneous catalysts falter. To this end, there are numerous industrial processes, especially in the production of several important commodity chemicals, where homogeneous catalysts aret he most desirable and widely used catalysts. We will show how metal centers in MOFs, in particular those derived by post-synthetic metal ion exchanges, are able to catalyze processes of industrial relevance such as ethylene oligomerization[1] and catalytic alcohol upgrading.[2]

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OC23

Effect of the acid and metallic properties of Ni/H-zeolite catalysts on the obtention of biofuels from 5-hydroxymethylfurfural

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2,5-Bis(ethoxymethyl)furan (BEMF) is a promising liquid biofuel candidate that can be obtained by reductive etherification of the biomass-derived platform compound 5-hydroxymethylfurfural (5-HMF) using catalysts with acid and metallic active sites[1]. This makes metal loaded H-zeolites effective catalysts for this reaction, as shown by the 79,8 % BEMF yield achieved by Hu et al. using Cu/HZSM5[2]. This work aims to explore the effect of the acid and metallic properties of several Ni/H-zeolite catalysts on the reductive etherification of 5-HMF. Thus, H-Beta (HBZ), H-mordenite (HM) and H-ZSM-5 (HZSM5) were prepared by cation exchange of commercial Na-Beta (Si/Al = 10), Na-Mordenite (Si/Al = 6.5) and Na-ZSM-5 (Si/Al = 20), and impregnated with different Ni loadings to obtain the catalysts xNi/HBZ, xNi/HM and xNi/HZSM5 (x = wt % of Ni), whose results are shown in Figure 1.

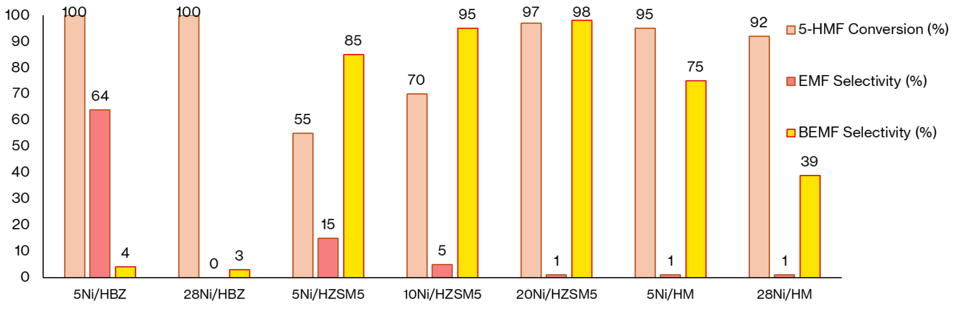

Figure 1. Catalytic results for the reductive etherification of 5-HMF at 140 °C under 10 bar of H_2 for 2 h

X-Ray diffraction patterns of all catalysts exhibited the characteristic peaks of their respective zeolites as well as those of metallic Ni, while acidity and N_2 physisorption measurements showed that the number of available acid sites and external area of the supports followed the trend HBZ > HZSM5 > HM. Ni/HBZ catalysts reached total 5-HMF conversion but very low BEMF selectivity (< 5 %) (Fig. 1). This could be explained by the higher number of available acid sites of HBZ favouring the etherification of 5-HMF to the intermediate 5-ethoxymethylfurfural (EMF) but hindering its hydrogenation to BEMF. In contrast, Ni/HM and Ni/HZSM5 catalysts showed moderate to high 5-HMF conversion, but much higher BEMF selectivity (Fig. 1) due to the lower amount of acid sites of HM and HZSM5 allowing a greater hydrogenation of EMF to BEMF by Ni metallic sites. Notably, 20Ni/HZSM5 achieved a 97 % 5-HMF conversion and a 98 % BEMF selectivity (Fig. 1), showcasing the effectiveness of bi-functional catalysts with an optimal proportion of acid and metallic sites in this reaction. This work was supported by project PID2019-110735RB-C22, funded by MICIU/AEI/10.13039/501100011033. L. Arrieche-Hernández thanks Generalitat de Catalunya for the grant 2024 FI-1 00418.

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Clip-Off Chemistry as a novel approach to obtain Metal-Organic Nanosheets

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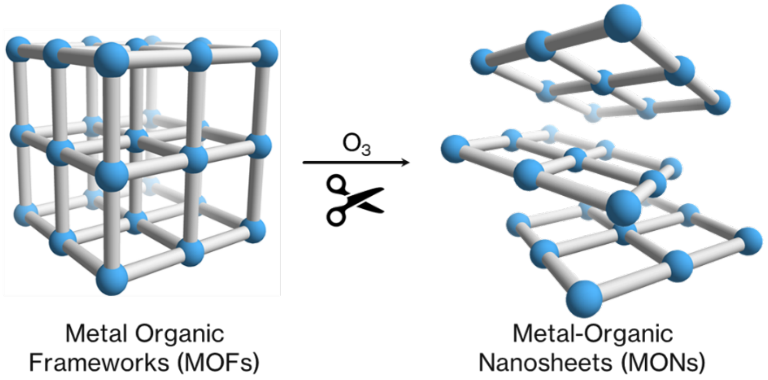
Two-dimensional (2D) nanomaterials have gathered great attention in the field of Materials Science due to their high surface to volume ratio, which results in excellent physical and chemical properties valuable in different fields such as catalysis, energy storage or separation[1]. In this regard, Metal-Organic Frameworks (MOFs), which consist of highly crystalline architectures of periodically connected inorganic metal-based nodes through organic linkers, offer a significant advantage because of their superior ease of design. The obtention of 2D MOFs, particularly of Metal-Organic Nanosheets (MONs) has been explored both by bottom-up and top-down approaches[2,3]. In the first case, intricate synthesis conditions or the use of surfactants are required. In the second case, exfoliation of MOFs is limited to architectures that possess strong chemical bonds in two-directions but weaker interactions in the third, dealing as well with low yields and homogeneity.

Herein, we propose the application of Clip-Off Chemistry as a bottom-up-top-down approach to obtain 2D MONs by precise cleavage of double bonds present in known positions of 3D MOFs which contain strong chemical bonds along the three-dimensions of the material. As a proof of concept of this methodology, we took a previously reported MOF, namely LIMF-66[4], which contains a cleavable tetracarboxylate linker and a non-cleavable tricarboxylate linker. We selectively and quantitatively broke their cleavable linkers through ozonolysis, and successfully obtained novel MONs, which could be characterized by means of Powder X-Ray Diffraction (PXRD) and Scanning Electron Microscopy (SEM). We strongly believe that the use of this methodology further expands the potential for synthesizing and obtaining new materials in this field.



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Make the design molecular again: metal cage complexes for spintronic devices

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Despite the proliferation of spintronic devices that revolutionized data storage, the potential of the molecular approach, which offers unrivaled control over the properties of a device, remains largely untapped. Molecular spintronics aims to create devices with a unique 'spinterface,' a crucial yet elusive element encompassing a 'ferromagnet–molecular compound' interface[1]. These devices are often built as vertical heterostructures of two ferromagnetic electrodes separated by a film of a molecular compound and an optional oxide tunnel barrier. However, a significant challenge of this approach is the variability in molecular structures due to chemical modifications used to tailor their behavior. This variability causes even closely related molecules to produce films with diverse structures and morphologies, resulting in inconsistent electronic and spin transport properties. This mismatch between chemical modifications and their impact makes it extremely challenging to identify the underlying factors, such as structural changes or variations in magnetic or redox properties, responsible for observed device performance fluctuations. Without addressing this issue, the vast potential of molecular design for fine-tuning device properties remains unfulfilled.

We propose to overcome this limitation by introducing cage complexes into molecular spintronic devices. These complexes feature a macrocyclic ligand that securely encapsulates a metal ion, shielding it from environmental influences and ensuring structural rigidity – attributes often lacking in compounds used in current molecular spintronic devices. Their neutrality, high chemical and thermal stability, and ability to sublimate easily while forming ordered crystalline structures make them particularly suited for reproducible manufacturing processes, such as vacuum sublimation. Notably, even when small amounts of paramagnetic ions are embedded in a diamagnetic matrix to achieve extended phase memory times, this dilution is preserved after sublimation. This approach has enabled the development of molecular qubit prototypes with memory times in the microsecond range. Furthermore, the use of various metal ions and functionalizing ligands, while maintaining the core structure of the cage complexes, allows for the induction of a wide range of magnetic behaviors, including single-molecule magnetism[2] or spin-crossover[3]. This versatility enables the fine-tuning of transport properties and the creation of stimuli-responsive multifunctional devices. The possibility of selective, step-by-step modification of cage complexes makes them ideal candidates for introducing incremental changes into the molecular layers of spintronic devices.

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OC26

Interplay of Curcuminoid design and deposition methods for their electronic applications

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Curcuminoids (CCMoids) are efficient molecular platforms with a direct correlation between structural tuning and target applications. [1] They have simple syntheses with rational yields. Well known for their biomedical applications, they are increasingly explored in other fields of nanoscience and nanotechnology. [2] In this direction our group is working on the creation of new CCMoids with special interest in the study of their integration into different substrates/devices. The combination of molecular design and nanostructuring methods (the latter by sublimation, dissolution or soft deposition techniques) has allowed us to create monolayers of CCMoids and their use as sensors, as well as the creation of different types of crystals, aggregates and films in FET-type devices for their electrical characterization. [3]

Related to the latter, in the field of molecular electronics, CCMoids are used as nanowires, where one or a few molecules are employed to study the phenomenon of single-electron transport, connecting graphene electrodes via - bonds. [1] We also study the formation of crystals and films, using a simple, fast and low-cost technique to study the I-V characteristics of these systems. [3]

This is a learning by doing process in which the results allow redesigning new generations of molecular materials. We will show our latest results related to these topics and future perspectives.

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Unveiling the Chemical Reactivity of Ge-based 2D Materials with Thiolated Molecules: Functionalization, Passivation and (Bio)Applications

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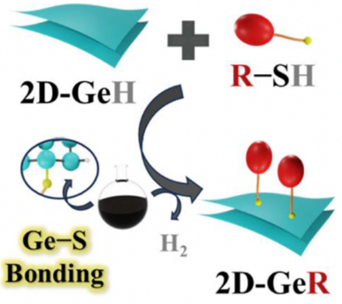
Succeeding graphene, the Materials Science community has moved to explore alternative inorganic 2D materials (i2DMs) exhibiting complementary properties[1]. Among the wide library of i2DMs, monoelemental 2D materials akin to graphene, known as 2D Xenes, are especially appealing since most of their (opto)electronic properties can be tuned on-demand via molecular functionalization. Particular attention has been devoted to the predicted properties of 2D germanene (2D–Ge) owing to its large band gap and buckled structure plenty of reactive sites. Nonetheless, the main chemical challenge in the field relies on making 2D–Ge functional and stable for task-specific applications, since it prone to oxidation under ambient conditions. Consequently, further research is needed to accurately develop simple functionalization methods for the synthesis of ligand-terminated forms of 2D–Ge (viz. 2D–GeR, being R an organic terminal ligand) to prevent oxidation and enlarge the field of implementations. To date, some 2D–GeR have been synthesized by a tedious topochemical reaction involving the reactivity of Zintl-phase $CaGe_2$ with alkyl halides (RX) via Ge–C bond formation [2]. However, the weak Ge–C bonding rapidly descomposes under ambient conditions, resulting in GeO_2.

To solve this, we present a robust and general chemical approach for the direct functionalization of H-terminated 2D germanene (2D-GeH) with a wide range of thiolated molecules (R-SH) via Ge–S bond formation (see Figure 1 for illustration)[3]. While the material characterization data provide direct experimental evidence of the Ge–S chemical bonding, density functional theory (DFT) calculations also predict its existence. Remarkably, the anchored thiolated molecules also favor the passivation of the 2D Xene against air oxidation, enlarging its benefits for real implementation. Overall, the reported a-la-carte molecular engineering approach provides the basis toward the rapid development of high-stable 2D-GeR derivatives exhibiting molecule-programmable properties for the development of memory devices and biosensing systems.



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OC28

2ona REUNIÓ DE QUÍMICA INORGÀNICA
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Redox-active and -inactive molecules inside expanded halide perovskite analogs can behave as charge reservoirs

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Pristine semiconductors and insulators can become high-temperature superconductors upon doping (e.g., La_2CuO_4, Nd_2CuO_4).[1] For high-temperature cuprates,[2–4] the doping mechanism arises from a charge-transfer from a charge-reservoir sublattice to a high-mobility sublattice.[5] By envisioning materials with both sublattices, similar mechanisms are currently explored for other semiconductors, such as $Bi_2O_2Se_6$ and halide perovskites and analogs.[7,8] For halide perovskites, introducing charge-reservoirs into their high-mobility sublattice formed by BX_6^{n-} octahedra represents a promising avenue to control electronic doping[9,10] and potentially realizing superconductivity ($B = Pb^{2+}$, Sn^{2+}; $X = Br^-$, I^-).[1] Such doping will impact their current applications, such as light-emitting and absorbing applications,[11–14] and reveal new potential ones.[1,9] In this presentation, we will show our progress[15,16,17] in introducing charge-reservoirs inside 3D expanded analogs of halide perovskites.

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Flash Communications

FC1

2ona REUNIÓ DE QUÍMICA INORGÀNICA
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Schiff Bases as platform for synthetising Molecular Magnets

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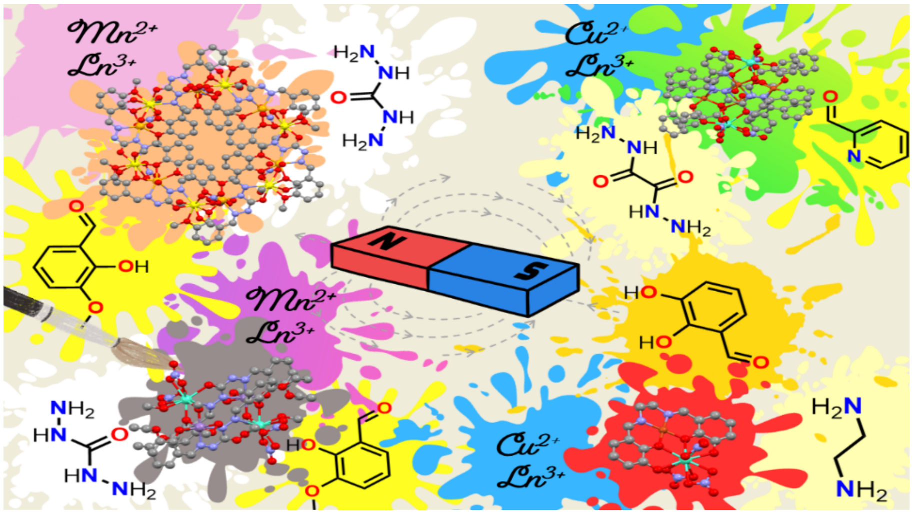

Schiff Bases, the N analogue of carbonyl groups (C=O) obtained from the condensation of a primary amine and an aldehyde or a ketone, are promising candidates for synthetising coordination compounds for different purposes such as luminescence[1], catalysis [2], biological activity[3] and magnetism[4].

By carefully selecting the precursors, multiple properties can be modulated such as the denticity of the ligand, the charge of the deprotonated ligand, the nature of the donor atoms, the nature of the chelating moieties and/or the nuclearity of the complex giving a platform to design specific ligands for each purpose.

Carbohydrazide and Oxalyl hydrazide are primary amines, which have barely been explored in the use for synthesizing complexes for quantum information technologies purposes, that have an interesting potential due to the presence of 1 or 2 carbonyl groups able to bond with metals.

Upon the combination of these ligands with the appropriate paramagnetic cations, magnetic properties can be studied to elucidate whether the synthetised complexes behave as Single Molecule Magnets for quantum information storage. To do so, alternating current (ac) susceptometry has been performed focusing specially on the out-of-phase response which evidences if the complex retains the magnetization upon switching the magnetic field.

Data from ac susceptometry has been analysed and fitted to obtain the relaxation time (τ_0) and the relaxation processes involved in giving information about which modifications would be necessary to enhance the SMM behaviour.

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FC2

2ona REUNIÓ DE QUÍMICA INORGÀNICA I ORGANOMETÀL·LICA de la SCQuímica

Effect of 2,2'-Bipyridine Ligand on Ruthenium Nanoparticles for Hydrogen Evolution Catalysis

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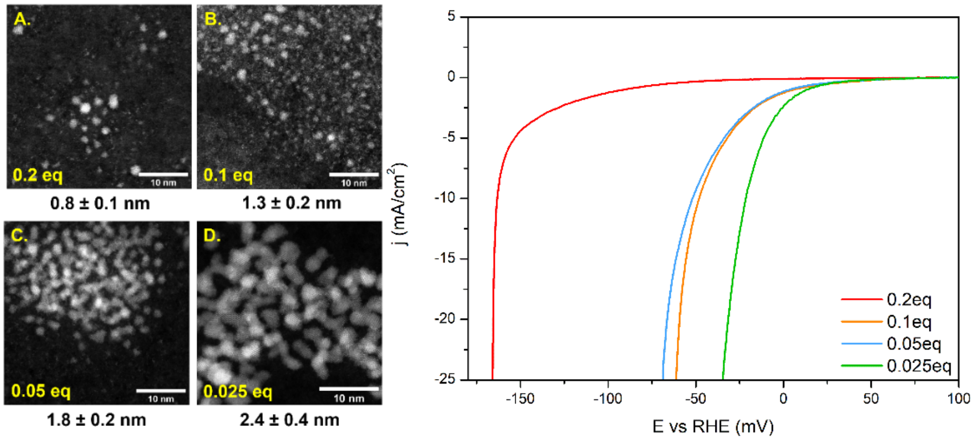
In recent years metallic nanoparticles (NPs) have increased their popularity for numerous catalytic applications. This is largely due to their size-related properties. When compared to typical homo- and heterogeneous catalysts, metallic NPs gather some of the best properties of both worlds.[1] One particularly interesting method for the synthesis of metallic NPs is the organometallic approach. This procedure entails the controlled decomposition of an organometallic precursor in the presence of a stabiliser, usually a ligand of interest, under mild conditions. In this way, the synthesised NPs present a clean surface free of contaminant by-products.[2] Interestingly, the ligands attached to the surface of NPs have been shown to alter the physicochemical properties of the system and even increase their catalytic efficiency, similarly to organometallic complexes.[3,4] Herein we present various systems consisting of Ru NPs stabilised with different amounts of 2,2'-bipyridine (bpy). It was found that there is an inverse relationship between the amount of bpy used and the NP size. These differences in size also translate into their catalytic performances towards HER, being the smallest system the worst and the largest one the best. This behaviour can be justified by the effect of the bpy ligand on the active sites of the NPs by a combination of experimental (electrochemistry, XPS, synchrotron) and computational studies.



0.8 ± 0.1 nm
1.3 ± 0.2 nm
1.8 ± 0.2 nm
2.4 ± 0.4 nm

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Designing Switchable Materials: The Role of Supramolecular Interactions in Fe(II) Spin-Crossover

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Structure and function are intimately associated, and this is especially evident in the field of spin crossover (SCO). SCO complexes are versatile materials capable of switching between two electronic configurations, low spin (LS) and high spin (HS), triggered by various external stimuli such as temperature, light, and pressure. These transitions, governed by intricate structural and electronic factors, hold significant potential for applications in molecular devices and sensors. A key feature of SCO materials is their tunability, achieved by modifying the weak non-covalent interactions within the structure. Among these, hydrogen bonding stands out as a powerful tool for constructing supramolecular networks that significantly influence SCO behavior. In this work, we explore the potential of H-bonded SCO materials by designing ligands that incorporate pyrazolyl-pyridinyl chelating units together with specific H-donor or H-acceptor groups (Figure 1).[1,2] Remarkably, the incorporation of additional units bearing H-donor/acceptor groups (whether anionic or neutral) enables both the precise design of tailored architectures through crystal engineering, and the integration of additional functionalities. These functionalities can interact synergically with the SCO properties, allowing their modulation or enhancing their response to external stimuli.

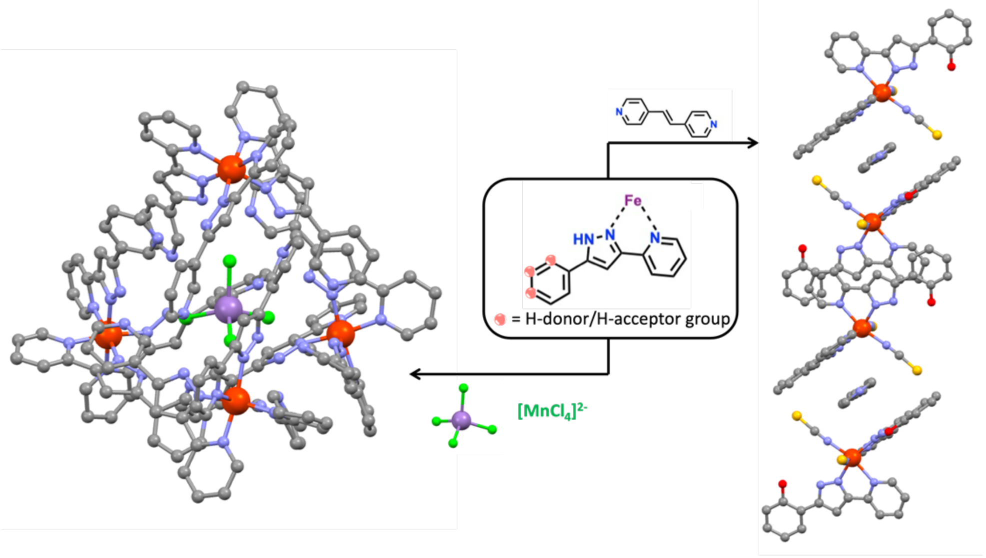

Figure 1. Representation of different architectures of SCO Fe(II) complexes achieved through crystal engineering using ligands with H-donor/acceptor groups and external anionic (left) or neutral (right) units.

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Synthesis of Metal-Organic Cages via Orthogonal Bond Cleavage in 3D Metal-Organic Frameworks

S. Ruiz-Relaño[1,2], D. Nam[1,2], J. Albalad[1,2], A. Cortés-Martínez[1,2], J. Juanhuix[3], I. Imaz[1,2], D. Maspoch[1,2,4]

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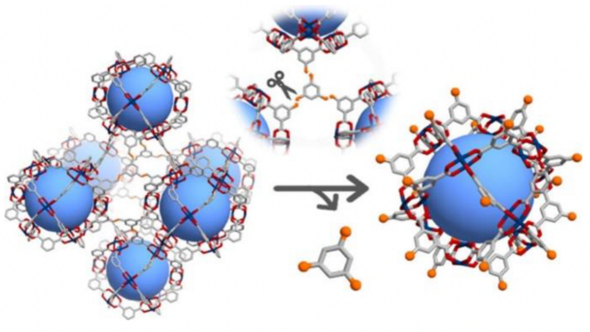
New molecules and materials are and will continue to be key to our society, so that their design and synthesis will remain a vibrant challenge for chemists. While chemical processes have traditionally focused on bond formation, the control of bond cleavage is emerging as a powerful tool for the same purpose. In this context, our group has introduced the Clip-off Chemistry, a novel synthetic approach that generate new molecules and materials through the selective and rational cleavage of covalent bonds in molecular structures. Among the various molecular structures, reticular materials are particularly promising as precursors for Clip-off Chemistry.[1-3] These structures can be viewed as the linkage of repetitive units and fragments that are formed when inorganic and/or organic building blocks are connected.[4] These units or fragments, which include clusters, macrocycles, cages, chains, and others, are a new source of molecules and materials when isolated from a reticular precursor.

Herein, we present the Clip-off Chemistry strategy to obtain zero-dimensional (0D) metal-organic cages or polyhedra (MOCs/MOPs) via disassembly of porous 3D metal-organic frameworks (MOFs).[5] We demonstrate that the insertion of cleavable olefinic bonds into the 3D MOF precursor, followed by a selective ozonolysis reaction, enables the breakage of the MOFs into its individual cavities, in a pore-by-pore disassembly, yielding the MOPs.



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RQIO 2025

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Supramolecular Mask Regio-Converter: Orthogonal Diels-Alder C_{70} bis-adducts by Mask-Mediated regioselective synthesis

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Fullerenes, a class of carbon allotropes, are molecules composed entirely of carbon atoms arranged in a spherical, ellipsoidal or cylindrical structure. Due to this, their functionalization is not regio-controlled, often resulting in mixtures of regioisomers that are not amenable for applications.[1] In this context, only readily accessible mono-functionalized fullerenes are used as electron transport layers in solar cells (SC) devices. Pure regioisomers of poly-adducts, however, are considered a promising alternative for enhancing SC efficiency.

In this study, we extend the mask strategy [2-5] to Diels-Alder (DA) cycloaddition reaction with C_{70} and acenes, which produces a regio-divergent outcome depending on the length of the diene. When C_{70} is encapsulated within the confined space of the nanocapsule and reacts with anthracene, the major product is the 12 o'clock bis-An_2-C_{70} (>90% bis-adduct ratio).[6] The crystal structure of the host-guest complex reveals the tight fitting of the anthracene moieties at contiguous gates of the tetragonal prismatic nanocapsule. In contrast, when pentacene is used, the regio-selectivity shifts to the 5 o'clock bis-Pn_2-C_{70} (>96% bis-adduct ratio). Additionally, taking advantage of the different degrees of background of retro-DA, the mask functions as a supramolecular regio-converter, fully transforming mixtures of 2 and 5 o'clock bis-An_2-C_{70} into 12 o'clock bis-An_2-C_{70}. Moreover, the mask can completely regio-convert the 12 o'clock bis-An_2-C_{70} into 5 o'clock bis-Pn_2-C_{70}.

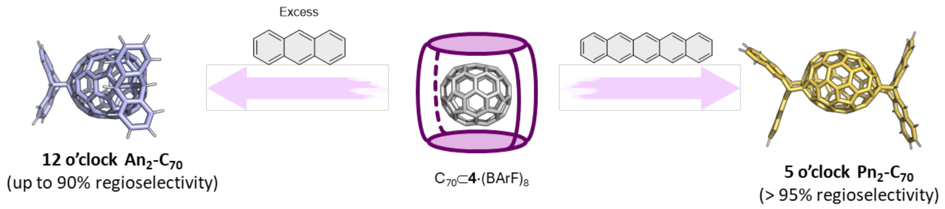

Figure 1. Schematic representation of the supramolecular mask in the DA cycloaddition on the C_{70}.

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Estudi computacional del moviment d'un guest planar dins d'un metal·lorectangle

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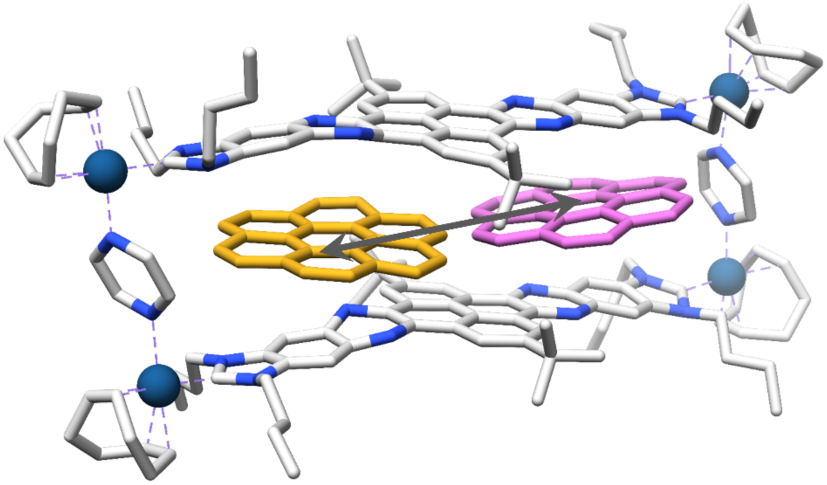
Les metal·locaixes són estructures auto-acoblades que poden actuar com a hostes de molècules petites, generant un entorn intern adequat per a promoure i dirigir reaccions catalítiques[1]. Concretament s'ha treballat amb una metal·locaixa d'Ir(I) que conté dues pirazines i dos lligands de 2.4nm de llargada de caràcter poliaromàtic que confereixen al complex una forma rectangular i una gran afinitat per a molècules orgàniques planes[2-3]. Degut a la geometria de l'amfitrió, les molècules que acull poden situar-se asimètricament dins la cavitat, amb la possibilitat de moure's lliscant d'un costat a l'altre.

Utilitzant tècniques basades en dinàmica molecular s'ha pogut fer una descripció del comportament del sistema amb diversos lligands, estudiant les estructures formades més estables i les transicions entre elles.



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FC7

Un Enfocament Microcinètic Híbrid per Connectar Teoria i Experiments en l'Oxidació de l'Aigua

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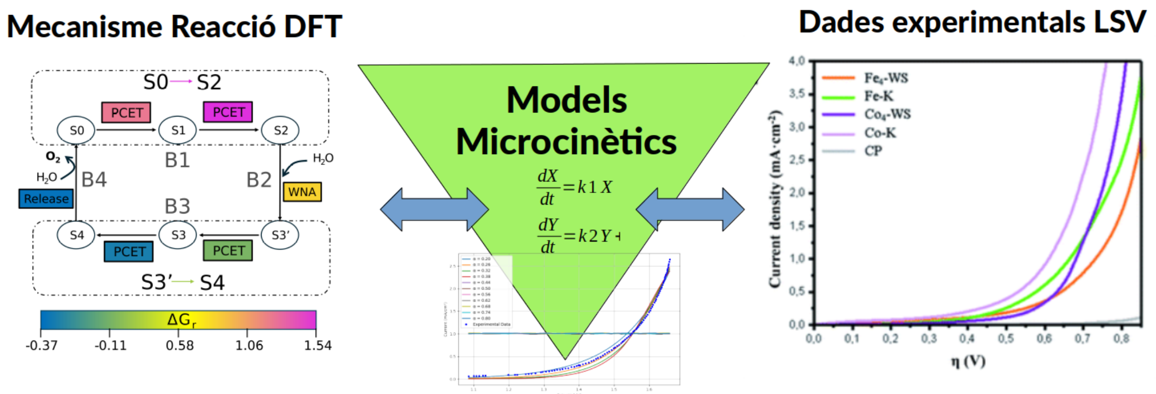
El mecanisme d'oxidació de l'aigua és un procés complex de múltiples passos que implica tant passos químics com electroquímics. Identificar els passos clau que influeixen críticament en la corrent i el sobrepotencial és essencial. . Els rols particulars de cada pas dins del procés, així com el seu efecte concret en el sobrepotencial i en la generació de corrent són poc clars.

Presentem un nou enfocament microcinètic híbrid mitjançant la integració de dades experimentals de voltamperometria d'escombratge lineal (LSV), amb mecanismes de la teoria de funcional de densitat (DFT). Aquest mètode permet el desenvolupament i la parametrització de models microcinètics per simular la relació corrent-potencial. Els nostres resultats mostren que el sobrepotencial no només es veu influït per passos electroquímics, sinó també per passos químics. A més, connectem les propietats cinètiques de cada pas amb el comportament electroquímic mesurable, posicionant el coeficient de transferència de càrrega com un enllaç entre el potencial de l'elèctrode i la corrent. Aquests resultats demostren els principis electrocinètics, establint un pont entre els enfocaments teòrics i experimentals per proporcionar una visió més profunda dels factors claus que governen els mecanismes electrocatalítics multi-passos.



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FC8

Remote 1,4-Carbon-to-Carbon Boryl Migration: From a Mechanistic Challenge to a Valuable Synthetic Application of Bicycles

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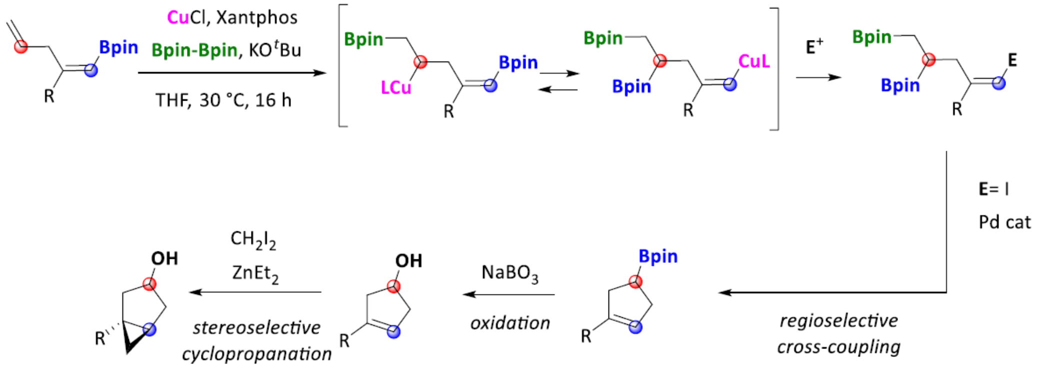
The 1,4-migration facilitated by transition metals has emerged as a novel strategy for relocating various atoms along molecular frameworks.[1] Building on our prior work with boron-copper 1,3-rearrangement,[2] we have developed a method for a 1,4-boryl copper shift, enabling a remote 1,4 carbon-to-carbon boryl migration without requiring heteroatom assistance.[3]

Using CuCl and Xantphos, the borylcupration of borylated skipped (*E*)-dienes produced diborated terminal compounds through the unexpected migration of the Bpin group from C1(sp^2) to C4(sp^3). This unprecedented carbon-to-carbon boryl migration occurred with stereospecificity at the alkene, enabling stereoselective electrophilic trapping via in situ addition of H$^+$, I$_2$, or NBS. Furthermore, the newly synthesised diborylated (*E*)-iodo-substituted alkenes served as key intermediates for constructing functionalised cyclopentenes through palladium-catalysed regioselective coupling. This approach was further enhanced by employing an OH-directed Simmons-Smith cyclopropanation, yielding stereoselective, structurally valuable bicyclic systems.



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FC9

Ni nanocatalysts in an inorganic matrix for OER at pH 7

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Electrochemical conversion of solar energy into energy vectors is prospected to play a key role in the decarbonization of future societies. The process consists in the use of renewable sources to catalytically produce species which store energy into chemical bonds. Hydrogen is a promising candidate for this use. Indeed, it can be obtained as the product of the Hydrogen Evolution Reaction (HER), taking place at the cathode of a water splitting electrochemical cell. Carbon-based fuels and chemicals can also be renewably produced by reducing carbon dioxide (CO2RR) at the cathode. In both cases, when working in aqueous electrolytes, the anodic counterpart of these reactions is the Oxygen Evolution Reaction (OER), providing protons and electrons required by HER and CO2RR alike. However, OER is a sluggish reaction that may become kinetically limiting. Therefore, an improvement of OER kinetics through catalyst design can benefit overall efficiency.

Ni-based materials are state-of-the-art OER catalysts in alkaline media[1-3], but their performance generally worsens at pH 7. This hinders their implementation in neutral-water electrochemical processes. The catalytic Ni nanostructures presented in this contribution are produced via the organometallic approach[4]. This synthetic method consists in the decomposition of an organometallic in the presence of a stabilizing agent (i.e., a ligand). This routine allows for fine control over the morphology and surface chemistry of the resulting nanoparticles, as well as facilitating their post-functionalization. We employed bis(cyclooctadiene)nickel(0), hydrogenated in the presence of a bifunctional ligand. The resulting particles were proven active and stable during OER at neutral pH. Additionally, they could be implemented in semiconducting oxide-based photoanodes. Therefore, our catalyst represents a viable candidate for both electrochemical and solar-driven energy conversion devices.

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FC10

Predicció de l'especiació aquosa de heteropolioxometalats: el fosfomolibdat i l'arsenomolibdat

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La química dels polioxometal·lats (POMs) està en l'actualitat mostrant la seva versatilitat en aplicacions en diversos camps com ara la medicina, els sensors i la catàlisi. No obstant això, els processos que condueixen a l'auto-assemblatge d'aquests compostos inorgànics continuen sent poc coneguts, cosa que incrementa la necessitat d'eines per explorar-ne l'especiació. Durant els darrers anys hem desenvolupat una metodologia nova, que anomenem POMSimulator, per modelar els complexos processos d'equilibris multi-espècie en solucions aquoses de POMs. Utilitzant càlculs DFT, Teoria de Grafs i les equacions de l'equilibri químic, POMSimulator genera automàticament xarxes de reaccions químiques, construeix models d'especiació i determina constants de formació (Kf). En aquesta comunicació es presentaran les darreres millores del mètode a través de dos enfocaments principals.

En primer lloc, un tractament "data-driven" que prediu els paràmetres d'escalat lineal necessaris per ajustar les constants de formació derivades de DFT en absència de referències experimentals, usant un model de Regressió Lineal Múltiple (MLR) basat en una extensa base de dades de models d'especiació[1]. En segon lloc, s'introdueix un procés de "clustering" per gestionar la gran quantitat de dades generades, integrat en un protocol estadístic[2]. Ambdós mètodes han estat validats utilitzant sistemes estudiats prèviament i s'alineen amb els principis de "FAIR data" publicant el codi de POMSimulator[3].

Aquesta nova metodologia ha estat aplicada a dos heteropolioxometal·lats (HPA) com el fosfomolibdat i l'arsenomolibdat. Amb el primer sistema es va aplicar el tractament estadístic mostrant un molt bon acord amb els resultats experimentals, incloent per primer cop un diagrama de fases per a un HPA. En el segon sistema es van aplicar simultàniament el tractament estadístic i el model MLR obtenint també resultats molt comparables amb els experimentals. Aquests avanços implementats en el POMSimulator marquen el camí per a nous estudis en l'especiació de polioxometal·lats.

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FC11

Integrating molecular spin qubits in multidimensional systems

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Molecular materials have gained considerable attention during the past two decades. Specifically, molecules with interesting magnetic properties have become a hot topic in the research landscape. Molecules which can retain their magnetization and quantum coherence between opposite spin orientations have found potential applications in high-density data storage[1,2] and quantum computing[3] respectively.

To turn these systems into potential usable devices, a control between spin-spin distances is required (Fig 1). Given that such control grants tunability over the spin-spin interaction. As a result, the integration of these systems into multidimensional coordination networks becomes primordial[4,5]. This work reports recent results obtained from the study of the magnetic properties of 3*d* and/or 4*f* ions embedded into such frameworks. Specifically, we have chosen porphyrin and/or Schiff-based derived metal-organic frameworks embedded with one or multiple metal ions. The magnetic properties of these paramagnetic metal ions have been studied with both static and dynamic magnetometry measurements. And show a slow relaxation of the magnetization. CW and pulse EPR has been carried out to evaluate their performance as potential molecular spin qubits.

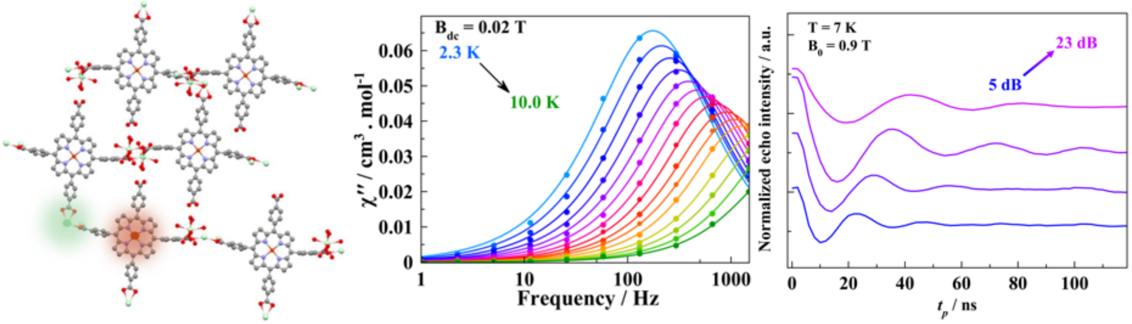

Fig. 1. Left: structure of the porphyrin-based network containing two paramagnetic metal ions. Center: Out-of-phase magnetic susceptibility component indicating a slow relaxation of the magnetization. Right: Rabi oscillations.

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Ru-based heterogeneous catalytic systems for organic photoactivated oxidations

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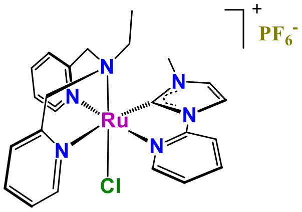
Chemical catalysis is of paramount importance to face the challenges associated to the global warming and the increasing demand of renewable energy sources. In this sense, the reaction conditions used in many organic transformations should be optimized to move from traditional, energetically-inefficient procedures, to cleaner reaction schemes that better fulfil the main requirements of green chemistry. However, optimal progress entails a detailed knowledge of the intrinsic mechanisms operating at the key stages of catalyzed chemical transformations.

In the specific context of catalytic organic oxidations, polypyridyl ruthenium catalysts have been widely used due to their robust nature and the versatile structural and electronic properties of the active center, which can be easily modulated by miscellaneous combinations of oxidation states, geometries and ligands. Additionally, the photochemical properties of these types of complexes make them excellent candidates for their use in photoactivated reaction schemes.[1]

To further improve the efficiency of (photo)catalytic systems, the anchoring of the catalyst into solid, insoluble materials can improve its reusability and enlarge its durability thanks to the protective effect of the support. Mesoporous silica nanoparticles (MSN) appear as strategic candidates for this purpose, thanks to their advantageous properties such as large specific surface area, highly ordered mesoporous structure, tunable pore size, controllable morphologies and unique stability.[2] Moreover, they can be easily functionalized through either ionic exchange or covalent modification. This facilitates the dispersion of the anchored species while minimizing aggregation, and allow convenient photoactivated catalytic setups thanks to their transparency in a wide optical window.

In this work, we describe the anchoring of the [RuCl(Cb-Me)(bpea)](PF_6) complex into several types of silica-based materials and the catalytic performance of the heterogeneous composites in the oxidation of alcohols and olefins. The effect of different solvents and oxidants on the overall efficiency is evaluated, along with the effect of visible light as activator.



[RuCl(Cb-Me)(bpea)](PF_6)

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FC13

Molecular Anodes for Electrocatalytic Water Oxidation based on Self Assembled Bilayers Driven by Electron Transfer Mediators

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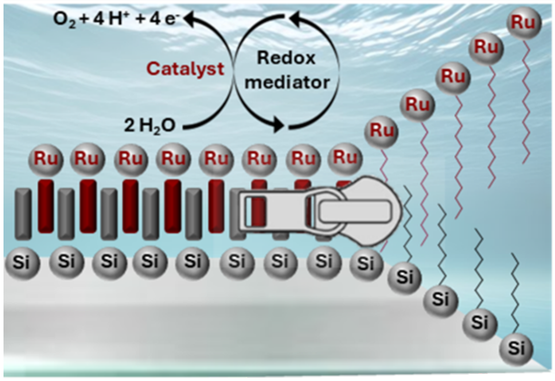
The design of robust and efficient molecular water oxidation catalysts (WOCs) for integration with conductive oxide electrodes remains a significant challenge for artificial photosynthesis. Herein, we report the development of self-assembled bilayer (SAB) systems[1] incorporating a Ru-based oligomeric WOC, $\{[\mathrm{Ru}^{II}(\mathrm{tda})\mu\text{-}\mathrm{b12}]_{12}(\mathrm{b12})\}$[2] (tda^{2-} is [2,2':6',2''-terpyridine]-6,6''-dicarboxylate and b12 is 3,3'-didodecyl-4, 4'-bipyridine), with long alkyl chains facilitating robust anchoring on fluorine-doped tin oxide (FTO) and nano-antimony-doped tin oxide (nATO) electrodes. The nATO-based molecular anodes exhibit two orders of magnitude higher catalyst loading compared to FTO, owing to the porous architecture and enhanced alkyl-alkyl interaction. Electrochemical studies reveal efficient water oxidation at pH 7 with faradaic efficiencies exceeding 92% and turnover numbers above 2200. The assemblies demonstrate exceptional stability attributed to the dynamic rebound mechanism of the Ru-tb12 oligomer and the hydrophobic protection of the alkyl-silanotrisolate layer. Furthermore, electron relay effects mediated by $[\mathrm{Ru(bpy)_3}]^{2+}$ and the Ru centers enhance catalytic performance and minimize deactivation. These results underscore the potential of SABs for creating durable and efficient molecular anodes for solar fuel applications.



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Towards efficient asymmetric hydrogenation of tetrasubstituted enones: new catalyst design and mechanistic insights

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The asymmetric hydrogenation of olefins is a highly efficient method for preparing enantiopure compounds, owing to its selectivity, atom economy, and operational simplicity.[1] Tetrasubstituted olefins are particularly challenging due to their congested structure, which limits reactivity and transfer of the chiral information.[2] However, their hydrogenation is highly desirable, enabling the direct installation of two vicinal chiral centers. Specifically, the asymmetric hydrogenation of tetrasubstituted enones offers an efficient strategy for preparing valuable intermediates for drugs or natural products.[3]

In this context, we developed a new Ir-P,N catalyst library that proves to be completely enantio- and diastereoselective (ee >99%, dr >25:1) and highly active (complete conversion in 5 minutes) for the hydrogenation of tetrasubstituted enones.[3] The system was found to be robust, achieving high enantio- and diastereocontrol for 22 different olefins, while tolerating various functional groups and substitution patterns, including acyclic and exocyclic olefins. To investigate the origins of this selectivity and activity, we conducted mechanistic studies using deuterogenation experiments and DFT calculations, revealing a novel Ir I/III mechanism. Additionally, we found that coordination of the ketone was crucial to provide the excellent enantioselectivity, as suggested by the quadrant models we developed.

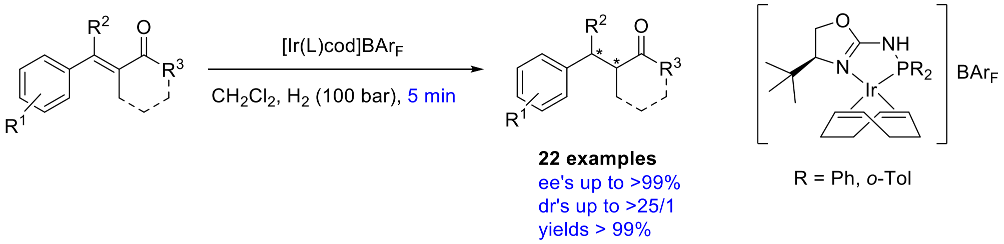

Figure 1. Novel Ir-P,N catalyst for the asymmetric hydrogenation of tetrasubstituted enones.

In conclusion, in this study, we designed a new Ir-P,N catalyst library that proves to be highly efficient for the hydrogenation of challenging tetrasubstituted enones, whose hydrogenation had previously remained elusive. Our full mechanistic study reveals a novel Ir I/III pathway, that agrees with the short reaction times and the excellent enantiocontrol.

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FC15

2ona REUNIÓ DE QUÍMICA INORGÀNICA
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Cu-Catalyzed Asymmetric Synthesis of γ-Amino Alcohols Featuring Tertiary Carbon Stereocenters

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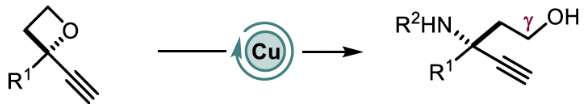
The synthesis of compounds featuring quaternary stereogenic carbons represents one of the most demanding tasks in organic synthesis due to the large steric repulsion present in such core units.[1] To address this challenge, Cu-promoted enantioselective propargylic substitution is a versatile transformation that can provide access to compounds with challenging carbon stereocenters in a simple and effective manner.[2] γ-Amino-alcohols are found in a wide range of natural products and biologically active compounds such as sedum alkaloids, paliclavine and benzo[1,4]oxazepines. Therefore, they are attractive synthons for the pharmaceutical industry. Moreover, they can also act as organocatalysts and chiral auxiliaries in organic synthesis. Despite their huge potential, enantioselective approaches for the preparation of such targets comprising quaternary stereocenters has remained largely unexplored.[3]



- high atom-economy
- functionalized γ-amino-alcohols
- versatile enantio-enriched BBs

Herein, we present a simple, scalable, and attractive method for the enantioselective synthesis of γ-amino alcohols with quaternary stereocenters. Enantioselective Cu-catalyzed ring-opening amination of oxetanes is demonstrated to provide access to these compounds in high yields and appreciable-to high enantiocontrol. The γ-amino-alcohols obtained are able to undergo further modifications without any observable loss of chirality. These functional propargylic compounds are illustrated to be suitable and versatile synthons for the preparation of a series of biologically important intermediates such as γ-unnatural amino acids.

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Asymmetric γ-C-H Lactonization as a New Approach for the Synthesis of Quaternary Chiral Malonates

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All-carbon quaternary chiral centers are present in a plethora of pharmaceutical and biologically active molecules. Considering this, there is an increasing interest in the development of new and efficient catalytic methodologies for the enantioselective construction of these motifs.[1] Malonic esters are interesting starting materials due to their low cost and chemical versatility. During the last years, different approaches based on hydrolysis[2], reduction[3] and Michael addition reactions[4] have been developed to construct chiral malonates from simple substrates. To the best of our knowledge the desymmetrization of malonates based on C-H bond functionalization has not been explored.

Having in mind that γ-lactonization reaction provides high stereocontrol in the oxidation of non-activated C-H bonds,[5] herein we show that γ-lactonization can be applied in the desymmetrization of homo-disubstituted malonates. The reaction provides outstanding levels of regio- and enantiodiscrimination when using sterically encumbered Mn catalysts and H_2O_2 as the oxidant. Our approach enables the straightforward and general access to quaternary chiral centered scaffolds that can be valuable intermediates for the synthesis of pharmaceutical and bio-active products.

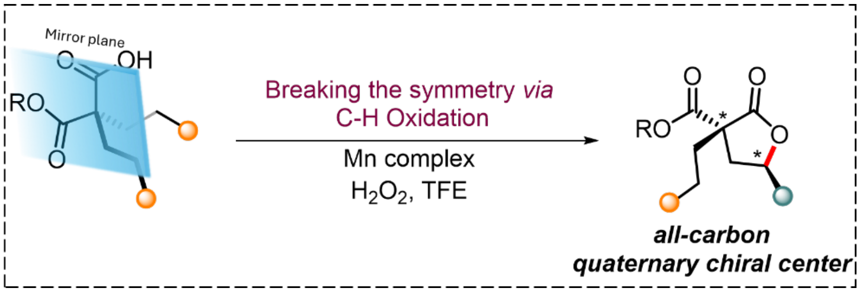

Figure 1. Desymmetrization of malonates *via* γ-C-H bond lactonization catalyzed by Mn complexes.

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Rh-catalyzed Single-Carbon Insertion of 1,3-Dienes

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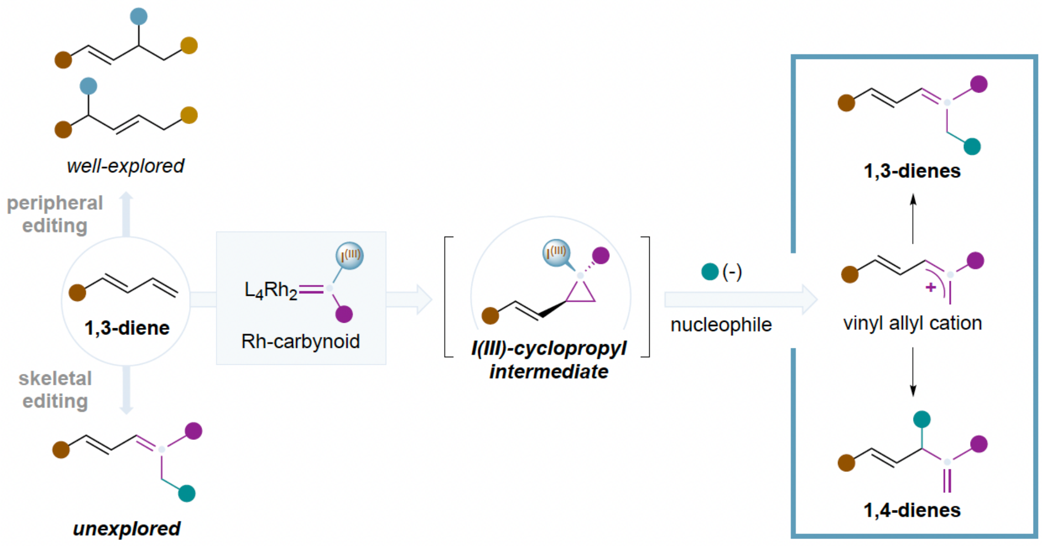
Since the discovery of the Diels-Alder reaction over a century ago,[1] 1,3-dienes have become common scaffolds, frequently used as key intermediates in the total synthesis of bioactive natural products, drug molecules, and polymers.[2] However, catalytic processes that can difunctionalize 1,3-dienes through σ- and π-bond activation of C(sp^2)–C(sp^2) double bonds remain unexplored and are limited to cross metathesis of 1,3-dienes and alkenes.[3]

Herein, we report the first catalytic difunctionalization of 1,3-dienes based on skeletal manipulation via single-carbon insertion with Rh-carbynoids.[4a-c] This process involves the catalytic generation of a Rh-carbynoid, which formally induces the insertion of a cationic monovalent carbon unit (:$^+$C-R) into the C(sp^2)–C(sp^2) double bond of the diene through the transient formation of an cyclopropyl-I$^{(III)}$- intermediate. Disrotatory ring opening leads to a vinyl-substituted allyl cation that undergoes regioselective nucleophilic attack resulting in the formation of multi-substituted 1,3- or 1,4-dienes with a broad range of carbon and heteroatomic nucleophiles.



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Cu-Catalyzed Enantioselective Borylative Desymmetrization of 1-Vinyl Cyclobutanols and Axial-to-Point Chirality Transfer in a Diastereoconvergent/Stereoretentive Allylation Scenery

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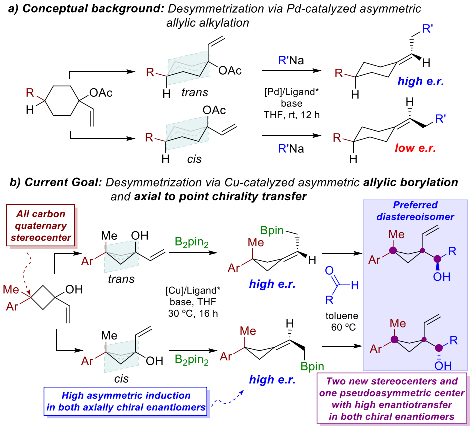
The stereoselective generation of chiral molecular entities remains at the central core of research in organic synthesis.[1] The preparation of axially chiral compounds already entails a challenging task by itself. While the stereocontrolled synthesis of axially chiral allenes has been widely covered, the enantioselective access to axially chiral alkylidenecycloalkanes remains underexplored with scarce examples.[2] In particular, Zheng, Shi and co-workers designed a method to synthesize axially chiral alkylidenecycloalkanes via Pd-catalyzed asymmetric allylic alkylation[3] in which diastereomeric nature of the substrate resulted critical (Scheme a). Inspired by this desymmetrization process, we speculated that Cu-catalyzed asymmetric allylic borylation of 3,3'-disubstituted 1-vinylcyclobutan-1-ols would provide axially chiral allylboranes with high asymmetric induction in both enantiomers. Moreover, the enantioenriched alkylidenecyclobutanes would serve as chiral platform to prove the transference of the axial-to-point chirality via diastereoconvergent allylation of aldehydes (Scheme b).[4]


a) Conceptual background: *Desymmetrization via Pd-catalyzed asymmetric allylic alkylation*

b) Current Goal: *Desymmetrization via Cu-catalyzed asymmetric* ***allylic borylation*** *and* ***axial to point chirality transfer***

All carbon quaternary stereocenter

Preferred diastereoisomer

High asymmetric induction in both axially chiral enantiomers

Two new stereocenters and one pseudoasymmetric center with high enantiotransfer in both chiral enantiomers

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FC19

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Dearomatizative oxidation of arenes

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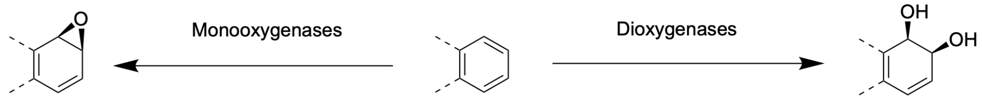
The abundance of arenes in nature makes them very interesting substrates in organic synthesis. Through their dearomatizative oxidative reactions, they can be easily converted into very elaborated molecules, containing multiple stereogenic centers with potential biological interest.

In nature, heme and non-heme iron oxygenases can oxidize arenes disrupting their aromaticity while using mild conditions. On one hand, monooxygenases can produce the epoxides of arenes, and on the other hand, Rieske Dioxygenases can perform the *syn*-dihydroxylation of alkenes and arenes.[1] The most studied enzyme within this family is naphthalene-1,2-dioxigenase (NDO) which can realize enantioselectively the *syn*-dihydroxylation of naphthalene.

Even though enzymes can perform those reactions with good yields and excellent enantioselectivities, due to the complexity of those reactions very little is currently known about their realization using artificial systems.

In literature we can find an example that imitate the behavior of those dioxygenases. It consists in an iron catalyst that can perform the same reaction of the NDO enzyme, unfortunately, the yield obtained for the product is very low and cannot be used for synthesis.[2]

1.



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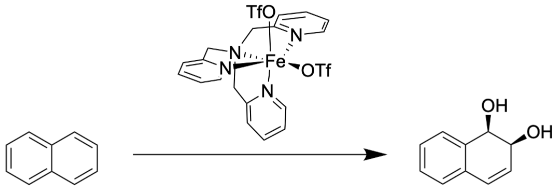

Taking this into account, in this work we want to use transition metal-based catalysts to perform oxidative dearomatizative reactions using naphthalene as a model substrate and hydrogen peroxide as oxidant. We want to break the aromaticity while generating different stereogenic centers through the oxidation. Our main objective is to achieve yields that can be used for synthesis.

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Sulfanilic acid-capped Ru-NPs for enhanced HER activity in neutral media

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Metal-based nanoparticles (NPs) have experienced rising popularity due to their unique properties compared to their corresponding bulk metals or molecular metal complexes. They are now utilized in a broad range of applications, such as electrocatalysis, photo(electro)catalysis, and medicine. The advantage of NPs lies in their high surface-to-volume ratio, due to their small size. As a result, the availability of potential active sites on the surface is increased, which can lead to higher activity in catalytic reactions.[1] In our group, nanoparticles are synthesized via the organometallic approach, which allows for a clean modification of the surface and a narrow size distribution of the particles. By decomposing an organometallic precursor with hydrogen under mild conditions in the presence of the ligand of interest, the nanoparticle contains only the chosen ligand on the surface, with no contaminants or by-products that could alter the activity.[2] In particular, the hydrogen evolution reaction (HER) requires new materials that can maintain high activity in seawater or wastewater.[3] To work towards this objective, in this contribution we report sulphonate-capped Ru-based NPs where the negatively charged ligand is intended to repeal chloride anions from seawater. This catalyst has been preliminary tested in freshwater at pH 0 and pH 7, showing comparable activity in both media (**Fig. 1**).

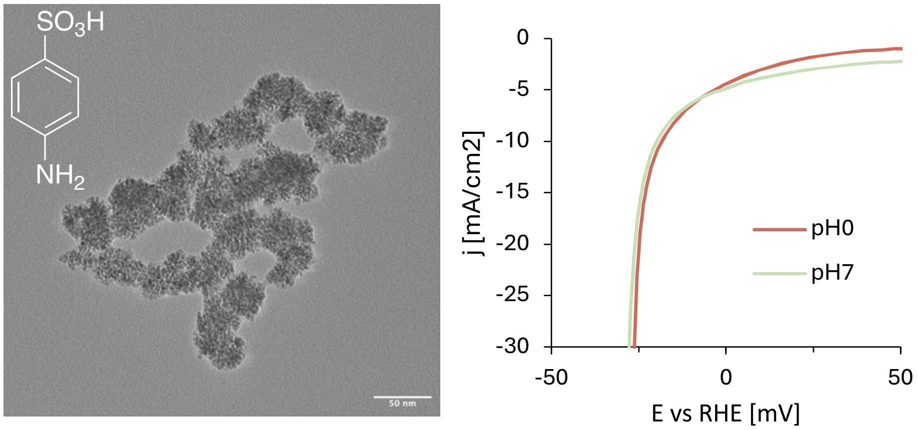

Fig. 1 TEM image of Ru-NP bearing the sulfanilic acid ligand (left), polarization curves in 1M H_2SO_4 shown in red and 0.1 M phosphate buffer shown in green (right).

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FC21

Synthesis and characterization of well-ordered mesoporous carbons from almond shells as the biomass source

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Renewable energy technologies are pivotal in the fight against climate change, offering innovative pathways to address global challenges. Among these, transforming biomass waste into valuable resources like chemicals and fuels, and reducing the carbon footprint trough carbon dioxide capture and the mitigation of greenhouse gas emissions, are some of the biggest challenges. The development of efficient catalysts is essential for this purposes, as current technologies lack the energy efficiency required for large-scale industrial applications.[1-2]

There has been an increasing interest in utilizing biomass as a source for carbonaceous materials in catalyst production due to its wide availability, renewability, and cost-effectiveness.[3] In Spain, almond shells are one of the most abundant biomass resources, consisting of approximately 40% cellulose, 30% hemicellulose, and 30% lignin.

This study explores the synthesis of ordered mesoporous carbons (OMCs) using compounds derived from almond shells as carbon precursors, with SBA-15 serving as the template. SBA-15 was synthetised, and lignin and xylose were extracted from almond shells via microwave-assisted extraction and impregnated into the SBA-15. These samples underwent carbonization under nitrogen flow at 650 ºC and 900 ºC, following a template removal. The successful formation of OMCs was confirmed by the presence of the 100-diffraction peak in the XRD diffractograms of all samples, with some also displaying the 110 and 200 peaks, indicative of the SBA-15 inverse structure. TEM analysis further confirmed the well-ordered mesoporous channels. As prepared catalysts have been employed for electrochemical CO_2 reduction.

This work was supported by the project (PID2022-139176OA-I00) funded by MCIN/AEI/ 10.13039/501100011033. J. Lozano thanks to URV for the 2022PMF-INV-4 grant.

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FC22

La química supramolecular i l'efecte plantilla com a eines estratègiques per a la construcció d'arquitectures heterolèptiques dinuclears de Ni(II)

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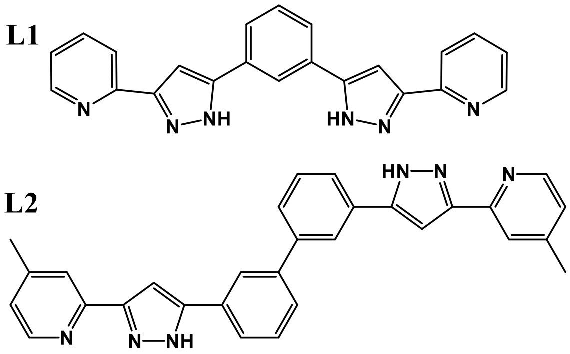
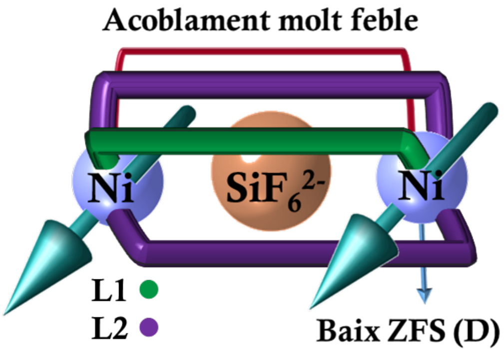
Diversos helicats supramoleculars heterolèptics s'han estudiat utilitzant una família de lligands ditòpics bis-pirazolilpiridina, sintetitzant arquitectures amfitrió-convidat del tipus helicat de triple cadena.[1] L'anió SiF_6^{2-} ha estat utilitzat com a convidat exercint un fort efecte plantilla, permetent la formació exclusiva de compostos heterolèptics on es garanteix la no equivalència química al voltant dels cations coordinats.[2] En una geometria octaèdrica distorsionada i amb un camp de lligands adequat, el catió Ni^{II} dona lloc a una feble divisió del camp zero (ZFS, el seu acrònim en anglès) que fa que sigui un candidat ideal per a una possible aplicació com a qubit molecular.[3,4] En aquest treball, es van sintetitzar dos complexos amb fórmula molecular $SiF_6@[Ni_2(L1)(L2)_2](BF_4)_2$ (1) i $SiF_6@[Zn_2(L1)(L2)_2](BF_4)_2$ (2) (on L1 = 1,3-bis[3(piridin-2-il)pirazol-5-il]benzè, L2 = 3,3'-bis(3-(4-picolin-2-il)-1H-pirazol-5-il)-1,1'-bifenil) que es van caracteritzar i es va estudiar la dinàmica dels estats d'espín del Ni^{II}. Per primera vegada, s'han estudiat els ions Ni^{II} com a dos qubits adreçables de manera independent dins d'un mateix assemblatge molecular en el complex $SiF_6@[Ni_2(L1)(L2)_2](BF_4)_2$, fent servir els nostres lligands bis-pirazolilpiridina.





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A Versatile Synthesis Method of 0D–Metal Nanoparticle@2D–Germanane Nanoarchitectonics for Energy Conversion and Biosensor Implementations

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The modern chemical and material science communities have moved to explore alternative monoelemental 2D materials with complementary properties towards advanced real implementations including energy conversion, (bio)sensing, (bio)recognition, etc. Particularly, germanene (2D–Ge) attracts enormous attention owing to its graphene-like configuration and thus its predicted (opto)electronic properties.[1] However, the insufficient stability of 2D–Ge hinders the relative investigation and thus forces attention to its stabilized derivatives. In this case, H-terminated 2D–Germanane (2D–GeH) as the only commercially available 2D–Ge derivative becomes the focus of the exploration of the 2D–Ge family. At present, its primary challenge is the lack of robust functionalization approaches, inhibiting the subsequent real implementation for specific tasks.

With the perspective to expand the applicability of 2D–GeH, herein, a general and straightforward organometallic (OM) approach is exploited to realize custom integration of 0D noble metal nanoparticles (M-NPs) on 2D–GeH. Pt-NPs and Au-NPs have been explored as model noble metals to study the effects of M-NPs immobilization. As a proof-of-principle, M@GeH was developed as an unconventional electrocatalytic platform toward energy conversion applications. Compared to the pristine 2D–GeH counterpart, Pt@GeH and Au@GeH exhibited boosted HER and ORR activity, respectively.[2]

Further, the 0D/2D Au@GeH nanoarchitectonic was utilized as a nanotemplate for anchoring a thiolated single-stranded DNA (ssDNA) aptamer based on gold-thiol interaction. Regarding the specific task, the ssDNA/Au@GeH heterostructure was exploited as a novel electrochemical biosensor with a selective ability to impedimetrically determine cocaine model drug at the attomolar level (4.87 aM), the lowest detection limit found in literature so far.[3]

In summary, we present a versatile and facile OM approach as a robust functionalization strategy of 2D–GeH with 0D M-NPs immobilization. This work directly results in a new library of 0D/2D M@GeH nanoarchitectonics with implanted electrochemical properties, which can be easily tuned according to the desired electrochemical applications including energy conversion, biosensing, and beyond.

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Slow magnetic relaxation in Ag(II) macrocyclic systems

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During the last decades, magnetic molecules have been proposed for a wide range of technological applications, such as magnetic memories, quantum computing and spintronics[1]. Specifically, in the field of quantum computing, paramagnetic coordination complexes that exhibit slow relaxation of magnetization have been suggested as a qubits, taking advantage of the high versatility provided by the chemical design of different molecular systems by employing multiple ligands and metallic cations of the d/f blocks. This versatility gives the possibility to tune and optimize the key parameters for a proper qubit performance in future applications.

Recently, the magnetic properties of coordination complexes with S=1/2 have been studied[2,3], exhibiting values of spin-lattice relaxation time (T_1) and phase memory time (T_m) considerably high. These molecular systems differs from the classical single molecule magnets by the fact there are not excited spin levels that can foster the magnetic relaxation and the most important decoherence source is the interaction between the nuclear and electronic spins.

In this line, we present the study of the magnetic behavior of different Ag(II) complexes (Figure 1, left) with an analysis of the spin dynamics studied my means of AC susceptibility (Figure 1, center) and EPR measurements (Figure 1, right)[4].

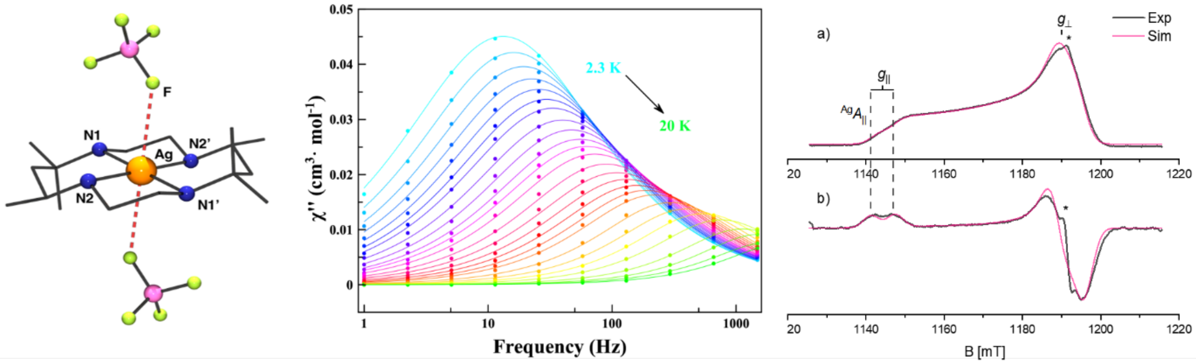

Figure 1. Left, Ag(II) coordination complex as an example of the studied compounds. Center, example of frequency dependence of the out-of-phase susceptibility as a function of the temperature of the studied compounds. Right, example of the CW-EPR spectrum (bottom) and the ESE detected EPR spectrum (top) of the studied compounds.

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FC25

2ona REUNIÓ DE QUÍMICA INORGÀNICA I ORGANOMETÀL·LICA de la SCQuímica

Computational evaluation of the role of the overcharge protector in electrochemical cross-electrophile coupling

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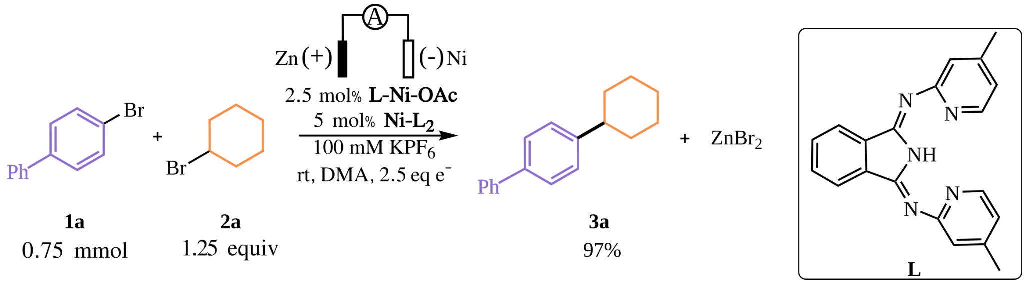
The selective formation of C-C bonds is a fundamental aspect in organic chemistry. Conventionally, these bonds are constructed through the cross-coupling between an electrophile and a nucleophile. An alternative strategy for C-C bond formation is cross-electrophile coupling (XEC), where two electrophiles are employed. However, this method typically requires large quantities of chemical reductants, such as metal powders. Replacing chemical reduction with electrochemical reduction offers a promising alternative, providing not only a more sustainable approach but also enhanced reactivity.

We have chosen the nickel-catalyzed electrochemical cross-electrophile coupling between aryl bromides and alkyl bromides, reported by Sevov and coworkers, as our case study. This reaction is remarkable in the field due to its exceptional selectivity and high yields. These results are attributed to the use of an overcharge protector, which prevents catalyst overreduction under the high potentials required for the reaction. However, evaluating the exact role of the overcharge protector remains a complex challenge.

Herein, we report a complete computational description of the reaction mechanism introducing the overcharge protector. We first defined the mechanism in solution and then characterized the cathodic reactions, where the catalyst degradation and the protector reduction are competing. To account for this competition, we incorporated the electric current into the microkinetic simulations by defining the rate of electron release.[2] Ultimately, we integrated all the elements into the model, simulating the reaction both with and without the protector, achieving strong agreement with experimental results.



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FC26

Pivotal Synthesis of Tetrasubstituted Epoxides from Ketones and α-halo B/Si Ylides

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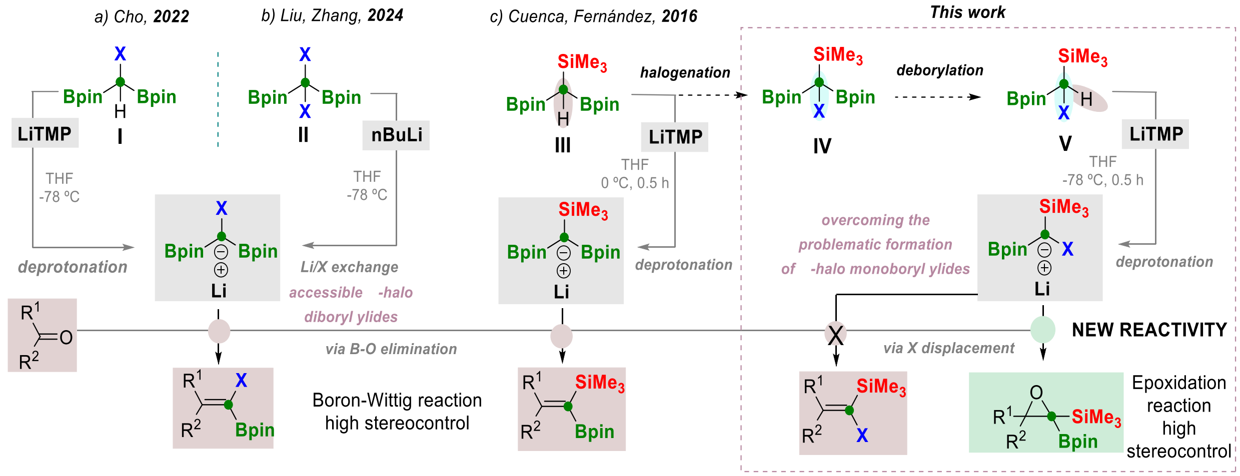
α-Halo boron ylides are considered prominent synthons with remarkable applicability in organic synthesis due to the two vacant p-orbitals of the boryl groups. Their relevance has been shown by Cho (Scheme, a) [1] and Liu, Zhang (Scheme, b)[2] in the reactions of these compounds with ketones and aldehydes, accomplishing the synthesis of tetra- and tri-substituted (*Z*)-haloborylalkenes throughout the Boron–Wittig reaction.

The Boron-Wittig reaction between boron ylides and carbonyl compounds is characterized by the stereoselective B-O elimination step. Our group also contributed to apply the α-boronsilicon ylide LiC(Bpin)$_2$(SiMe$_3$) to perform stereoselective synthesis of tetra- and tri-substituted *gem*-borylsilylalkenes throughout the Boron–Wittig reaction with ketones and aldehydes, respectively (Scheme c).[3]

In this work, we envisioned the use of the new reagents α-monohalo diborylsilylmethane (**IV**) and α-monohalo borylsilylmethane (**V**) to explore the stereoselective formation of tetrasubstituted gem-halosilylalkenes through the Boron–Wittig reaction. However, the boronsilicon ylide Li[C(Bpin)(SiMe$_3$)(X)], formed from reagent **V** and LiTMP, reacted with the carbonyl compounds to render tetrasubstituted epoxides, opening a new reactive pathway (Scheme, right).



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Posters

Advanced metallacarborane photocatalysts for efficient removal of organic compounds in surface and wastewater effluent

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In recent decades, the presence of pollutants in water sources has steadily increased. posing a risk to both the environment and human health. Conventional water treatment methods may not adequately remove these contaminants, underscoring the necessity for advanced treatment technologies to ensure the quality and safety of reclaimed water. Photocatalytic oxidation degradation has emerged as a promising approach for the removal of organic pollutants from polluted water, using semiconductor-based photocatalysts such as titanium dioxide (TiO_2), among others. However, these conventional metal oxide photocatalytic methods often fall short in effectively degrading persistent pollutants, while their high costs and the risk of generating toxic by-products further constrain their practicality[1]. Consequently, the development of green photocatalysts, often derived from abundant and renewable materials such as carbon-based nanomaterials, has gained attention. These materials offer significant advantages, including low cost, high stability, minimal toxicity, and greater environmental compatibility, positioning them as promising alternatives for the efficient degradation of micropollutants[2]. Recently, θ-metallacarboranes have been applied as efficient photocatalysts in oxidation processes in water[3] and have been successfully heterogenized without creating any covalent linkage on the metallacarborane framework[4].

This study focuses on the immobilization of $H[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]$, abbreviated as H[*o*-COSAN], onto graphene oxide functionalized with amine groups, GO@NH_2-H[*o*-COSAN]. It further investigates the application of both the heterogenized H[*o*-COSAN] and its molecular form as photocatalysts in UV-assisted processes without the need of adding an oxidant. These photocatalysts were employed to degrade a range of environmental pollutants, including galaxolide (HHCB), tonalide (AHTN), chlorpyrifos (CPS), and triclosan (TCS), across various water matrices, such as ultrapure water, drinking water, and wastewater effluent. This work represents a groundbreaking milestone in water purification, showcasing the first-ever application of metallacarboranes. The results highlight a highly promising and innovative strategy for addressing water pollution, paving the way for transformative advancements in the field.

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P2

Synthesis of new aminophosphine/phosphoramidite-pyridine ligands for Ir-catalyzed asymmetric hydrogenation of olefins

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Metal-catalyzed hydrogenation concerns one of the most powerful and efficient methods to produce enantiomerically pure substances such as pharmaceuticals, flavors, fragances and agrochemicals. Even though asymmetric hydrogenation (AH) of olefins has been widely explored during the last decades, several challenging substrates remain unresolved. Most catalysts are effective for a narrow range of alkenes, requiring specific catalysts for each type of olefin to achieve optimal enantioselectivity. In that respect, AH of chelating alkenes is a mature field, where Ru- and Rh-diphosphine complexes are used as catalyst. In contrast, AH of non-chelating olefins is far less developed and is typically catalyzed by Ir-P,N-based systems.[1] In this context, while the application in AH of different ligands containing a P-oxazoline motif have delivered excellent results, using other ligand scaffolds containing different sp² N-donor groups could lead to promising outcomes . Among these, pyridine-based ligands seem to be successful candidates because of their ring modularity, robustness and easy of accessibility. Remarkably, Pfaltz´s group was the first to perform AH with pyridine–phosphinite ligands obtaining excellent enantioselectivities but applicable in a limited scope of alkenes.[2] Building on these findings, our group further modified Pfaltz's ligands by replacing the phosphinite moiety with a phosphite group, allowing fine-tuning of ligand parameters for various substrate classes.[3] More recently, we have demonstrated that replacing phosphinite or phosphite groups with chiral aminophosphines further enhances catalytic performance.[4]

Considering these advances, we have developed a new family of P-stereogenic aminophosphine–pyridine ligands for the Ir-catalyzed asymmetric hydrogenation of olefins. These ligands combine the chiral aminophosphine moiety with Pfaltz's ligand scaffold. For comparison purposes and based on the previous successful phosphite-based ligands reported in the group, we also prepared a series of related phosphoramidite-pyridine ligands.

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The development of readily accessible phosphinite/phosphite-triazole ligands for Ir-catalyzed asymmetric hydrogenation of alkenes

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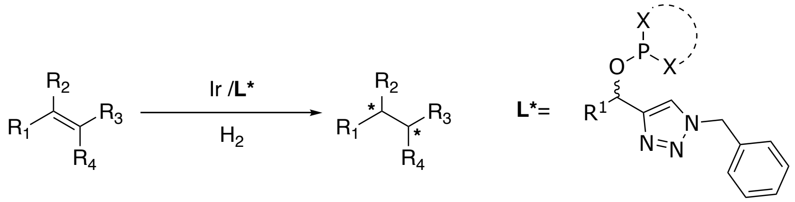
Asymmetric hydrogenation (AH) of alkenes using metal catalysts is one of the most sustainable and efficient approaches for producing a wide range of pharmaceuticals and fine chemicals, drawing significant interest from top pharmaceutical companies.[1] Expanding the substrate scope in AH remains essential to enable the synthesis of a broader array of chiral molecules and maximize the technology's industrial applications.

Our group specializes in creating modular and easy-to-handle ligand libraries from readily available materials. In this effort, click chemistry offers a powerful tool for synthesizing chiral ligands, leveraging reactions that are not only high-yielding and regioselective but also proceed under mild conditions with straightforward reaction and purification steps. A prime example is the Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) reaction, which enables the synthesis of 1,2,3-triazoles that can be incorporated into P,N-ligand scaffolds. Notably, in 2015, Reek, van Maarseveen, and collaborators developed a series of tunable chiral N-phosphine-triazole ligands for Ir-catalyzed asymmetric hydrogenation of three non-chelating olefins with various substitution patterns (di-, tri-, and tetrasubstituted), achieving promising enantioselectivities of 75%, 90%, and 87% ee, respectively.[2] However, only N-phosphine P-donor moieties were explored in their work, highlighting the need for further research on triazole-based ligands with diverse P-donor groups. In this study, we extend the work of Reek and van Maarseveen by investigating additional related ligands (Scheme 1) and evaluating their performance across substrates with varied geometries, substitution patterns, and neighboring polar groups.



Scheme 1. Ir-catalyzed asymmetric hydrogenation of non-chelating olefins using phosphite/phosphinite-triazole ligands.

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Pd-Catalyzed Allylic Substitution using Nucleophilic Amines: Access to Functionalized Mono- and Bis-N-Allyl Synthons

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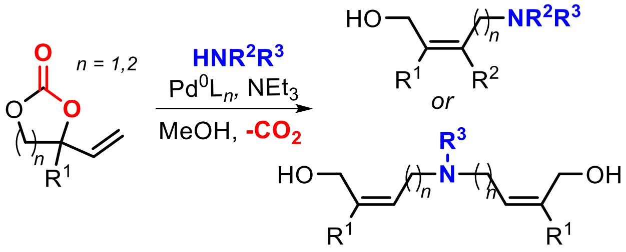
We here report an effective catalytic strategy to enable the decarboxylative allylic amination of vinyl cyclic carbonates[1] using various aliphatic and nucleophilic amines. The use of a protic medium and chelating diphosphine ligands is a main driver towards chemo-selective allylic amine formation, [2] thereby minimizing undesired ligand-driven complex speciation and aminolysis of the involved substrate. [3] [4] This improved approach amplifies the repertoire of allylic amine synthons that can be prepared from a variety of substrate combinations.



- *5- and 6-membered substrates*
- *structural pool much amplified*
- *improved Pd(0) preactivation*
- *1°/2° aliphatic amines*
- *mono- and bis-allyl amines*

Figure 1. Pd-Catalyzed Allylic Substitution.

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Synthesis of 2-Oxabicyclic [2.2.1] Heptanes using a Binary Al (III) Complex/Halide Catalyst

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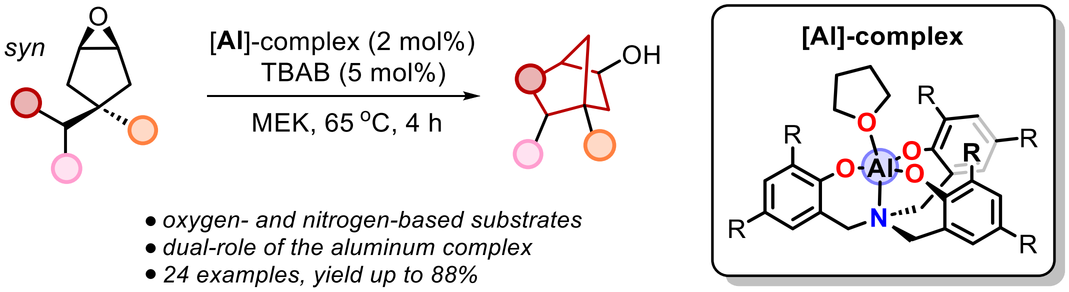
The incorporation of rigid fragments containing a high fraction of sp^3-hybridized carbons as bioisosteres of unsaturated molecular scaffolds is now a well-established approximation in medicinal chemistry to improve the solubility and metabolic stability of a target molecule.[1] Despite the fact that synthetic methods in this area have been diversified, approaches to obtain structurally rigid, saturated analogs remain rather limited, while primarily focusing on the synthesis of nitrogen-based heterocycles.[2,3] In recent years, there have only been a few reports on oxygen-based product and methods for their synthesis thus remain underdeveloped.[4,5] Here, we report a new catalytic approach that allowed us to prepare a wide series of 2-oxabicyclic [2.2.1] heptanes. Key to the selectivity of the process is the use of a binary catalyst based on an Al(III)-centered aminotriphenolate complex and a halide source that cooperatively promote the conversion of the *syn*-epoxy substrates.[6] Various precursors, including those containing nitrogen substituents can be smoothly transformed through this method. The use of a chiral catalyst for this sequential process is also discussed.



- *oxygen- and nitrogen-based substrates*
- *dual-role of the aluminum complex*
- *24 examples, yield up to 88%*

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Synthesis of luminescent curved nanographene-like compounds via the Scholl reaction

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In the recent years, polycyclic aromatic hydrocarbons (PAHs) compounds such as nanographenes and graphene nanoribbonds (GNRs) have received more attention due to their wide applications in material science, optoelectronic devices and supramolecular chemistry. Hence, the development of efficient and novel strategies for the synthesis of these compounds stands as a research topic of interest.[1,2] In the last years, our group reported a Ni-catalyzed system to activate selectively C_{sp2}-F and C_{sp2}-OMe strong bonds, using 8-aminoquinoline as directing group and internal alkynes as non-activate coupling partners obtaining as the major product the aromatic homologation.[3,4] Recently, we reported the stepwise synthesis of new nanographenes and polycyclic aromatic hydrocarbons using aromatic homologation compounds as starting substrates (Figure 1a).[5] In this work, we exploit the formation of a fluoroanthene aromatic homologation precursor and then, the subsequence Scholl reaction. For our surprise, we obtained a perylene-based derivative (**P1**) in a quantitative manner. Interestingly, P1 exhibited red-fluorescent properties with a remarkable quantum yield of 44 %, leading to an ideal platform for rational derivatization and tuning of physical properties (Figure 1b).

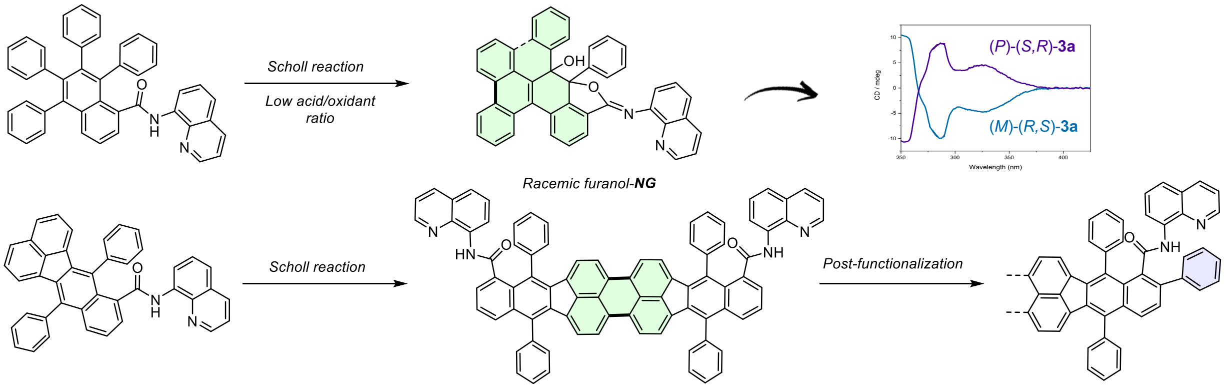

Figure 1. a) Synthesis of chiral furanol-NG compounds. b) Synthesis and post-modification of perylene-NG.

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A Versatile, Readily Available and Bench Stable Iron Catalyst Active in Carbene Transfer Reactions

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The development of C-H functionalization reactions catalyzed by non-precious metals is an important aim for gaining sustainability in chemical synthesis. In 1992, Hossain reported the first example of carbene transfer reactions using iron as a catalyst, $[CpFe(CO)_2(THF)]BF_4$.[1] With this as a starting point, over the past decades iron has exhibited promising results in this field.[2]

Our group has previously described a synergy between an iron catalyst, $[Fe(^{F}pda)(THF)]_2$, and a lithium aluminate salt, $Li[Al(OC(CF_3)_3)_4]$. The aforementioned catalyst activates azoesters under mild conditions promoting both intramolecular and intermolecular functionalization of strong Csp^3-H bonds via carbene insertion.[3,4]

During our research we have been able to identify a much simpler and manageable catalyst, $[Fe(acac)_3]$, that, upon previous activation, exhibits superior performance. $[Fe(acac)_3]$ has shown excellent selectivity practically avoiding the formation of "hydride shift" side products. Of important to note is that $[Fe(acac)_3]$ is commercially available, cheap, and air/moisture stable. Finally, $[Fe(acac)_3]$ has proven to be a versatile catalyst achieving good yields in intermolecular C-H insertion and cyclopropanations reactions, and it is also able to access to Buchner ring expansion products generating cycloheptatrienes derivatives.

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Synthesis and characterization of new Mn complexes and their application in the asymmetric directed oxidation of non-activated C-H bonds

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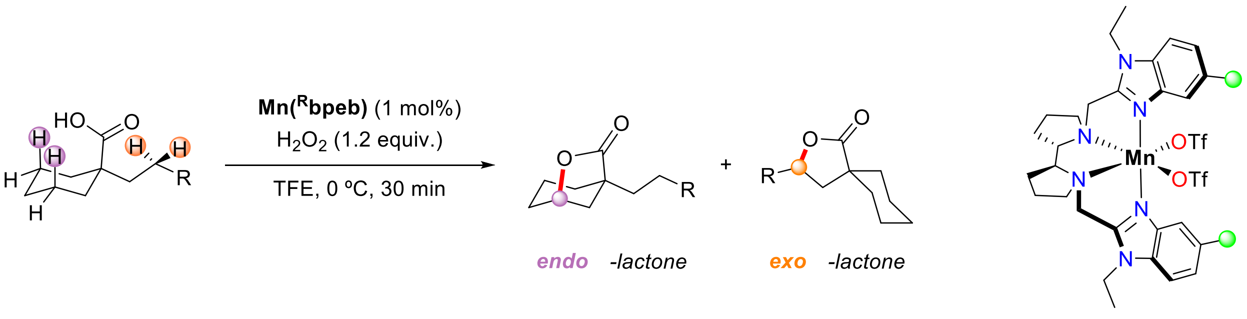
The selective oxidation of non-activated C(sp^3)-H bonds is a reaction with enormous potential in organic synthesis since it allows the transformation of these poorly reactive bonds, which are very abundant in organic molecules, into alcohol or ketones which are recognized as one of the most versatile functional groups in organic synthesis.[1] The oxidation of non-activated C-H bonds in regio-, chemo-, and enantioselective manner is one of the main challenges toward the development of new methodologies for organic chemistry.[2, 3]

This work shows new sterically congested manganese catalysts capable of efficiently and selectively oxidizing non-activated C(sp^3)-H bonds, using hydrogen peroxide as an oxidant under mild conditions and short reaction times. The catalytic system enables the site-selective and asymmetric lactonization of primary and secondary γ-C-H bonds in carboxylic acid substrates. The high modularity and versatility of the present systems allow them to exert control over site selectivity when multiple γ-C-H bonds are present. By manipulating the electronic and steric properties of the catalysts, the γ-lactonization at methylenic sites can be tuned by allowing unprecedented control over the stereoselectivity. Such control has been successfully exploited in the oxidation of carboxylic acid substrates bearing diverse γ-C-H bonds.[4]



(S,S)-[Mn(OTf)$_2$(^{R}bpeb)

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P9

Organometallic Complexes of Au(I) with Azobenzene Derivative Ligands: Study of The Photodynamic Process

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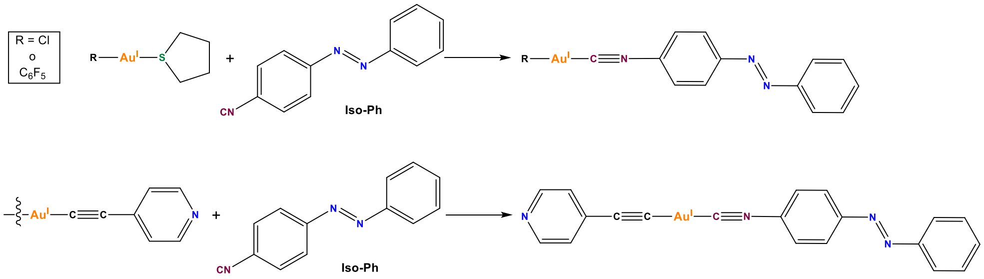
Azobenzene and their derivatives are molecules that can change their structure from the thermodynamically stable *trans* form to the metastable *cis* form by interaction with light of the appropriate wavelength. The reverse process is spontaneous and, for these reasons, this family of compounds can be considered molecular switches.

In the research group where the studies here presented have been carried out, one of the active research lines relates to the effect of the coordination of azoderivatives to anionic or cationic metal moieties. This is in order to determine the effect in the actuation isomerisation mechanism in these photochemical switches.[1,2]

In this work, a family of Au(I) organometallic compounds with one of the ligands being an azobenzene derivative, having an isocyanide functional group in the *para* position to the azo group, have been studied. The strategy followed to prepare these complexes consists in either the substitution of a tetrathiophene ligand (tht) or the breakage of the [-Au-C≡C-py] polymer (in the case of ethynilpyridine).



All the synthesized compounds have been characterised by 1D ^{1}H, ^{13}C, 2D HSQC and HMBC NMR, IR and MS techniques. For some of them their structure have been determined by X-ray single crystal diffraction.

Moreover, their photoactivity and the possible influence of the aurophilic interactions in the process have been studied. Kinetic studies of the spontaneous *cis* to *trans* reaction have been carried out at different concentrations, temperatures, pressures and using different solvents in order to determine the effect of coordinating a metallic Au(I) fragment on the azo isomerisation mechanism.

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Cu-catalyzed Boron-Wittig reactions of carbonylic compounds

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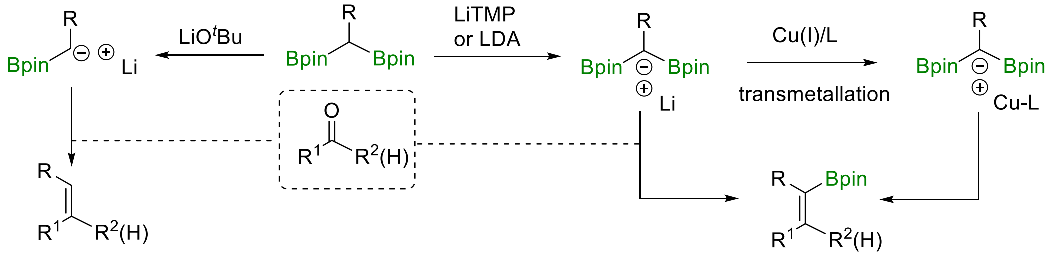
The Boron-Wittig olefination reaction, between carbonyl compounds and gem-diborylalkanes, offers precise control over the cis/trans selectivity of carbon-carbon double bond formation, thereby yielding stereoselective boronfunctionalized alkenes.[1] The mechanism of Boron-Wittig reaction involves the formation of a four-membered ring intermediate throughout O-B interaction/elimination, delivering the alkene and the corresponding boronic ester, as the driving force.[2] The activation of gem-diborylalkanes with main group metals allows the formation of corresponding carbanions, via deprotonation or deborylation strategies, however the alkenylboranes are only generated when the two boryl moieties are present along the Boron-Wittig olefination reaction (Scheme 1). In order to extend the applicability of transition metal complexes in the Boron-Wittig reaction, we describe here the transmetallation of lithium diborylmethide salt to Cu(I), with the aim to explore the influence of copper diborylmethide salts in the stereoselectivity of the Boron-Wittig olefination reaction.



Scheme 1

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Supramolecularly directed enantioselective γ-lactonization of carboxylic acids using bioinspired manganese catalysts

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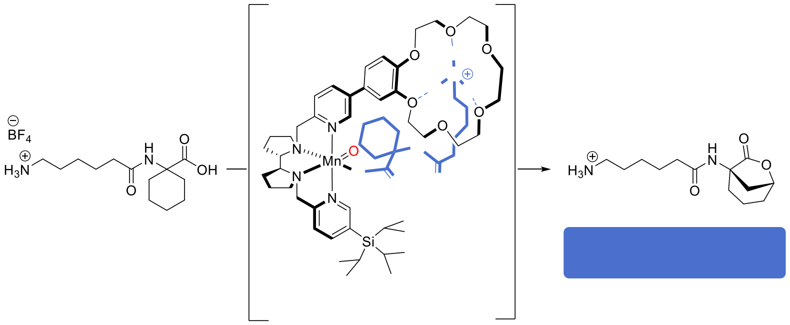
Lactones are known for their diverse and often potent biological activities, making them a fascinating group of molecules for biomedical and chemical research. One of the most desirable processes for obtaining novel lactone compounds is the direct lactonization of carboxylic acids. During the latest years, different examples using iron and manganese biomimetic complexes with tetraazadentate nitrogen-containing ligands have been reported as efficient catalysts for the γ-lactonization using hydrogen peroxide, a waste-free oxidant and operating under mild temperature conditions. [1,2]

Although different catalysts have been developed, some limitations stand in terms of substrate scope. Herein, we present a novel strategy to solve this issue. Our approach relies on supramolecular recognition of the protonated amine of an α,ω-amino acid to a crown ether receptor located in the remote position of the ligand, while the acid moiety activates the hydrogen peroxide at the metal center.[3] This specific spatial rearrangement of the substrate governed by remote binding at the crown ether receptor, may impact in the site- and enantioselectivity of the lactonization.



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Towards the quantum properties' manipulation of metallohelicate-based host-guest supramolecular assemblies.

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Dinuclear triple-stranded helicates serve as versatile scaffolds for the synthesis of nanoscale materials with technological functionalities, through the encapsulation of anionic complexes. For instance, the various guests that have been encapsulated in $[Fe^{II}_2L_3]$ helicates can greatly affect the Spin-Transition Temperature for each of the Fe^{II} ions[1, 2], while the $[Cr^{III}(ox)_3]^{3-}$ complex exhibits an unprecedented Single-Ion Magnet behavior upon its encapsulation[3]. Moreover, the guest's electronic density in $[Co^{II}_2L_3]$ helicates improves the relaxation rates of their magnetization through Spin-Orbit Coupling[4] (SOC). In this work, we report the synthesis and characterization by single-crystal X-ray diffraction of the complexes: $[Fe(ClCNAn)_3]@[Ni_2L_3]$ (**1**), $[Cr(ClCNAn)_3]@[Ni_2L_3]$ (**2**), $[Fe(ClCNAn)_3]@[Co_2L_3]$ (**3**), $[Al(ClCNAn)_3]@[Co_2L_3]$ (**4**), $[Fe(ClCNAn)_3]@[Zn_2L_3]$ (**5**) and $[Al(ClCNAn)_3]@[Zn_2L_3]$ (**6**) (Figure 1). In the cases of (**1**) and (**2**), the use of the asymmetric $ClCNAn^{2-}$ ligand can potentially lead to 2-qubit systems comprised by inequivalent and individually addressable qubits. Moreover, the encapsulation of the electron-rich $[M(ClCNAn)_3]^{3-}$ (M = Fe^{III}, Al^{III}) complex in (**3**) and (**4**) should enhance the SOC and therefore improve the relaxation rates. Meanwhile, complexes (**5**) and (**6**) constitute diamagnetic analogues enabling the possibility for magnetic dilutions. Finally, the luminescent properties of the $ClCNAn^{2-}$ ligand could lead to multifunctional materials which are sensitive to external stimuli.

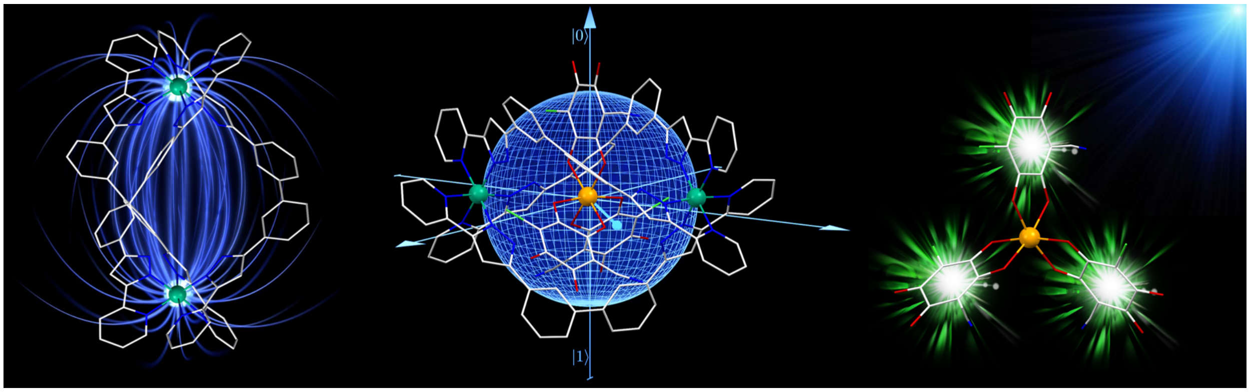

Figure 1. Graphical representation of the potential quantum properties of the complexes (**1**) - (**6**).

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Nous complexos polinuclears de lantànids per a aplicacions de computació quàntica i conversió ascendent de fotons

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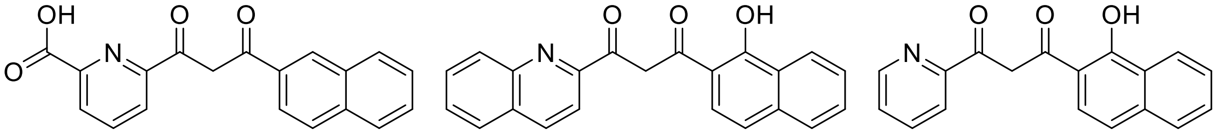
Prèviament, el nostre grup de recerca ha demostrat que amb la utilització de lligands polidentats que combinen restos moleculars tipo 2,6-dipicolinat i 1,3-dicetona es pot promoure l'autoassemblatge de complexos polinuclears i heterometàl·lics de lantànids. En aquests complexes, els ions metàl·lics es distribueixen selectivament als llocs de coordinació dependent del seu radi iònic [1].



H_2LB H_2LQ H_2LC

Figura 1. Lligands picolinat-dicetona utilitzats.

Aquests complexes ens donen la possibilitat d'estudiar fenòmens i propietats emergents de la combinació de distints lantànids en la mateixa molècula [1] i aprofitar aquestes propietats per a la fabricació de imants monomoleculars [2], qubits [3] i materials de conversió ascendent de fotons [4]. El objectiu que es proposa en aquest treball es sintetitzar nous lligands que promoguin noves arquitectures moleculars i utilitzar-los per a accedir a combinacions de lantànids que encara no eren possibles amb els lligands reportats a la literatura. A més, es reporten tres noves estructures de complexes homo- i hetero-metàl·lics no descrits a la bibliografia.

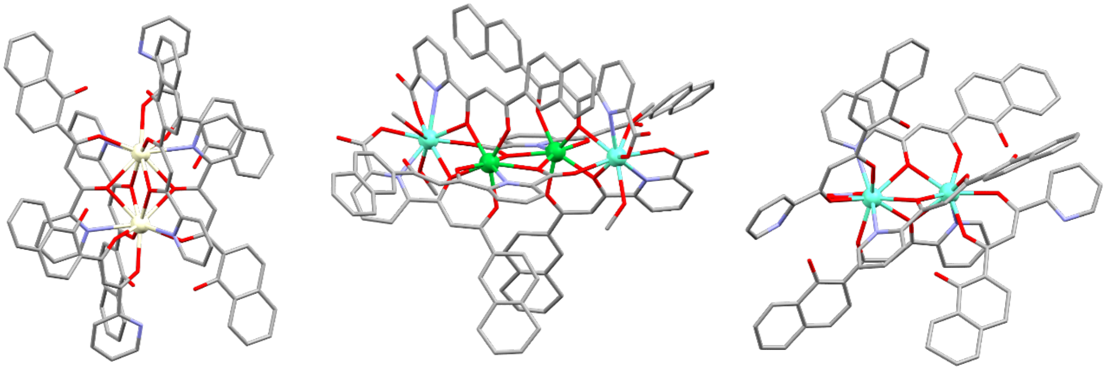


Figura 2. Complexos sintetitzats. $[Ce(HLC)_3]_2$ (esquerra); $[EuYb(LB)_3(OHMe)]_2$ (centre); $[Eu_2(HLC)_5(NO_3)]$ (dreta).

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Exploring Copper *β*-Diketiminate Complexes for Heterogeneous Ammonia Oxidation on Graphitic Surfaces via CH-π and π-π Interactions

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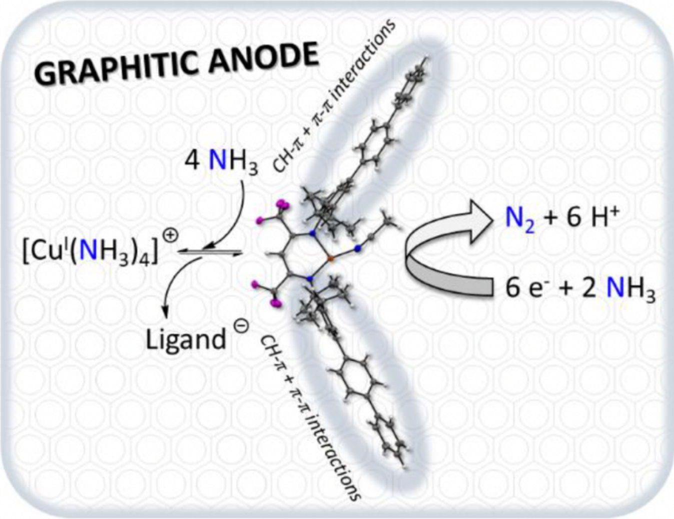
Ammonia is a strong candidate as a carbon-free energy carrier, with potential applications both as a hydrogen vector and as a fuel itself.[1] Building on recent work with a fluorinated Cu(I) β-diketiminate catalyst for homogeneous ammonia oxidation,[2] we report the first example of constructing hybrid electrodes based on first-row metal complexes for heterogeneous ammonia oxidation. During these studies, we prepared various analogues that could be immobilized onto graphitic surfaces via CH-π and π-π interactions. In all cases, we found that these Cu complexes generate an equilibrium with $[CuI(MeCN)_4]^+$, leading to ligand loss and catalysis deactivation. Despite this, we demonstrate that heterogeneous ammonia oxidation is feasible with this approach, although the low catalyst loading and deactivation hindered proper product analysis. Therefore, further work is required to prevent ligand loss and improve catalyst immobilization, ensuring robust and efficient heterogeneous ammonia oxidation performance with this system.



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P15

2ona REUNIÓ DE QUÍMICA INORGÀNICA
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Bimetallic Alloy Nanoparticles Immobilized Over TiO_2 Nanostructures for Enhanced CO_2 Photoreduction

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The development of the CO_2 reduction technologies has been a hot topic for the past several decades.[1,2] The photocatalytic approach has gained popularity in recent years as it involves the utilization of renewable energy. Photocatalytic CO_2 reduction thus emerged as a promising approach for converting this greenhouse gas into value-added chemicals and fuels under ambient conditions.[3–5]

To date, this research field has been prevalently dominated by the use of wide bandgap semiconductors (i.e.: TiO_2, ZnO, Cu_2O etc.), which have been extensively modified to meet selectivity and efficiency standards.[6] Unfortunately, these traditional semiconductors predominantly yield C_1 compounds (i.e: CO, CH_4) which from the commercial standpoint lack in both value and spectrum of industrial applications, making semiconductor photocatalysts capable of producing C_2+ products extremely desirable.[7],[8]

Herein , we report on the synthesis of bimetallic alloy nanoparticles (BNPs) immobilized on the surface of titanium dioxide (TiO_2) nanostructures, for application as photocatalysts in the photoreduction of CO_2 to valuable compounds.

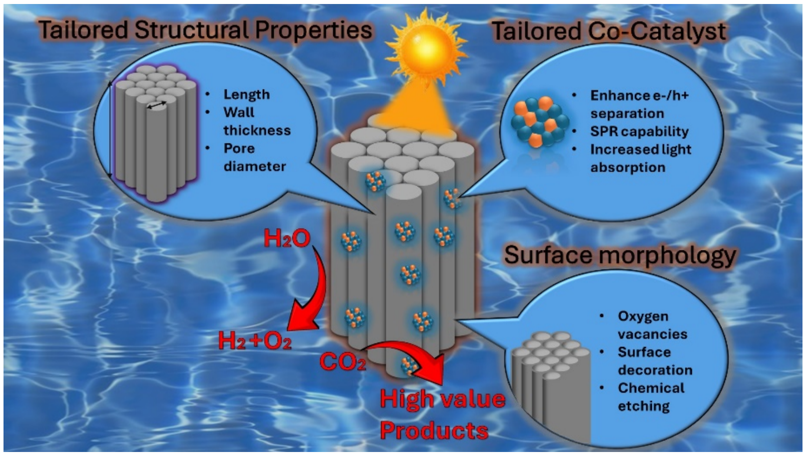

Figure 1. *Graphical abstract.*

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Encapsulation of Fullerenes and Stabilization of Their Radicals Anions for Characterization and Functionalization via Supramolecular Mask Strategies

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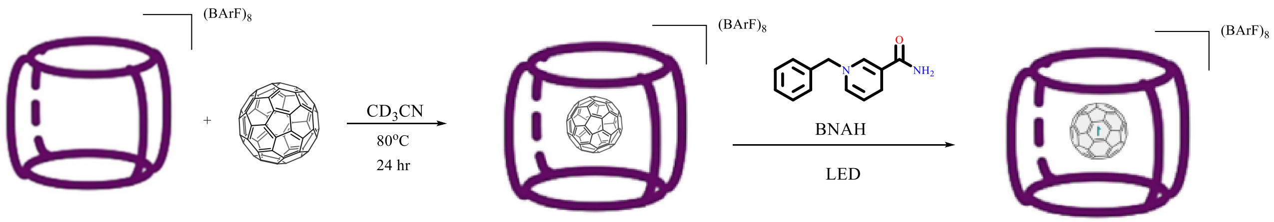
Fullerene derivatives exhibit enhanced properties compared to pristine fullerenes in various fields, including organic photovoltaics, perovskite solar cells, and biological applications. In recent years, researchers synthesized regioisomerically pure fullerene isomers via supramolecular mask strategy by utilizing Bingel-Hirsch reaction[1], Prato reaction[2] and Diels alder reaction[3]. A rapidly evolving approach is the radical anion pathway[4,5], which offers promising opportunities for fullerene functionalization.

In this work, we design heteroleptic supramolecular cages using bimetallic macrocycle based in Pd and H-TCPP (Tetrakis (4-carboxyphenyl) porphyrin), Zn-TCPP[6] and Pd-TCPP. The self-assembly reaction yields tetragonal prismatic cage capable of encapsulating large guests, such as fullerene. This supramolecular platform allows us to study the generation and stabilization of fullerene radicals within confined spaces provided by the cavities of the cages. Stability studies of the C_{60} radical anion within these cages revealed that the electronic and structural properties of the porphyrin cores significantly influence radical generation and stabilization. The long-lived C_{60} radical anions within confined spaces enable us to investigate the selectivity imposed by the cage towards the functionalization of C_{60} through radical-based pathways, coupled to the regioselectivity imposed by the supramolecular nanocage.



M = Zn (4.(BArF)$_8$)
M = H (10.(BArF)$_8$)
M = Pd (11.(BArF)$_8$)

$C_{60}\subset$ M.(BArF)$_8$

$C_{60}^{\cdot-}\subset$ M.(BArF)$_8$

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P17

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Exploring Mechanistic Insights of Cp*CoIII-catalyzed C–H Functionalizations with Organometallic Nucleophiles

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Over the past decade, Cp*CoIII catalysts have emerged as very powerful tool within directed C–H functionalization reactions.[1] While they have shown their tremendous potential coupling a wide variety of electrophiles, the number of nucleophilic C–H couplings is very limited,[2] and the mechanistic intricacies remain obscure. Intrigued by this scenario, we have already disclosed the involvement of oxidatively-induced reductive elimination (ORE) events in Cp*CoIII-catalyzed C–S nucleophilic couplings via high-valent cobalt(IV) intermediates.[3] In this work, we expand our horizons to interrogate C–H functionalizations using organometallic nucleophiles. Our results suggest (i) a key role of the transmetalation step in the Cp*Co-catalyzed C–H functionalization reaction and (ii) a mechanistic departure on the reductive elimination step from literature precedents with analogous Cp*-based group 9 TM systems[4] and our previous results in C-S bond-forming reactions.[3]

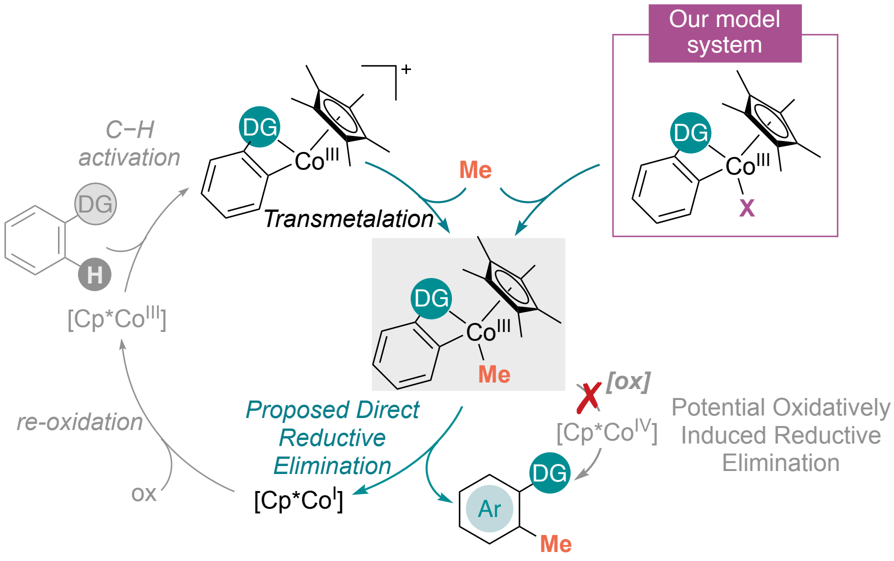

Figure 1. C–H nucleophilic coupling mechanism.

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Computational study of Rh(II)/Pd(0) dual catalysis in the synthesis of 2,2-disubstituted tetrahydroquinolines

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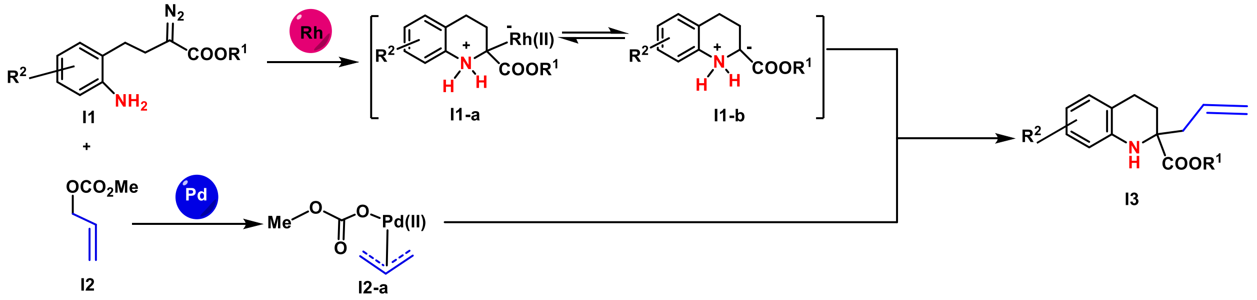
Multimetallic catalysis represents a rapidly advancing area in modern chemistry, offering enhanced control over reaction pathways and significant versatility. While experimental applications are well-established, theoretical investigations remain in their developmental stages[1-2]. This work investigates the with density functional theory (DFT) calculations the mechanism for the synthesis of 2,2-disubstituted tetrahydroquinoline derivatives through cooperative Rh (II)/Pd (0) dual catalysis[3]. Calculations reveal a synergistic interaction between the two catalysts: Rh (II) activates the diazo compound (**I1**), generating an electrophilic Rh (II)-carbenoid intermediate (**I1-a**), while Pd (0) activates the carbonate substrate (**I2**) through oxidative addition to produce an allyl-Pd (II) intermediate (**I2-a**). The Rh (II)-carbenoid intermediate (**I1-a**) can evolve through two pathways: formation of an associated ammonium ylide or a dissociated intermediate (**I1-b**). DFT calculations indicate that the dissociated intermediate (**I1-b**) is the key reactive species, engaging with allyl-Pd (II) (**I2-a**) to form the tetrahydroquinoline product (**I3**). Although side product formation cannot be entirely ruled out, computational results highlight a substantial energy preference for the desired pathway, offering valuable insights into the reaction mechanism.



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Photoinduced water oxidation using organic photosensitizers and a Copper (II) catalyst

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Water oxidation is currently an important bottleneck in the development of artificial photosynthetic systems, and mainly relies on the use of catalysts containing rare elements. Indeed, first-row transition metals, although desirable because inexpensive, possess the disadvantage of lower stability in catalytic conditions due to easier demetallation. However, the combination of tetra-amidate macrocyclic ligands with Copper (II) has recently[1] demonstrated the possibility of obtaining a robust electrocatalyst for water oxidation that is able to produce molecular oxygen even at neutral pH.

In this report, we explore the possibility of coupling this Copper (II) electrocatalyst to organic dyes that possess a long-lived excited thanks to thermally-activated delayed fluorescence, with the goal of building a three-component photocatalytic system that can produce O_2 without the use of noble metals.

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P20

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Study of the spin dynamics of a new family of Schiff base heterometallic complexes containing 3d-4f metals.

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In recent decades, paramagnetic coordination complexes have been explored for various technological applications, including magnetic memory devices, quantum computing, and spintronics [1]. Within quantum computing, magnetic molecules complexes with slow magnetization relaxation have emerged as promising candidates for such applications. This is due to the extensive versatility offered by coordination chemistry, allowing the use of diverse ligands and metallic cations from either or both d- and f-block elements[2,3]. This flexibility enables precise tuning and optimization of key parameters essential for achieving efficient performances in future technologies.

Following this premise, Schiff base complexes appear to be good candidates for these applications due to their capability to coordinate both 3d and 4f metals. A novel series of coordination complexes has been synthesized, including a rare trinuclear structure where the 3d metal exhibits a distinct coordination environment within the same molecule (Figure 1, left). To investigate the spin dynamics of these systems, AC susceptibility measurements and continuous-wave EPR spectroscopy were conducted. The results reveal that some of these complexes exhibit slow magnetization relaxation.

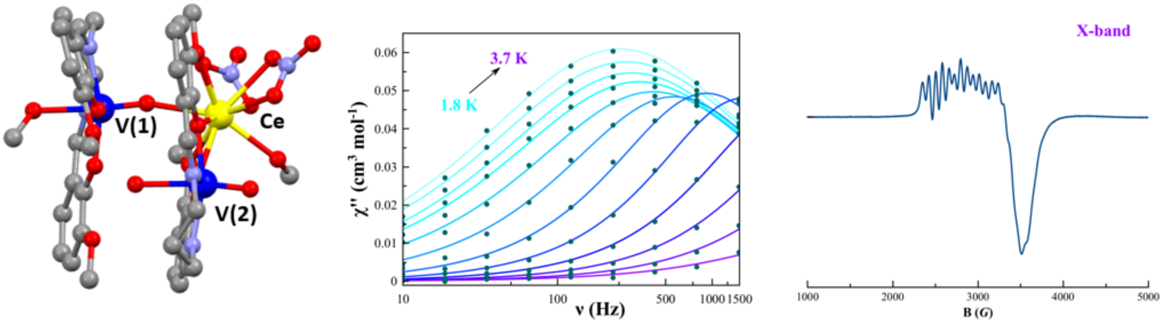

Figure 1. *Left*, trinuclear VO^{2+}-Ce^{3+}-VO^{2+} coordination complex as example of the studied compounds. *Middle*, frequency dependence of the out-of-phase magnetic susceptibility as a function of temperature. *Right*, X-band *cw*-EPR at 4K of the trimer.

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