

BOOK OF ABSTRACTS

Barcelona, February 2-3, 2023

1st Meeting of **Inorganic and
Organometallic Chemistry** of the
Catalan Chemical Society





1a REUNIÓ DE QUÍMICA INORGÀNICA I ORGANOMETÀL·LICA de la SCQ

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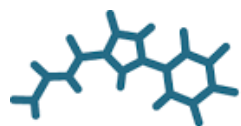


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Scientific Program

Thursday, February 2		Friday, February 3	
9:00-9:30	Registrations		
9:30-9:45	Welcome. Prof. G. Aromí	SESSION V	Chair Laura Rodríguez <i>Sponsored by Adv. Catal. Elsevier.</i>
	Opening. Prof. G. Ujaque	9:20-10:00	Plenary 3. Corine Mathonière
SESSION I	Chair Miquel A. Pericàs <i>Sponsored by AstraZeneca</i>	10:00-10:20	Oral Communication 15. <i>J. Puigmartí-Luis</i>
9:50-10:30	Plenary 1. Ruben Martin	10:20-10:40	Oral Communication 16. <i>R. Núñez</i>
10:30-10:50	Oral Communication 1. <i>S. Rafael</i>	10:40-11:00	Oral Communication 17. <i>M. Martínez</i>
10:50-11:10	Oral Communication 2. <i>M. Biosca</i>	11:00-11:30	Coffee Break-Poster Session
11:10-11:40	Coffee Break-Poster Session	SESSION VI	Chair Daniel Maspoch
SESSION II	Chair E. Carolina Sañudo <i>Sponsored by AstraZeneca</i>	11:30-11:50	Oral Communication 18. <i>A. Figuerola</i>
11:40-12:00	Oral Communication 3. <i>X. Sala</i>	11:50-12:10	Oral Communication 19. <i>L. Capdevila</i>
12:00-12:20	Oral Communication 4. <i>L. Francàs</i>	12:10-12:30	Oral Communication 20. <i>E. C. Sañudo</i>
12:20-12:40	Oral Communication 5. <i>I. Fort-Grandas</i>	12:30-12:50	Oral Communication 21. <i>A. Carné-Sánchez</i>
12:40-13:00	Oral Communication 6. <i>A. de Aquino</i>	12:50-13:10	Oral Communication 22. <i>A. Cortés-Martínez</i>
13:00-13:20	Oral Communication 7. <i>R. Matheu</i>	13:10-13:15	Presentation of the Young Section of the SCQ
13:20-15:30	Lunch – Poster Session	13:15-13:20	Group Picture
		13:20-15:30	Lunch – Poster Session
SESSION III	Chair Arjan. W. Kleij <i>Sponsored by Organometallics and Inorg. Chem.</i>	SESSION VII	Chair Xavier Sala <i>Sponsored by Adv. Catal. Elsevier.</i>
15:30-16:10	Plenary 2. Eva Hevia	15:30-16:10	Plenary 4. Guillermo Mínguez
16:10-16:30	Oral Communication 8. <i>M. Sethuraman</i>	16:10-16:30	Oral Communication 23. <i>R. Diego</i>
16:30-16:50	Oral Communication 9. <i>M. Galeotti</i>	16:30-16:50	Oral Communication 24. <i>S. Ruiz-Relaño</i>
16:50-17:20	Coffee Break-Poster Session	16:50-17:20	Coffee Break-Poster Session
SESSION IV	Chair Anna Company <i>Sponsored by Organometallics and Inorg. Chem.</i>	SESSION VIII	Chair Montserrat Ferrer
17:20-17:40	Oral Communication 10. <i>C. Casadevall</i>	17:20-17:40	Oral Communication 25. <i>E. Petrus</i>
17:40-18:00	Oral Communication 11. <i>J. Margalef</i>	17:40-18:00	Oral Communication 26. <i>N. Pagès-Vilà</i>
18:00-18:20	Oral Communication 12. <i>S. Barranco</i>	18:00-18:20	Oral Communication 27. <i>P. Font</i>
18:20-18:40	Oral Communication 13. <i>A. García-Roca</i>	18:20-18:40	Closing Ceremony. Prof. M. Diéguez
18:40-19:00	Oral Communication 14. <i>J. Eusamio</i>		
20:30	Conference Dinner		

Table of contents

Plenaries		9
PL1.	<i>Taming multifaceted nickel catalysts: an academic fascination</i>	10
	Ruben Martin	
PL2.	<i>Tailoring organosodium reagents for new synthetic and catalytic applications</i>	11
	Eva Hevia	
PL3.	<i>Switchable cyanometallate compounds : Metal-to-metal charge transfer or spin crossover?</i>	12
	Corine Mathonière	
PL4.	<i>Porous materials with electroactive building blocks</i>	13
	Guillermo Mínguez	
Oral Communications		14
OC1.	<i>Synthesis and application of internal ynamides in the Pauson-Khand reaction</i>	15
	Sergi Rafael	
OC2.	<i>Readily available tailor-made Ir-catalysts for the enantioselective reduction of challenging substrates</i>	16
	Maria Biosca	
OC3.	<i>Surface-functionalized nanomaterials for the production of solar fuels</i>	17
	Xavier Sala	
OC4.	<i>Deciphering the key factors for the good performance of different Ni/NiOOH electrocatalysts</i>	18
	Laia Francàs	
OC5.	<i>Study of conductive MOFs based on triphenylene derivatives for chemiresistive greenhouse gas sensors</i>	19
	Ignasi Fort-Grandas	
OC6.	<i>Efecte de les interaccions Au(I)···Au(I) en les propietats fotofísiques</i>	20
	Araceli de Aquino	
OC7.	<i>Charge reservoirs in an expanded halide perovskite analog: enhancing high-pressure conductivity through redox-active molecules</i>	21
	Roc Matheu	
OC8.	<i>Oxidative desymmetrization of cyclic amides via enantioselective C-H bond oxidation using bioinspired manganese catalysts</i>	22
	Muthuramalingam Sethuraman	
OC9.	<i>Manganese-catalyzed C-H bond oxidation of cyclopropane containing hydrocarbons</i>	23
	Marco Galeotti	
OC10.	<i>Carbon-based materials for solar-driven catalysis</i>	24
	Carla Casadevall	

OC11.	<i>Reversed regioselectivity in the Rh-hydroformylation of styrene</i> Jèssica Margalef	25
OC12.	<i>Merging Cp*Co catalysis and statistical analysis for interrogating deuterium source selection in directed hydrogen isotope exchange</i> Sergio Barranco	26
OC13.	<i>A comprehensive mechanistic scenario for the Cu-mediated asymmetric propargylic sulfonylation forging tertiary carbon stereocenters</i> Alèria Garcia-Roca	27
OC14.	<i>P-Stereogenic non-symmetric diphosphanes with a methylene bridge: coordination chemistry to late transition metals</i> Javier Eusamio	28
OC15.	<i>Microfluidic technologies as an advanced tool for chemistry and materials synthesis</i> Josep Puigmartí-Luis	29
OC16.	<i>Inorganic boron clusters as unique entities to trigger and modulate molecule and material properties</i> Rosario Núñez	30
OC17.	<i>Building molecular mixed-valence cyanido-bridged CoIII/FeII redox active complexes: from dinuclear to cubic species</i> Manuel Martínez	31
OC18.	<i>Synthesis and applications of group 11-based ternary Semiconductor nanocrystals with tunable morphology and composition</i> Albert Figuerola	32
OC19.	<i>Synthesis of curved perylene-based nanographenes</i> Lorena Capdevila	33
OC20.	<i>Devices for quantum computing: towards a measurement of on-surface qubit phase memory time</i> E. Carolina Sañudo	34
OC21.	<i>Reactivitat i assemblatge de poliedres metal-orgànics</i> Arnau Carné-Sánchez	35
OC22.	<i>Síntesi de materials oligomèrics porosos</i> Alba Cortés-Martínez	36
OC23.	<i>Quantum fluctuations in single molecule magnets on magnetic substrates</i> Rosa Diego	37
OC24.	<i>Síntesi de noves estructures metal·loorgàniques mitjançant la química de "Clip-Off"</i> Sara Ruiz-Relaño	38
OC25.	<i>Predint l'especiació en dissolució aquosa i els mecanismes d'auto-assemblatge dels òxids metàl·lics moleculars de Mo, W, V, Nb i Ta</i> Enric Petrus	39
OC26.	<i>Proton triggered chemoselective halogenation of aliphatic C-H bonds with nonheme Fe(IV)-oxo complexes. An alternative model for nonheme halogenases</i> Neus Pagès-Vilà	40

OC27.	<i>Hemilabile MIC^N ligands allow oxidant-free Au(I)/Au(III) arylation-lactonization of γ-alkenoic acids</i> Pau Font	41
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Posters		42
P1.	<i>[Dy₂(μ-2,6-2FBz)₄(NO₃)₄]²⁻ and [Dy₂(μ-2,6-2FBz)₄(2,6-2FBz)₄]²⁻ : Two anhydrous different structural motifs depending on the solvent</i> Ànnia Tubau	43
P2.	<i>Triphenylene derivative MOFs for greenhouse gas sensing and green catalysis</i> Yuzelfy Mendoza-Gamero	44
P3.	<i>Enhancing Pd-catalyzed asymmetric allylic substitution reactions with improved catalysts for the construction of chiral C-C and C-X bonds</i> Pol de la Cruz-Sánchez	45
P4.	<i>DFT guided ligand design for iridium catalyzed asymmetric hydrogenation. Filling the gap by in silico optimization</i> Jorge Faiges	46
P5.	<i>New supported phosphine-stabilized palladium nanocatalysts for the hydrogenation of CO₂ into formate</i> María Dolores Fernández-Martínez	47
P6.	<i>Propane dehydrogenation over small platinum clusters supported on g-C₃N₄</i> Jie Pan	48
P7.	<i>Is size all that matters? A discussion on the fine-tuning of metallic nanoparticles</i> Álvaro Lozano-Roche	49
P8.	<i>A new Ir-P,N catalyst design to solve the asymmetric hydrogenation of challenging alkenes</i> Daniel Tarr	50
P9.	<i>Stereoselective multi-component allylic alkylation enabled by dual photoredox/Ni catalysis</i> Qian Zeng	51
P10.	<i>Understanding polyoxometalates as water oxidation catalysts through iron vs. cobalt reactivity</i> Khalid Azmani	52
P11.	<i>Cianuro complexos de Fe(II) amb grups azo solubles en aigua: estudi mecanístic de la seva isomerització tèrmica cis-trans</i> Montserrat Ferrer	53
P12.	<i>Kinetico-mechanistic studies on the lability of Cu(II)-carbon bonds: homo- or heterolysis?</i> Manuel Martinez	54
P13.	<i>Cyclometallated iridium catalysts for the asymmetric hydrogenation of imines</i> Yisong Wen	55
P14.	<i>Three-component Suzuki-Miyaura/allylic substitution: a regioselective approach to 2-aryl allyl sulfones</i> Marina Bellido	56

P15.	<i>Mechanistic insights into the oxidation of Cp*Co(III) species with F⁺ oxidants</i> Sara López-Resano	57
P16.	<i>Tuning nanoparticles for artificial photosynthesis applications</i> Aureliano Macili	58
P17.	<i>Switchable MOP solubility through surface chemistry: engineering molecular self-sorting systems</i> Laura Hernández-López	59
P18.	<i>Polimerització covalent de caixes moleculars poroses: síntesi, funcionalització i aplicacions</i> Akim Khobotov-Bakishev	60
P19.	<i>L'efecte plantilla de l'anió SiF₆²⁻ i els ponts d'hidrogen: L'aliança perfecta per aconseguir la formació exclusiva de nous sistemes de coordinació heterolèptics</i> Leoni Alejandra Barrios	61
P20.	<i>Synthesis of Ni(II) helicates for the chemical tuning of spin clock transitions</i> Manuel Imperato	62
P21.	<i>Design of functional inorganic 2D materials via molecular engineering</i> Jose Muñoz	63
P22.	<i>Disseny de compostos dinuclears de lantànid per portes lògiques quàntiques</i> David Aguilà	64
P23.	<i>Highly selective heterometallic [LnLn'Ln] molecules as 3-qubit quantum gates</i> Diamantoula Maniaki	65
P24.	<i>Light-driven hydrogen evolution using Ni, Cu and Pt nanoparticles supported on carbon nitride and covalent triazine-frameworks</i> Heting Hou	66
P25.	<i>Millora dels temps de relaxació de imants unimoleculars</i> Adriana Silvestre-Llora	67
P26.	<i>Dearomatizative syn-dihydroxylation of arenes</i> Najoua Choukairi Afailal	68
P27.	<i>C-H Bonds as functional groups. simultaneous generation of multiple stereocenters by enantioselective hydroxylation at unactivated tertiary C-H bonds</i> Andrea Palone	69
P28.	<i>Synthesis and reactivity of organometallic nickel complexes relevant in carbon-carbon and carbon-heteroatom bond formation reactions</i> Adrià Juvanteny	70
P29.	<i>Exploring the intramolecular chemistry of iron(V)-oxo-carboxylato species</i> Andrea Álvarez-Núñez	71
P30.	<i>Carbene transfer reactions catalyzed by an iron/lithium dual system</i> David Capellán	72
P31.	<i>Development of a new protocol towards the synthesis of nanographene-like compounds via aromatic homologation catalysis</i> Judith Sala	73



1a REUNIÓ DE QUÍMICA INORGÀNICA I ORGANOMETÀL·LICA de la SCQ



P32.	<i>Orthogonal regioselective bis-functionalization of C₆₀ by Diels-Alder reaction via avant-garde supramolecular mask strategy</i> Tània Pèlachs	74
P33.	<i>Biologically inspired C-H hydroxylation catalysis with metallocavitand</i> Siu-Chung Chan	75
P34.	<i>Regioselective bis-functionalization of fullerene C₇₀ via supramolecular masks</i> Valentina Iannace	76
P35.	<i>Molecular and hybrid materials based on metallacarboranes</i> Syrine Affes	77
P36.	<i>Preparation of carbons with different morphologies from xylose obtained from almond shells: carbon microspheres and ordered mesoporous carbons</i> Angie Carlyne Rueda	78
P37.	<i>Catalitzadors de Ni suportats en carbons mesoporosos ordenats, obtinguts a partir de lignina procedent de biomassa, per a la hidroxigenació de guaiacol</i> Anna Casadó	79

Plenaries





1a REUNIÓ DE QUÍMICA INORGÀNICA I ORGANOMETÀL·LICA de la SCQ



Taming Multifaceted Nickel Catalysts: An Academic Fascination

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The recent years have witnessed a renaissance in the general area of Ni-catalyzed reactions. The popularity of these processes is mainly attributed to the unique features of nickel when compared to its d10 congeners, and the promiscuity of nickel to participate in multiple redox manifolds.^[1] Our research group has contributed to the general area of nickel catalysis for the valorization of chemical feedstocks as a vehicle to rapidly and reliably generate added-value compounds. Among these, we have shown the ability to incorporating carbon dioxide (CO₂) into organic skeletons or catalytic techniques that make use of simple (un)saturated hydrocarbons or native functionality to build up molecular complexity from simple precursors.^[2] These methods are characterized by their simplicity, and wide substrate scope.

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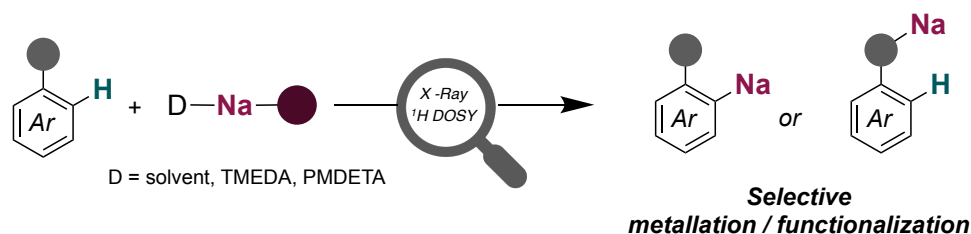
Tailoring Organosodium Reagents for New Synthetic and Catalytic Applications

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Lithium alkyls and amides reside at the front of organometallic synthesis as key players in countless transformations, owing to their availability, substantial stability and solubility in hydrocarbon solvents. However, these desirable traits are often pitfalls of sodium organometallics, meaning that their applications have remained underexplored. Recent reports have hinted at the untapped potential of these reagents, although the constitution of the organometallic intermediates that operate in these reactions has remained hidden.^[1]

Exploiting chemical cooperativity, by combining sodium amides with either organoboron reagents^[2] or metal-amides of other earth abundant metals (M= Fe, Co)^[3] this talk will describe new synthetic strategies for arene functionalisation. Upgrading stoichiometric successes to catalytic regimes, the applications of organosodium reagents as efficient catalysts in perdeuteration processes will also be discussed.^[4] Isolation of key reaction intermediates combined with DFT calculations advances the understanding on how the reactivity and regioselectivity of organosodium reagents can be boosted.



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1a REUNIÓ DE QUÍMICA INORGÀNICA I ORGANOMETÀ-LICA de la SCQ



Switchable coordination compounds: Metal-to-metal Charge Transfer or Spin Crossover ?

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The rational design of molecular systems, which exhibit light-switchable physical properties is still a subject of the intense research activity. Over the past, chemists have investigated magnetic and photoresponsive complexes through rational choices of cyanido-based building blocks.¹ This approach has been extremely successful, and various molecular architectures have been obtained with remarkable properties such as spin crossover, electron-transfer process, and photoinduced magnetism. The understanding of the electronic mechanism during the photo-excitation is not an easy task using only magnetic properties. The use of structural X-ray probes is necessary to better understand the photomagnetic mechanism.

In this presentation, the switching properties of three coordination compounds, namely the mononuclear $K_4Mo(CN)_8 \cdot 2H_2O$,² a dinuclear pair $[(Tp)Fe^{III}(CN)_3Co^{II}(PY_5Me_2)]^+$ ($PY_5Me_2 = 2,6$ -bis(1,1-bis(2-pyridyl)ethyl)pyridine,³ $Tp =$ hydridotris(pyrazol-1-yl)borate) and the tetranuclear $\{[(Tp^+)Fe(CN)_3]_2[Co(Me_2bpy)_2]_2\}(ClO_4)_2 \cdot 2DMF$.⁴ These compounds will be analysed using a combination of bulk photocrystallography, X-ray Absorption Spectroscopy (XAS) and X-ray Magnetic Circular Dichroism (XMCD) measurements. For $K_4Mo(CN)_8 \cdot 2H_2O$, the photocrystallography reveals a reversible photo-induced breaking of one CN bond in the solid state that leads to the triplet state trapping up to 60 K.² For the cyanido-bridged compounds, the bulk and local structural measurements have shown the thermal- induced electron transfer.^{3,4}

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Porous materials with electroactive building blocks

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The development of metal-organic frameworks (MOFs) has grown very rapidly in the last years, with numerous applications in a wide range of different fields resulting from the ample chemical versatility of this type of crystalline porous materials. An interesting aspect in this type of hybrid materials is the incorporation of electronic properties, which can be achieved with the use of electroactive building blocks.[1,2]

In this presentation, we will present the use of tetrathiafulvalene (TTF) derivatives, an archetypal electroactive molecule, for the formation of different types of porous molecular-based solids, ranging from mesoporous robust MOFs that present a flexible behaviour and modify its electronic structure upon exposure to different solvents,[3,4] to multifunctional MOFs combining magnetic, electronic and luminescent properties.[5]

In addition, we will show another type of porous molecular-based crystalline materials that are self-assembled through H-bonding interactions, namely Hydrogen-bonded Organic Frameworks, or HOFs. A major advantage of HOFs is the lack of formation of strong coordination bonds (as in MOFs) or covalent bonds (as in COFs), thus being easily synthesised in mild conditions, which facilitates their processing, one of the major drawbacks of MOFs and COFs. By tuning the synthetic conditions, open structures with suitable TTF stacking for efficient orbital overlap can be prepared, and depending on the solvent a zwitterionic character of the molecule, with a positively charged TTF core and a negatively charged carboxylate group, can be controlled, resulting in an efficient charge transport with no need of post-synthetic treatment (e.g., electrochemical oxidation or doping).[6]

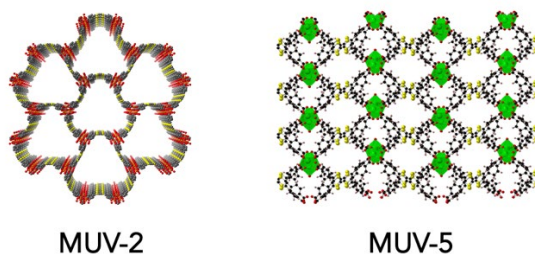


Figure 1. Crystal structures of two TTF-based MOFs, MUV-2 and MUV-5.

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Oral Communications



Synthesis and application of internal ynamides in the Pauson-Khand reaction

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The Pauson-Khand reaction (PKR) is a textbook method for the synthesis of cyclopentenones through the cycloaddition of an alkyne, an alkene, and a carbon monoxide molecule, catalyzed by cobalt or rhodium^[1]. This reaction can be performed both in intramolecular and intermolecular manner, making it a very powerful tool in organic synthesis. However, its synthetic application has been limited by the complex predictability of the regioselective outcome using asymmetric internal alkynes, and the limited range of alkenes that can be used in the intermolecular version. Therefore, there is synthetic interest for the study of new substrates that can undergo this reaction in a regioselective manner.

Our group has years of experience in the study of the PKR^[2,3], and we envisioned internal ynamides as the perfect candidate to use as the alkyne counterpart. These amide-substituted alkynes present very particular electronic properties, with a strong differentiation of charges between the two carbons^[4]. In our work, we have optimized the conditions for the use of these substrates in the PKR, both for the intramolecular and intermolecular version of it. We tested these conditions in a wide range of substrates, obtaining moderate to high yields in all cases. Finally, we have proven that only one regioisomer is formed in the intermolecular approach, characterized it via X-Ray diffraction, and rationalized the outcome in correlation with their electronic properties.

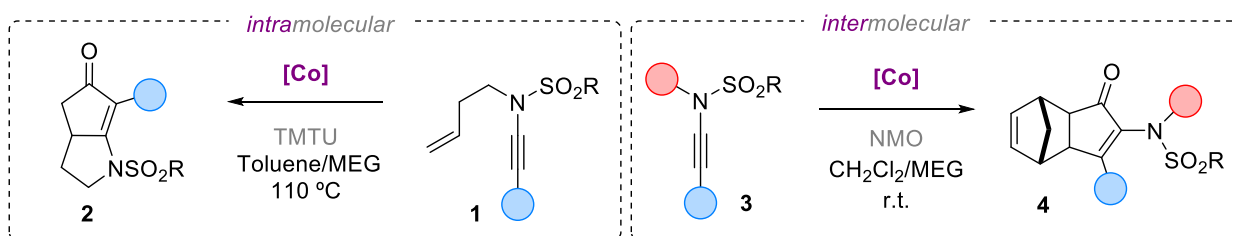


Figure 1. General scheme of the developed methodology for the application of internal ynamides in the Pauson-Khand reaction

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Readily available tailor-made Ir-catalysts for the enantioselective reduction of challenging substrates

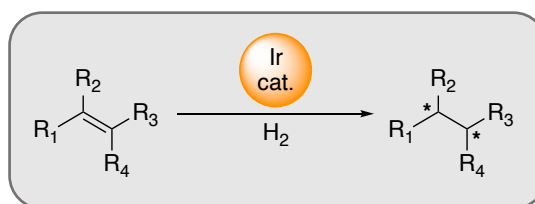
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Asymmetric catalysis is one of the most applied methodologies to satisfy the ever-increasing demand for chiral molecules. Among the enantioselective catalytic reactions that lead to enantiomerically pure products, the hydrogenation of olefins is one of the most powerful ones. In this field, the asymmetric hydrogenation of functionalized olefins has been comprehensively studied and can now be considered a mature field, however the hydrogenation of unfunctionalized olefins is less developed and the search for more efficient ligands is still needed.^[1] Our group has expertise in preparing modular and easy to handle ligand libraries from readily available materials. These ligands provided an improved generation of catalysts for the asymmetric hydrogenation of olefins, demonstrating high catalytic performance in the hydrogenation of a wide range of non-chelating olefins with different geometry, substitution pattern and degree of functionalization.^[2] These air-stable and readily available catalysts provided excellent enantioselectivities (ee's up to 99%) in the asymmetric hydrogenation of several challenging di- and trisubstituted alkenes and even in the more demanding tetrasubstituted olefins. Moreover, the combination of DFT-calculations and experimental studies led to the discovery of the factors responsible for the enantioselectivity, allowing the rationalization of the most suitable substrates for these catalysts.



Scheme 1. Ir-catalyzed asymmetric hydrogenation of minimally functionalized olefins.

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1a REUNIÓ DE QUÍMICA INORGÀNICA I ORGANOMETÀL·LICA de la SCQ



Surface-functionalized nanomaterials for the production of solar fuels

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To date 80% of worldwide energy is derived from fossil fuels, which is unsustainable in the mid-long term. Solar fuels are promising candidates for replacing fossil fuels as energy sources.^[1] However, its renewable and clean generation is still a great challenge. A particularly attractive solution is artificial photosynthesis, which follows the blueprint of the photosynthetic processes found in plants or phototrophic microorganisms in which carbohydrates are made from H₂O and CO₂ using solar energy. Various reactions are under study, including water splitting, where water is converted into hydrogen fuel and oxygen, and CO₂ reduction, where CO₂ and electrons are converted into carbon-based fuels (e.g. CH₄, CH₃OH, etc.) and/or useful chemical feedstocks (e.g. CO, ethylene, etc.). However, the practical development of these technologies is still hampered by the lack of selective, cost-efficient catalysts able to speed up the redox half-reactions involved, namely oxygen evolution, CO₂ reduction and hydrogen evolution reactions (OER, CO₂RR and HER, respectively). Both molecular and metal/metal-oxide species are plausible candidates for efficiently catalyze these processes. If durability and the attainment of high current densities are the main challenge for molecular HER/OER/CO₂RR catalysts, slow reaction rates are common when their counterparts at the nanoscale are employed. Furthermore, the reduced mechanistic knowledge and lack of well-controlled synthetic strategies to fine-tune these species prevents the rational development of more selective nanocatalysts for these transformations.^[2]

This contribution deals with the work carried out in our laboratories to unravel the key factors able to change these last general trends by means of tunable surface-functionalized nanocatalysts. This strategy allowed obtaining stable and efficient OER (photo)catalysts based on 1st-row transition metal oxide species,^{[3],[4]} fast and rugged Ru-based (photo)cathodes^{[5],[6],[7],[8],[9],[10]} superior to state-of-the-art Pt/C for HER, and selective photocatalyst for the CO₂RR.^[11]

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Deciphering the key factors for the good performance of different Ni/NiOOH electrocatalysts

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Hydrogen and other solar fuels have been highlighted as one of the future energy vectors. Having natural photosynthesis as inspiration, we can develop a device capable to split water using sunlight, obtaining oxygen and hydrogen.^{[1], [2]} Different strategies can be used to achieve this: from separated light harvesting and catalytic systems to all integrated devices able to transform directly sunlight into fuels. In both approaches the catalyst is pivotal to improve the system efficiency. Although rapid progress is being made in the field, understanding of the limiting factors of these catalysts has allowed remarkable improvements in their performance.

In this talk I will focus on the study of Ni/NiOOH based catalysts for oxidative reactions: Oxygen evolution reaction and organic substrate oxidation. In particular, I will discuss the effect of

doping on these earth abundant catalysts (both of Fe and Ru), using a wide variety of characterisation techniques (TEM, XAS, EXAFS, ATP, etc.).^[3-4] I will specially discuss the use of the combined electrochemical and optical technique to probe the catalytic function of metal oxides for redox catalytic transformations.^[5] This technique opens a new possibility of studying multielectron reaction mechanisms on non-ideal metal oxides (Figure1). All this acquired knowledge will help to systematically improve the next generation of catalysts for circular economy.

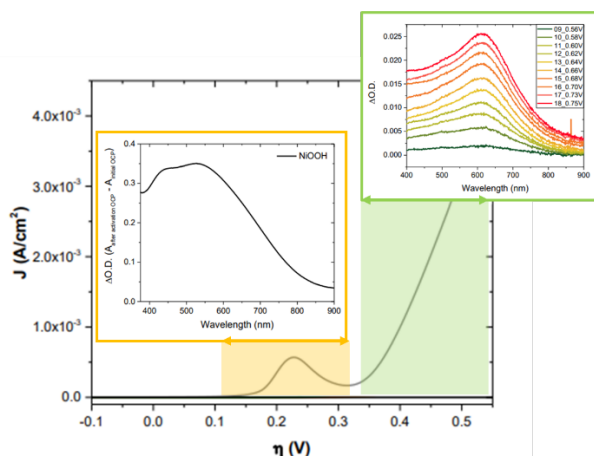


Figure 1. UV-Vis fingerprints before the catalytic onset (yellow) and after (green) for NiOOH electrocatalyst when used for oxygen generation, data extracted from [3]

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Study of conductive MOFs based on triphenylene derivatives for chemiresistive greenhouse gas sensors

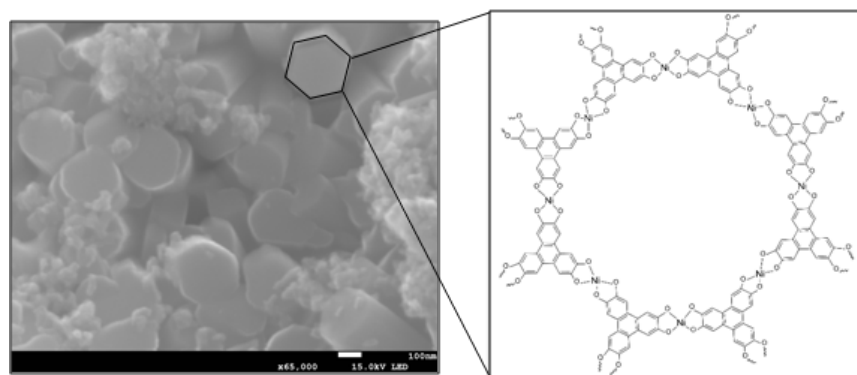
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The direction of sustainability and overall health concerns in which society is moving towards has brought an increasing demand of reliable and affordable new materials-based systems capable of monitoring key gas compounds of such concerns. Currently, sensitive and selective gas monitoring systems are complex, bulky and expensive and, thus, there are few of them and bound to fixed locations. To complement these systems, advanced, miniaturised, low cost and low power consuming gas sensing devices are required. Among them, sensors based on high conductivity nanostructured metal-organic frameworks (MOFs) materials, which present high porosity and specific surface area, are very interesting candidates.^[1]



In this work, highly conjugated triphenylene-derived ligands, namely hexahydroxytriphenylene (HHTP) or hexaminotriphenylene (HITP), were used, together with different metal centres (Mg, Ba, Co, Cu, Ni and Zn) that yield isostructural MOFs. We study the structural differences upon switching the metal or the ligand, and how this changes affect the electrical and CO₂ and CH₄ gas sensing properties of the MOFs. The synthetic route was adapted from elsewhere^[2] and modified to obtain new MOFs and various controlled morphologies at the nanoscale. The planar nature of the coordination of the beforementioned ligands with the metallic centres yields hexagonal 2D structures with a centre pore, and the vertical arrangement, probably provided by p-p stacking, gives rise to nanostructures with dimensions from 30 to 300 nm depending on the synthetic conditions and the nature of the MOF itself.

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Efecte de les interaccions Au(I)---Au(I) en les propietats fotofísiques

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Els compostos d'or(I) poden presentar interaccions febles que anomenem **interaccions aurofíliques**. Aquestes interaccions supramoleculares permeten modular les propietats luminescents dels compostos, i es poden donar entre diversos àtoms d'or dins de la mateixa molècula (intramolecular) o entre metalls de diferents molècules (intermolecular). ^[1-4]

En aquest treball volem estudiar **l'efecte de l'or, com a àtom pesant** en el procés d'*entrecreuament de sistemes* (conegut pel terme anglès *intersystem crossing*). Aquest estudi s'ha dut a terme amb dues famílies de compostos organometàl·lics, les quals presenten dos cromòfors diferents, units a àtoms d'or(I) i a difosfines amb diferents nivells de rigidesa, que ens permeten modular la presència i tipus de les interaccions Au...Au.

Tots els compostos s'han pogut caracteritzar mitjançant la difracció de Rajos X de monocristall, fet que ens ha permès tenir informació sobre quines interaccions tenen lloc en l'estat sòlid. D'altra banda, la utilització de la luminescència i tècniques més avançades com la *ns-Laser Flash Photolysis*, ens han permès saber l'eficiència de la població dels estats triplets.

A més a més, s'han complementat aquests resultats amb uns càlculs de TD-DFT, amb els quals s'han optimitzat les geometries dels compostos i s'han calculat els principals estats involucrats en les transicions observades a nivell experimental.

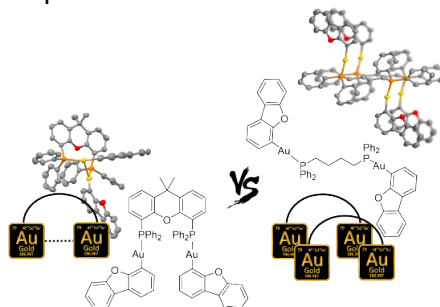


Figura 1. Imatge representativa dels objectius estudiats en el treball presentat.

Gràcies a aquest treball podem afirmar que hem trobat una tendència per compostos amb les estructures estudiades, que ens permet entendre les propietats luminescents resultants i que pretenem estendre a d'altres famílies per tal de poder extreure (o no) tendències generals.

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Charge reservoirs in an expanded halide perovskite analog: enhancing high-pressure conductivity through redox-active molecules

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As halide perovskites and their derivatives are being developed for numerous optoelectronic applications, controlling their electronic doping remains a fundamental challenge. We have recently discovered a novel strategy of using redox-active organic molecules as stoichiometric electron acceptors in new expanded perovskite analogs. Compressing the metal-halide framework drives up the valence band relative to the acceptor orbitals of the organic molecules. Thus, the material's electronic conductivity increases by a factor of 10^5 with pressure, reaching $50(17) \text{ S cm}^{-1}$ at 60 GPa, exceeding the high-pressure conductivities of most halide perovskites. This conductivity enhancement is attributed to an increased hole density created by reduction of the redox-active molecules. This work elevates the role of organic cations in 3D metal-halides, from templating the structure to serving as charge reservoirs for tuning the carrier concentration.

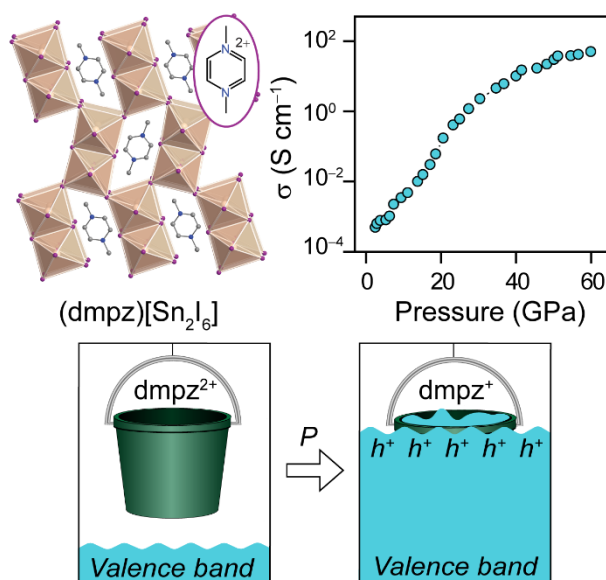


Figure 1. Redox-active organic cations can act as charge reservoirs in the expanded perovskite analog $(\text{dmpz})[\text{Sn}_2\text{I}_6]$. Material compression increases electronic conductivity by five orders of magnitude. This conductivity rise is attributed to an increased hole density in the valence band, caused by electron transfer to the redox-active molecules.



1a REUNIÓ DE QUÍMICA INORGÀNICA I ORGANOMETÀL·LICA de la SCQ



Oxidative desymmetrization of cyclic amides via enantioselective c-h bond oxidation using bioinspired manganese catalysts

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Asymmetric catalytic C-H oxidation constitutes the most appealing synthetic strategy for introducing chirality in saturated hydrocarbons because of the availability of these substrates. However, it is also a yet non-solved reaction. Enantiotopic selective C-H bond oxidation has so far been met with limited success: moderate to good enantioselectivity has been achieved only in the oxidation of activated benzylic and allylic C-H bonds.^[1] Stronger aliphatic C-H bonds remain inaccessible mainly due to the high stability of these C-H bonds, which compels vigorous reaction conditions or use of highly reactive oxidants for their oxidation and make realization of high enantioselectivity in this type of reaction difficult. However, enantioselective C-H oxidation of aliphatic C-H bonds, if realized, will be an extraordinarily powerful reaction because it has a virtually endless substrate scope, and will convert readily available simple molecules into precious chiral building blocks for chemical synthesis.^[2,3] Herein, we present the bioinspired approach for the oxidative desymmetrization of cyclic amines via enantioselective C-H activation by using manganese catalysts with tetradentate N4 ligands. This method is based in the enantioselective C-H oxidation of this class of substrates, where site selectivity controlled by the innate activation of C-H bonds adjacent to the amine moiety by medium effects effected by a fluorinated alcohol solvent. Under catalytic condition, the enantioselective oxidation of sp³ C-H bonds α to a nitrogen atom and results in the formation of the enamines.

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1a REUNIÓ DE QUÍMICA INORGÀNICA I ORGANOMETÀ-LICA de la SCQ



Manganese-catalyzed C-H bond oxidation of cyclopropane containing hydrocarbons

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C(sp³)-H bond oxygenation is an important class of C-H functionalization reactions that is attracting increasing interest because of the ubiquity of oxidized aliphatic frameworks in molecules of biological and pharmaceutical interest, and of the rich chemistry associated to C-O bond elaboration, amenable for broad product diversification.^[1] Iron and manganese complexes containing tetradentate aminopyridine ligands are powerful catalysts that, in the presence of hydrogen peroxide, are able to promote selective aliphatic C-H bond oxygenation. Mechanistic studies point towards a common mechanistic scenario for iron and manganese catalysts where C-H oxygenation proceeds via an HAT/rebound mechanism executed by high valent metal-oxo species.^[2]

Within this framework, cyclopropane containing hydrocarbons are particularly appealing probes to obtain mechanistic information on these processes. The presence of the cyclopropyl group has been shown to activate adjacent sites toward HAT via hyperconjugation, providing a powerful handle to implement site-selectivity in HAT-based functionalization reactions.^[3] In addition, because hyperconjugative effects also account for the stabilization of cyclopropylcarbinyl cations,^[4] these substrates can offer the opportunity to access cationic intermediates via sequential HAT-ET steps. With these concepts in mind, we have carried out a detailed mechanistic study on C-H bond oxidation of spiro[2.5]octanes with hydrogen peroxide catalyzed by manganese complexes. Unprecedented evidence for the formation of a cationic intermediate is provided, showing moreover that despite a complex mechanistic scenario, careful choice of the catalyst and fine tuning of the reaction conditions (solvent, temperature and carboxylic acid), have allowed the development of experimental conditions for a set of single product reactions where the unrearranged or rearranged products are obtained in good isolated yield.^[5]

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Carbon-based materials for solar-driven catalysis

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Carbon dots (CDs) and carbon nitrides (CN_xs) are promising carbon-based materials that have garnered increasing interest as they are easy and inexpensive to synthesize, biocompatible, environmentally benign, water soluble, and display excellent photoluminescence and fluorescence, together with tunable optical properties.^[1-3]

On the one hand, CDs are pseudospherical polydisperse nanoparticles (1-10 nm) that consist of a carbonaceous core stabilized by oxidized surface groups. We have applied them to produce solar fuels and chemicals. First, we deconvoluted the different sizes that form the bulk material. TEM and DLS confirm size-dependent separation and the monodisperse fractions show a size-dependent UV-vis and fluorescence spectroscopy response. A size-dependent effect on the photocatalytic H₂ evolution performance of the CDs in combination with a Ni cocatalyst has been demonstrated with a maximum activity at approximately 2-3 nm CD diameter. Then, for the first time, positively and negatively surface-functionalized CDs have been interfaced with the CO₂-to-formate reducing enzyme formate dehydrogenase to study the enzyme-material interface during photocatalytic CO₂ reduction.^[4] Finally, we show CDs for metal-free light-driven trifluoromethylation of aromatic compounds, including biological molecules, as well as cross-coupling of aldehydes, and a light-driven dual Ni/CDs photocatalytic system for photoredox catalysis.

On the other hand, CN_xs are emerging organic semiconductors that have had an increasing interest in organic photocatalysis, due to their scalable synthesis, recyclability and robustness due to their heterogeneous nature. In this line, graphitic carbonitride (CN_x), a polymeric material composed of heptazine units, has emerged as one of the most promising heterogeneous photocatalysts.^[5] CN_x has a broad absorption in the UV/Vis region and an optical band gap of approximately 2.7 eV, making it suitable for various photocatalytic applications.^[6-7] In this context, we have developed a Ni doped mpg-CN_x integrated heterogeneous photocatalysts that works as a Ni single-site photocatalyst for the cooperative photocatalytic C-O and C-N bond formation reactions.^[8,9]

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1a REUNIÓ DE QUÍMICA INORGÀNICA I ORGANOMETÀL·LICA de la SCQ



Reversed regioselectivity in the Rh-hydroformylation of styrene

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The hydroformylation of alkenes is one of the most worthwhile homogeneous metal-catalyzed reactions in industry since the obtained aldehydes are important building blocks for many important applications.^[1-2] In the hydroformylation of styrene, both the linear and branched products are essential. The linear aldehyde is widely used in the manufacturing of detergents and plasticizers, among others, while the branched isomer has anti-inflammatory properties. However, only few systems can favour the formation of the linear aldehyde over the branched.^[3-6] Vogt and co-workers showed that π -acceptor bis(phosphoramidite) ligands with an atropisomeric backbone provided high regioselectivities towards the typically less favoured linear aldehyde.^[6] We have further studied this system and found that after an extensive study of the reaction conditions, the linear/branched (l/b) ratios could be highly improved from 4.9 to 15. The key of success was to use a low partial pressure of CO together with a low temperature. Moreover, we have performed a DFT study to elucidate the obtained regioselectivity.

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Merging Cp*Co catalysis and statistical analysis for interrogating deuterium source selection in directed hydrogen isotope exchange

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Isotopically-labelled scaffolds have gained increasing interest in the last years as they are key components in chemical research.^[1] Particularly relevant is the introduction of deuterium in biologically-active molecules as a strategy for improving their pharmacokinetic and metabolic properties in drug discovery.^[2] Indeed, in 2017, the US Food and Drug Administration (FDA) approved the first deuterium-labelled drug, Austedo® for treating Huntington disease.^[3] Therefore, the design of innovative methodologies to deuterate organic molecules is a task of utmost importance.^{[4],[5]} Herein, we tackle two of the most prevalent challenges in the area of Hydrogen Isotope Exchange reactions: (i) the underexploitation of first-row transition metal catalysis in these transformations; (ii) the lack of rational mechanistic understanding regarding the choice of deuterium source needed for different systems.

In this work, we exploit the reversible nature of the C–H activation step by Cp*CoIII-based systems to engineer a deuteration methodology that enables the functionalization of arenes bearing a wide variety of directing groups, using D₂O or MeOD. Indeed, the utility of this transformation has been exploited in the late-stage functionalization of complex organic scaffolds such as drug-type molecules and pesticides. By modelling the data obtained in the reaction scope through multivariable linear regression, we were able to determine a substrate-dependent mechanism change that involves the presence of different reaction intermediates that dictate the need of the specific sources of deuterium for the different substrates.

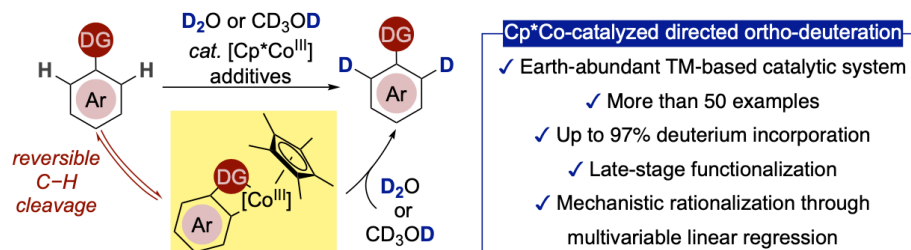


Figure 1. Cobalt-catalyzed ligand-assisted C–H deuteration.

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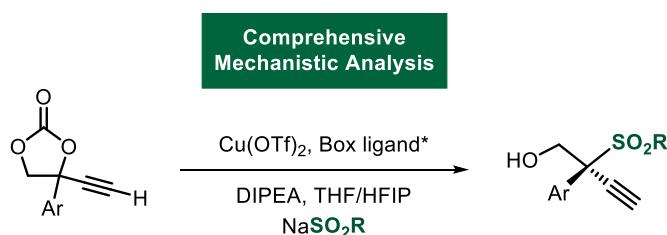
A comprehensive mechanistic scenario for the Cu-mediated asymmetric propargylic sulfonylation forging tertiary carbon stereocenters

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Metal-catalyzed propargylic transformations represent a powerful tool in organic synthesis to achieve new carbon-carbon and carbon-heteroatom bonds^[1]. However, detailed knowledge about the mechanistic intricacies related to the asymmetric formation of propargylic products featuring challenging heteroatom-substituted quaternary stereocenters is scarce, and therefore provides an inspiring challenge^[2]. Here, we present a meticulous mechanistic analysis of a propargylic sulfonylation reaction promoted by a chiral Cu catalyst through a combination of experimental techniques and computational studies. Surprisingly, the enantio-discriminating step is not the coupling between the propargylic precursor but rather the following proto-demetalation step, a scenario further validated by computing enantio-induction levels under other previously reported experimental conditions. The use of EPR, X-ray and IR *in situ* monitoring techniques helped us to picture a full mechanistic scenario for this propargylic substitution reaction, providing the understanding of the catalyst pre-activation stage, the productive catalytic cycle and an unanticipated non-linear effect at the Cu(I) oxidation level^[3].



- Proto-demetalation drives asymmetric induction
 - Crucial role for the base additive
 - NLE observed at the Cu(I) oxidation state
 - Isolation/characterization of key intermediates

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P-Stereogenic non-symmetric diphosphanes with a methylene bridge: coordination chemistry to late transition metals

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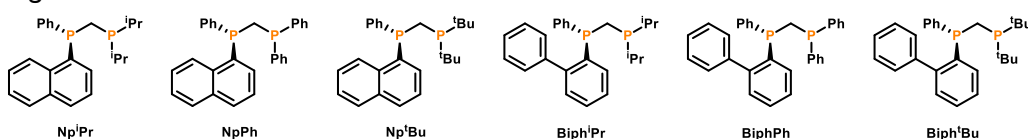
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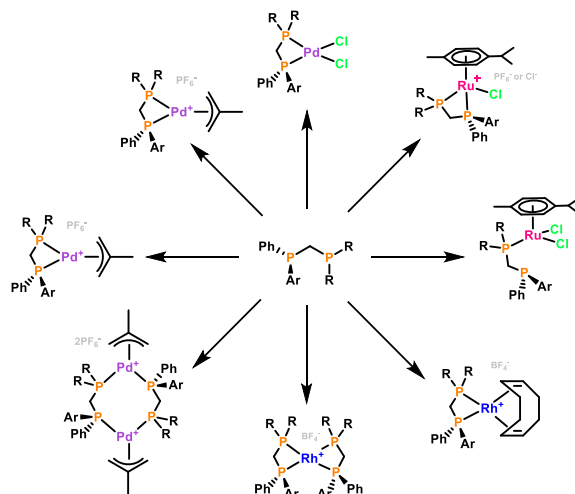
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The synthesis of *P*-stereogenic phosphanes has always been a challenge due the lack of methods. These molecules, however, are very interesting due to their applicability as ligands in a wide variety of enantioselective reactions catalyzed by organometallic complexes. Due to their scarcity and top-notch performance, new *P*-stereogenic ligands are always of interest in organometallic chemistry.

In this contribution, we present new family of six aryl *P*-stereogenic diphosphanes with the particularity of having a methylene linker^[1], a structural feature that has been very successful in the past with ligands like TCPF or MiniPhos^[2,3].



This family of diphosphanes has a very narrow bite angle due to the steric constraint imposed by the methylene bridge, which makes the ligands very interesting in terms of coordination chemistry^[4]. To explore their behavior, the ligands have been coordinated to Pd, Rh and Ru. A wide variety of structures has been identified, showcasing the great electronic and steric flexibility of the ligands.



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Societat Catalana de Química

Microfluidic technologies as an advanced tool for chemistry and materials synthesis

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Self-assembly has long been used to control covalent and non-covalent interactions where molecular design has been the major driving force to achieve a desired outcome. Like in nature, a full control over self-assembly processes could lead to rationalized structure-property correlations, a long-time sought in chemistry, physics and materials science. However, the pathways followed and the mechanisms underlying the formation of supramolecular aggregates are still a major challenge for the scientific community. Accordingly, the elucidation of nucleation and growth mechanisms will be highly required to push supramolecular chemistry to the next level, where access to nature inspired functions will be accomplished. In this contribution, I will present how reaction-diffusion (RD) conditions established within microfluidic devices can be used to uncover pathway complexity as well as to trigger pathway selection. Specifically, I will show that microfluidic RD conditions provide an unprecedented kinetic control over self-assembly processes; for example, enabling the isolation of well-defined kinetically trapped states as well as unprecedented metastable intermediates. This research provides a new tool to study and understand supramolecular chemistry and opens up new avenues for the engineering of advanced functional assemblies and systems.



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Inorganic boron clusters as unique entities to trigger and modulate molecule and material properties

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Icosahedral boron clusters, carboranes and metallocarboranes, do not exist in nature and are purely abiotic, inorganic and man-made compounds. The structure of boron clusters differs from that of organic ones, as they have a polyhedral cage-like structure that consists of different numbers of vertices occupied by boron atoms or heteroatoms to usually form an icosahedron. They are highly thermally and chemically stable due to their 3-D aromaticity.^[1] They have unique properties as rigidity, low toxicity, hydrophobicity or amphiphilicity (depending on the structure) and the ability to form dihydrogen and σ -hole bonding, that allow them to interact with biological molecules. All these properties make them useful for a wide range of applications such as materials science, nanotechnology and biomedicine.^[2]

Our research group has been working with boron clusters for about 35 years. Throughout this time, we have developed and optimised new methodologies to functionalise boron clusters, which have made possible to link these inorganic fragments to a huge number of organic molecules, dendrimers, polymers and surfaces.^[3] Linking these clusters to all those systems usually produces a great influence on their final properties, boosting and improving them. Moreover, they might allow the tuning of these properties what favours their applicability.^[4]

In recent years, one of my focus interest has been the design and development of luminescent boron clusters-based molecular materials to study the electronic and steric effect of these boron clusters on the emission properties of attached fluorophores. It has been very exciting to learn that depending on the isomer of the carborane cluster (ortho or meta), the substituent at the carbon atoms, the nature of the cluster (neutral or anionic), or the way to be attached to the fluorophore, the luminescent behaviour of the compounds can be modified. We have synthesized: I) boron cluster-based molecules as fluorescent probes for in vitro fluorescent bioimaging;^[5] II) electroactive fluorescent molecular switches based on metallocarboranes;^[6] III) high fluorescent systems in solid state and fluorescent water dispersible boron clusters-based nanoparticles due to the aggregation induced emission (AIE) phenomenon.^[7] Apart from previous luminescent compounds, we have also prepared carbon-based nanomaterials which consist of graphene oxide functionalized in the surface by radiolabeled cobaltabis(dicarbollide) units.^[8] These nanomaterial can potentially act as theranostic agents for diagnosis (radioimaging) and boron carrier for anticancer Boron Neutron Capture Therapy (BNCT).

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Building molecular mixed-valence cyanido-bridged Co^{III}/Fe^{II} redox active complexes: from dinuclear to cubic species

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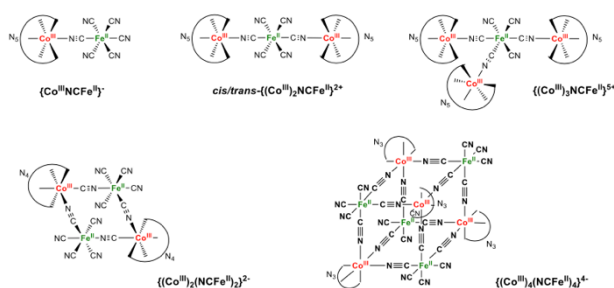
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Mixed-valence complexes represent an area of interest in the chemical world that goes from academicism (related to the Robin and Day classification as *Class I, II* or *III* species) to its potential applicability to photochemically triggered spin-crossover compounds. Closed-shell metal complexes of this family have been traditionally envisaged as 'precursors' for spin transitions to paramagnetic states.

The dimensionality of the species is also of great importance, given the fact the most of the magnetic characteristics of the complexes are studied in solid state. Furthermore, the association of these type of species to the primeval PrussianBlue is also rather relevant in view of inclusion and redox properties that can be potentially used for biological or sequestering applications. In all cases, though, most of the species reported are solid-state 3D structures that lack facile preparation procedures and aqueous solubility desirable for easy applicability.

By redox-triggered mechanistically-directed self-assembly procedures we have been involved for some time in the preparation of molecular, discrete and very robust structures having $\{[Co^{III}-NC-Fe^{II}]\}^{1+}$ mixed-valence units.^[2] These have been further assembled to trinuclear, square, and cubic molecules following the same procedure.^[3]



Interestingly, the study of the redox activity of the molecules indicated fully reversible Fe^{III}/Fe^{II} 1, 2 and 4 electron processes for the iron centres, which results very relevant for water activation processes. Furthermore, all these species have been proved capable of producing H₂O₂ in moderate alkaline medium, a process that can be reversed on peroxodisulfate reoxidation.^[4]

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Synthesis and applications of group 11-based ternary semiconductor nanocrystals with tunable morphology and composition

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The optimization of a material functionality requires both the rational design and precise engineering of its structural and chemical parameters.^[1] Colloidal chemistry is an excellent synthetic choice for the synthesis of homogeneous and compositionally complex novel nanostructured systems with potential application in several fields.^[2] We have exploited here several surfactant-assisted synthetic strategies in order to chemically transform our starting silver or copper chalcogenide nanocrystals into compositionally more complex nanostructured systems, such as hybrid and ternary I-I-VI semiconductor nanocrystals with different stoichiometries. Our results indicate the formation of new ternary materials, both with stoichiometric and non-stoichiometric compositions. Considering the complex chemical distribution of the species in the materials, the use of advanced atomic-resolution electron microscopy techniques was key for their appropriate characterization and elucidation of formation mechanisms. The work is complemented with the assessment of their potential as active materials for energy conversion devices and as contrast agents in clinical diagnosis.

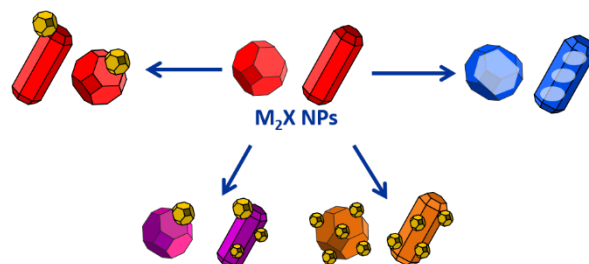


Figure 1. Chemical transformation of binary chalcogenide nanostructured materials into more complex noble metal-based chalcogenide systems with a ternary or hybrid composition. (M stands from Ag or Cu while X represents S or Se)

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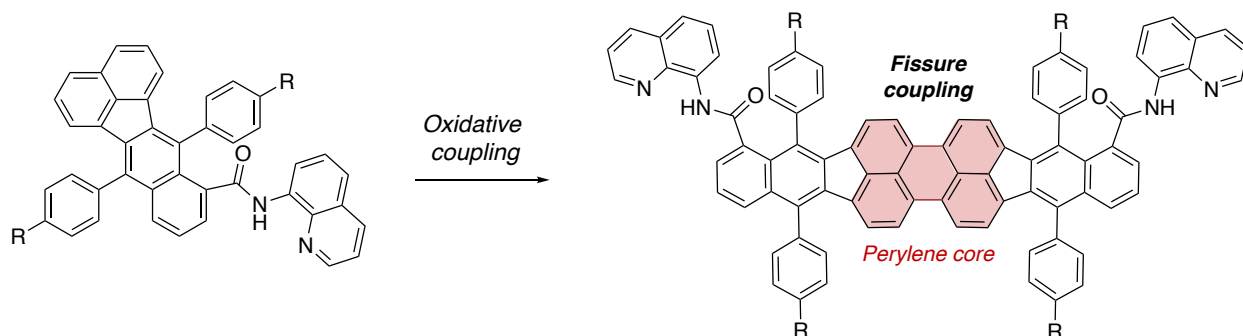
Synthesis of curved perylene-based nanographenes

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Nanographenes (NG) and graphene nanoribbons (GNRs) have been considered as promising candidates with application in material science, organic solar cells, among others.^[1] The “bottom-up” protocols for the synthesis of NG use organic synthesis tools to control their sizes, topologies and edge structures precisely, giving rise to well-defined molecular structures.^[2] It is well-established that the electronic structures of the nanographenes derivatives are mostly directed by their widths and edge topologies. Additionally, the introduction of nonplanarity into NG has been regarded as a promising parameter to alter their structural topologies as well as their optoelectronic properties to provide further opportunities in biomedical research or optoelectronic devices.^[3,4] Recently, our group described the formation of aromatic homologation products via C_{sp2}-F and C_{sp2}-OMe functionalization under nickel catalysis using 8-aminoquinoline (8-AQ) directing groups.^[5] Herein, we describe the synthesis of new aromatic homologation products bearing a fluoroanthene unit. Moreover, we have developed an efficient bottom-up synthesis of perylene-based nanographenes via fissure coupling by means of oxidative coupling reaction. The incorporated five-membered ring cause a flexible non-planar distortion depending on the 8-AQ orientation. Remarkably, the perylene-based nanographenes are pH-dependent fluorescent materials exhibiting NIR red-fluorescence with high quantum yield at alkaline media.



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Devices for quantum computing: towards a measurement of on-surface qubit phase memory time

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Applications of quantum computation are key for the new Quantum Revolution. So far, most of these applications rely on Josephson Junctions or defects doped on diamond as qubits. However, molecular qubits offer a wide variety of advantages towards other qubit options: molecules are all prepared equal, there is no size distribution, they can be functionalized at will with desired properties by ligand modification, they will require small voltages so that a molecular device will consume small amount of energy... The possible applications of molecules as qubits or for spintronics applications relies on the surface deposition of said molecules over large areas of a conductive material.^[1] In this work, we show how we can achieve chemisorption of molecular systems over functionalized Silicon wafers.^[2] Among the deposited molecules, we have chosen several examples of known qubits with the main objective of measuring the decoherence (or phase memory) time of a monolayer of qubits.

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Reactivitat i assemblatge de poliedres metal-orgànics

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Els poliedres metal-orgànics (del seu nom en anglès coneguts com a MOPs) són un tipus de material reticular format per la unió entre centres metàl·lics i lligands orgànics a través d'enllaços de coordinació els quals defineixen una cavitat discreta de mida nanomètrica.^[1] El seu caràcter monomèric i la seva poriositat permet conceptualitzar els MOPs com els anàlegs moleculars dels materials porosos estesos, tals com les xarxes metal-orgàniques (MOFs). Per tant, els MOPs combinen propietats típicament observades en molècules discretes (reactivitat estequiomètrica i solubilitat en líquids), en materials porosos cristal·lins (una mida de cavitat modulable) i en partícules nanoscòpiques (alta densitat superficial de grups reactius). En el nostre grup de recerca, em aprofitat totes aquestes virtuts per desenvolupar els MOPs basats en Rh(II) com a “nanopartícules moleculars” funcionalitzables mitjançant química covalent i de coordinació per a desenvolupar diferents propietats/aplicacions tals com bio-funcionalització, transport molecular i reconeixement i captura de contaminants.^[2-4] A més, la capacitat de introduir grups coordinants, tals com àcid carboxílic, a la superfície dels MOPs ens ha permès explorar l'ús d'aquests COOH-MOPs com a nos monòmers en la síntesis de materials porosos donant lloc a noves estructures que no es podrien obtenir mitjançant tècniques de auto assemblatge convencionals (Figura 1).^[5-7]

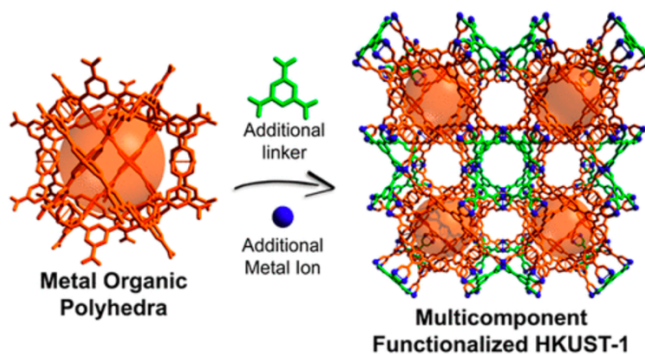


Figura 1. Assemblatge de un COOH-MOP amb ions metàl·lics i lligands orgànics addicionals per donar lloc a una nova estructura porosa cristal·lina.

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Síntesi de materials oligomèrics porosos

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Els poliedres metal·loorgànics, MOPs de les seves sigles en anglès, es sintetitzen via l'autoensamblatge entre centres metàl·lics i lligands orgànics mitjançant enllaços de coordinació, donant lloc a estructures discretes d'entre 1 nm i 5 nm. El seu caràcter molecular i porós permet conceptualitzar els MOPs com el resultat de la miniaturització extrema dels materials porosos. Entre les seves aplicacions, últimament s'ha estudiat l'ús dels MOPs com a monòmers porosos per la síntesi de materials porosos extensos explorant la seva reactivitat tant de coordinació ^[1] com covalent ^[2]. En aquesta comunicació descriurem un nou mètode sintètic que permet controlar el grau de polimerització d'aquests MOPs per donar lloc a materials porosos oligomèrics amb composició i massa definida (*Figura 1*). Aquests nous materials es troben a la frontera del món molecular i el polimèric, la qual cosa els hi obra un gran ventall de possibilitats, tals com combinar porositat extrínseca i canals de difusió definits amb una alta processabilitat en líquids.

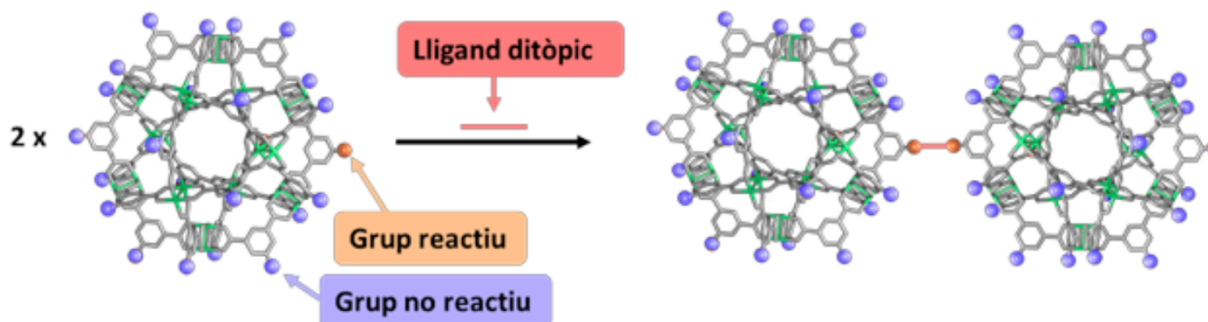


Figura 1. Reacció de dimerització d'un MOP, ressaltant la posició reactiva i les no reactives de l'estructura.

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Quantum fluctuations in single molecule magnets on magnetic substrates

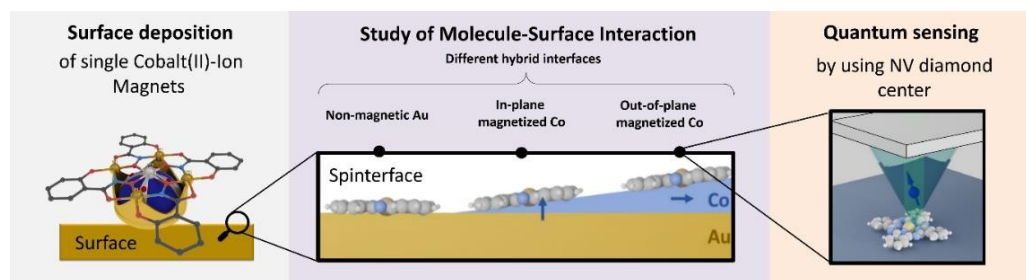
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SMMs are promising candidates as Qubits for quantum information processing or fabrication of molecular spintronic devices.^[1,2] While quantum tunnelling of the magnetization (QTM) is the limiting mechanism for the best SMMs due to the fast relaxation dynamics when crossing across the activation barrier, the possibility of exploiting QTM in quantum technologies opens a very attractive and new beneficial path. QTM allows performing basic quantum tasks faster than the classical ones. The research has mainly focused in the crystalline phase. However, surface disposition of molecules to integrate and manipulate them in the framework of solid-state qubit is the key step to exploit quantum properties in an integrated molecular-inorganic device. Herein, we aim to investigate and manipulate quantum fluctuations (e.g. tunnelling process) in SMMs down to the single-molecule limit by coupling them to a single nitrogen-vacancy (NV) diamond center. In this regard, the SMMs must preserve their integrity upon deposition on surfaces. [Co(II)Co(III)₄] metallacrown (MCs) with cobalt(II) ion as guests embedded into a diamagnetic scaffold, [12-MCCo(III)N(Shi)-4], are suitable SMMs since they show remarkable magnetic anisotropy and 3d-centered MC are easily evaporable under UHV conditions in most cases.^[3] On surfaces, the SMM properties are usually altered or sometimes even suppressed by the interactions between the molecules and the magnetic ordered surface at the interface. Achieving a high quality hybrid interface is a fundamental requirement. The Co(II)-centered MCs disposition on different metallic underlayers ranging from non-magnetic Au to in-plane and out-of-plane magnetized Co will provide screening of the ideal hybrid system and study the exchange interaction between them.^[4] While hybridization effects have been investigated semi-classically, studying relaxation dynamics in SMMs on surfaces demand quantum sensing.^[5] For this, scanning change in the quantum phase of the single NV diamond, which has emerged as a new powerful technique for investigating magnetic properties of single spins, will be used to probe quantum fluctuations using established sequences of microwave and optical pulses.^[6]



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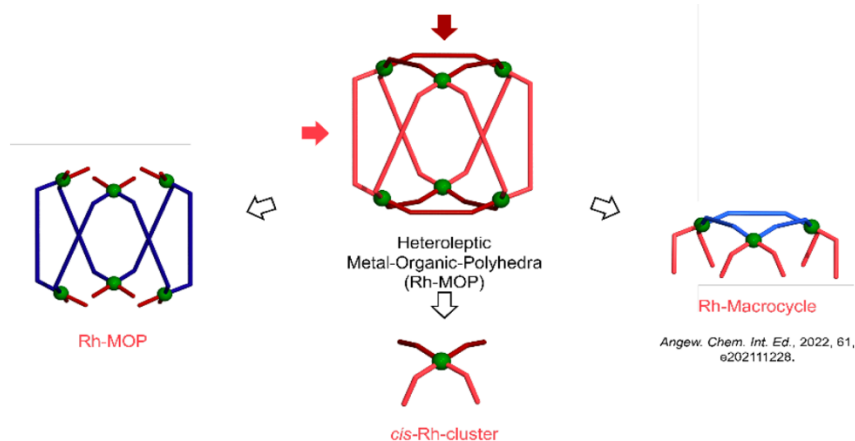
Síntesi de noves estructures metal·loorgàniques mitjançant la química de “Clip-Off”

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Les innovacions en síntesis química han atorgat, durant el pas del temps, el descobriment de nous materials i molècules. Cada nova metodologia i ruta sintètica no només ajuda a endinsar-nos més en el món de la química, sinó que també inspira a investigadors a obrir noves vies de pensament i a innovar de manera iterativa al disseny i preparació de noves estructures químiques. Els enfocaments sintètics més emprats consisteixen en estratègies *bottom-up*, on es formen enllaços que uneixen àtoms i molècules formant compostos de major mida. Recentment, el nostre grup de recerca ha desenvolupat una nova metodologia sintètica anomenada *Clip-Off Chemistry*. Al contrari dels enfocaments prèviament esmentats, la pretensió d'aquesta nova estratègia sintètica és generar nous materials i molècules mitjançant la ruptura selectiva i racional d'enllaços covalents en materials reticulars, com ara, les xarxes metal·loorgàniques (MOFs) i els poliedres metal·loorgànics (MOPs), proporcionant un control espacial precís sobre l'estructura resultant (Esquema 1)^[1]. Per exemple, aquesta ruptura controlable dels enllaços es pot produir a escala molecular mitjançant la reacció química d'ozonòlisis sobre dobles enllaços. En aquesta comunicació s'explica com utilitzant la Química de Clip-Off es pot utilitzar un MOP, format per dobles enllaços col·locats de manera estratègica, per sintetitzar noves estructures metal·loorgàniques, incloent dos nous clústers, un macrocicle i una estructura tubular.



Esquema 1. Esquema de la química de Clip-off per sintetitzar estructures complexes a partir d'un Rh-MOP.

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Predint l'especiació en dissolució aquosa i els mecanismes d'auto-assemblatge dels òxids metàl·lics moleculars de Mo, W, V, Nb i Ta

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El òxids metàl·lics moleculars constitueixen una família de compostos químics molt rellevants per aplicacions en catàlisi i nous materials per al desenvolupament de bateries i dispositius electrònics. En concret, els polioxometal·lats (POMs) són un tipus de clústers que combinen metalls de transició (normalment amb configuració d^0) i lligands oxo- en diferents estats de coordinació. Un dels majors reptes en l'àmbit dels POMs és controlar els equilibris químics que governen la síntesis d'aquests compostos. La formació d'aquests clústers és molt sensible al pH, concentració total, força iònica i temperatura. L'espectrometria de masses i la ressonància magnètica nuclear han permès determinar algunes d'aquestes espècies químiques en dissolució. Malgrat aquests avenços, les condicions per a sintetitzar els POMs son molt difícils de racionalitzar a causa de l'elevat nombre de equilibris complexos que hi intervenen. Per aquest motiu, hem desenvolupat un mètode computacional (al qual anomenem POMSimulator) per predir l'especiació aquosa i els mecanismes de reacció dels polioxometal·lats.^[1] La Figura 1 mostra un exemple de la dependència de les concentracions de diverses espècies front el pH (esquerra), i l'espècie majoritària segons la concentració total i el pH (dreta). Mitjançant aquest mètode hem pogut aportar constants d'equilibri i mecanismes per cinc famílies de POMs: molibdats, tungstats, vanadats, niobats, i tantalats.^[2,3]

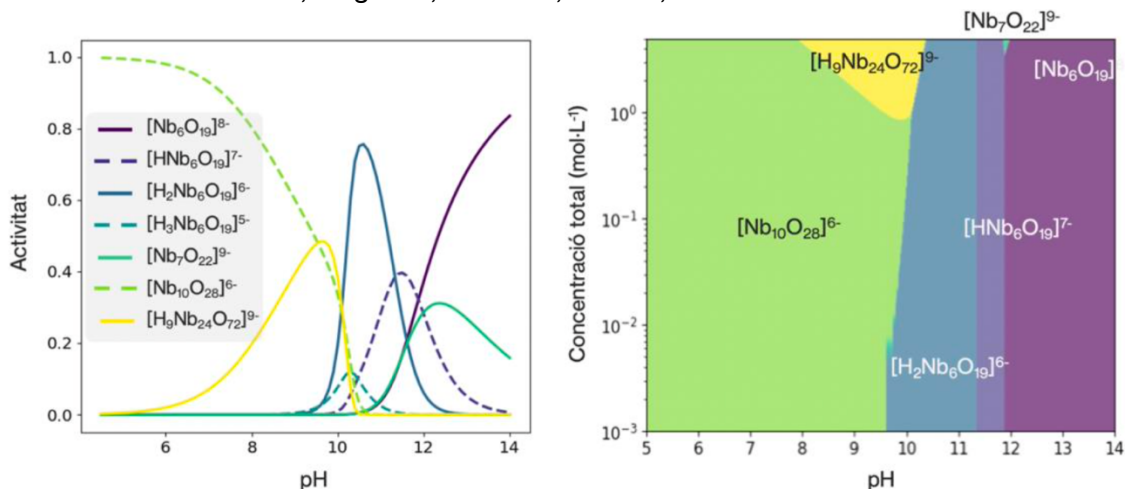


Figura 1. Diagrames d'especiació i fase pels polioxoniobats (resultats obtinguts amb el POMSimulator).^[4]

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Proton triggered chemoselective halogenation of aliphatic C-H bonds with nonheme Fe(IV)-oxo complexes. An alternative model for nonheme halogenases

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Halogenation of aliphatic C-H bonds is a relevant reaction in chemical synthesis because it introduces functionality into poorly reactive hydrocarbon skeletons. In nature, the reaction is performed by nonheme iron dependent enzymes such as SyrB2. The active site of these enzymes contains a mononuclear nonheme iron center and the crystal structure of SyrB2 has shown that it is bound to two histidines and a chloride atom.^[1] Its mechanism of reaction entails a transient high spin Fe^{IV}(O) species that has been detected and spectroscopically characterized, proposed to have a halide ligand *cis* to the terminal oxo unit.^[2,3] This species has been kinetically proven to be the C-H cleaving agent responsible of the initial hydrogen atom abstraction from the substrate, followed by rebound of the halide to the carbon centered radical.

Mimicking of this reaction with small molecule model compounds may provide clues to contribute to the understanding of the origin of the unusual chemoselectivity exhibited by halogenases. In this work, we show that a well-defined iron(IV)-oxo complex (**1^{IV=O}**), in the presence of an inorganic acid and a halide moiety reacts with hydrocarbon substrates via an initial HAT, producing their chemoselective halogenation.

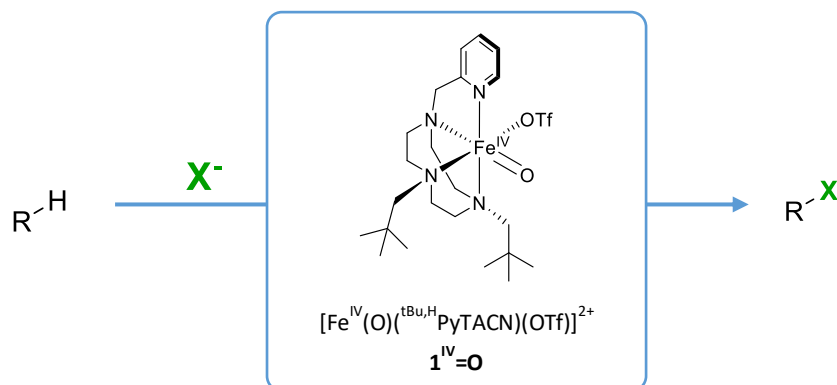


Figure 1. Chemoselective halogenation of aliphatic C-H bonds with iron(IV)-oxo complex **1^{IV=O}**.

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Hemilabile MIC[^]N ligands allow oxidant-free Au(I)/Au(III) arylation-lactonization of γ -alkenoic acids

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Carbene C[^]N and phosphine P[^]N hemilabile ligands have shown to be suitable platforms to chelate Au(III) centers formed from the respective Au(I) counterparts^[1,2]. Specially, P[^]N MeDalphos ligand showed great performance in promoting oxidative addition of aryl halides at Au(I), allowing the development of Au(I)/Au(III) catalysis for a wide scope of transformations, including C_{sp2}-N cross-couplings^[3] or oxy- and aminoarylations of alkenols and alkenamines^[4]. On the other hand, the use of bidentate C[^]N ligands remains scarcely explored. In this line, the group of Bourissou employed a mesoionic carbene (MIC) ligand bearing a hemilabile pyridine to obtain the corresponding (N,C)-cyclometalated Au(III) complex via oxidation^[5]. By employing similar MIC[^]N ligand scaffolds, we obtained (N,C)-cyclometalated Au(III) complexes either upon oxidation or, more importantly, upon oxidative addition^[6] (Fig. 1). Moreover, we demonstrate that the Au(I) species can undergo oxidant-free Au(I)/Au(III) catalysis, via aryl halide oxidative addition, to afford γ -substituted γ -butyrolactones upon arylation-lactonization of γ -alkenoic acids with iodoarenes (Fig. 1).

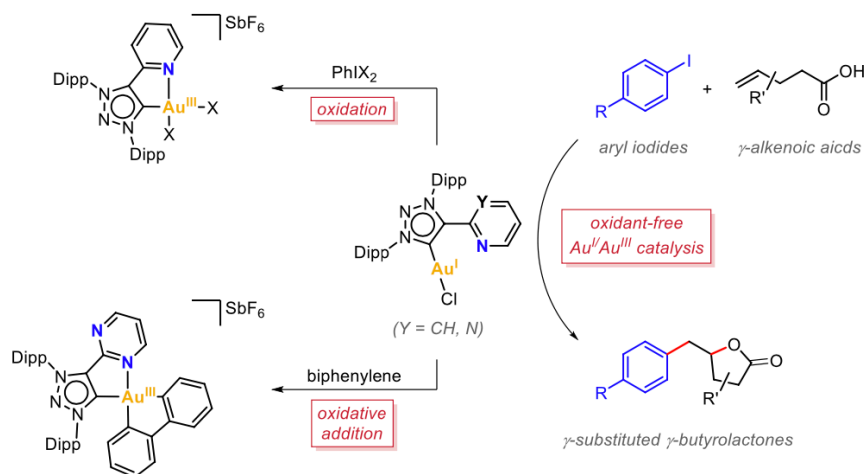


Figure 1. (N,C)-cyclometalated Au(III) complexes obtained upon oxidation and oxidative addition (left), and Au(I)/Au(III)-catalyzed arylation-lactonization of γ -alkenoic acids with aryl iodides (right).

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Posters



[Dy₂(μ-2,6-2FBz)₄(NO₃)₄]²⁻ and [Dy₂(μ-2,6-2FBz)₄(2,6-2FBz)₄]²⁻ : Two anhydrous different structural motifs depending on the solvent.

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The reaction of Dy(NO₃)₂·6H₂O with 2,6-Difluorobenzoic acid (H-2,6-2FBz) and pyridine allows the isolation of two different dinuclear compounds with the Dy³⁺ atoms bridged by four carboxylate ligands. Interestingly, when changing the solvent during the reaction, two different structural motifs are obtained. When a mixture of EtOH/H₂O is used, the compound with formula [Dy₂(μ-2,6-2FBz)₄(2,6-2FBz)₄]²⁻ is isolated (Fig1, left). However, when the reaction media is changed to an EtOH solution, the four 2,6-2FBz ligands that are in the chelating coordination mode, are replaced by four NO₃⁻ ions (Fig1, right) and the final compound is [Dy₂(μ-2,6-2FBz)₄(NO₃)₄]²⁻. The anhydrous dimeric structural unit [Dy₂(carboxylato)₄(NO₃)₄]²⁻ has never been reported as far as we know. Both compounds Single Molecular Magnet behaviour (Fig.1) and sensitized luminescence that changes from one structure motif to the other.

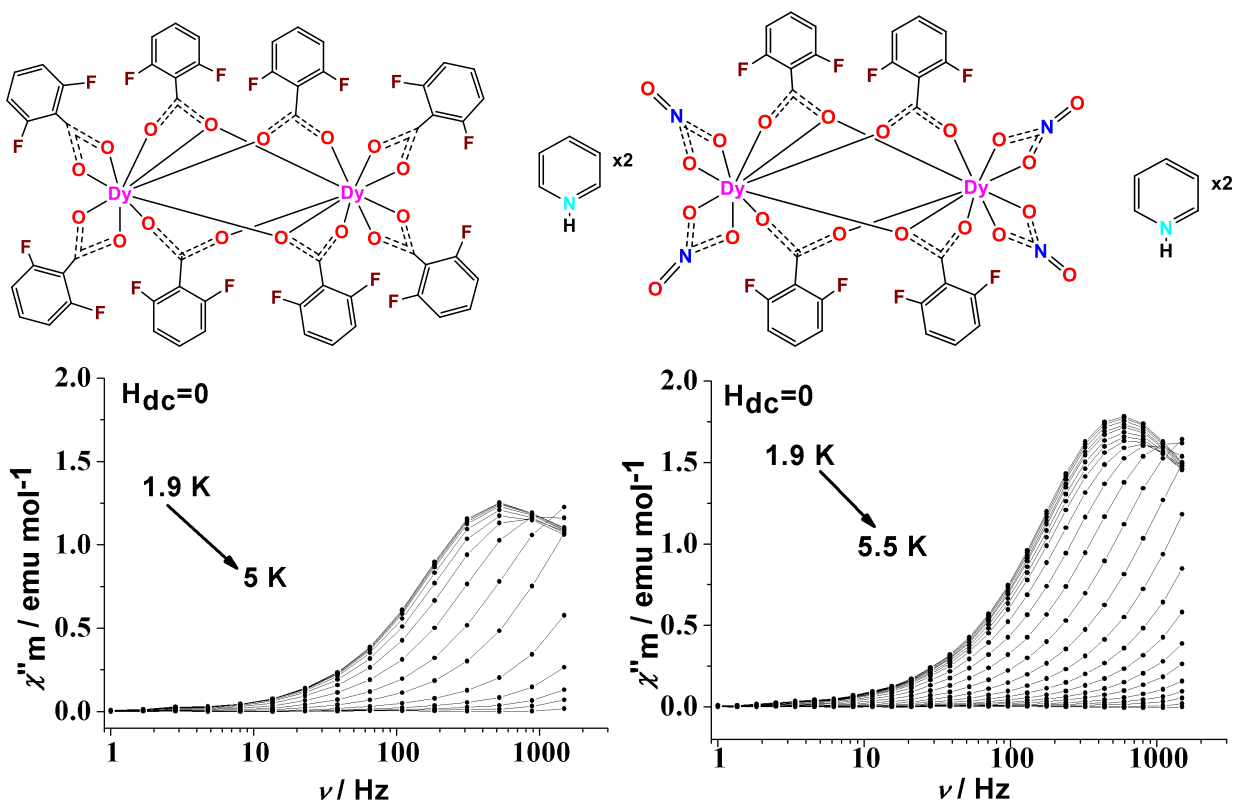


Figure 1

Triphenylene derivative MOFs for greenhouse gas sensing and green catalysis

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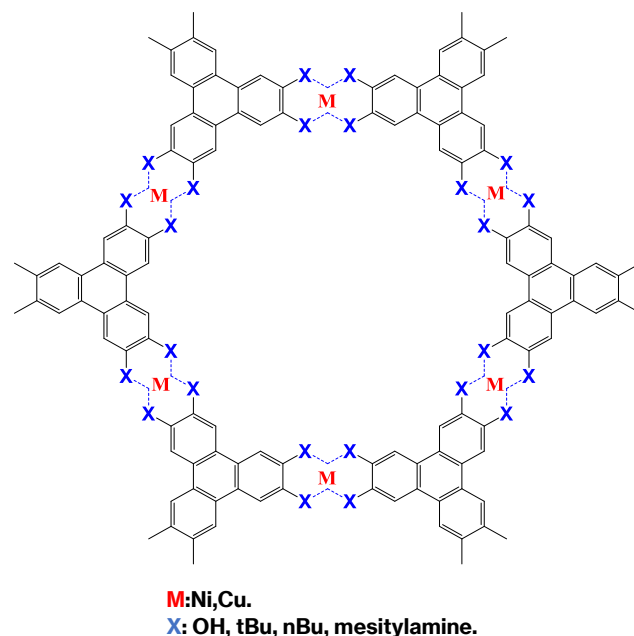
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The high concentration of greenhouse gases has arisen due to increasing human activity, industrial and social development; Some of these gases have a direct negative impact on human health, while others arise in a more indirect way over the long term^[1]. For the detention of these gases, commercial sensors are used, located in very specific areas, in addition to not meeting all the appropriate measurement requirements. The required devices must be sensitive, selective, and low power consumption; however, they do not provide the same level of accuracy and precision as reference instruments. The objective of our work is the development of advanced materials formed by Metal-Organic Frameworks. Which must be used in selective and miniaturized gas detection devices, as well as their potential application in catalysis.

Metal organic frameworks (MOFs) are porous crystalline solids and are obtained by coordination chemistry between ligands and metal cations. These structures present a high internal order combined with high porosity, thermal and chemical stability with large surface areas that allow us to give these structures different applications^[2].

Recently, studies of tri- and hex-substituted triphenylene ligands indicate the formation of rigid building blocks for porous crystals, demonstrating conductive, fluorescent, catalytic, and absorption properties mixed with metal precursors (metal salts). We use the commercially available 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) ligand and hexaaminotriphenylene ligands obtained from the Buchwald-Hartwig amination of hexabromotriphenylene which are synthesized according to the methods reported in the literature^[3,4].



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Enhancing Pd-catalyzed asymmetric allylic substitution reactions with improved catalysts for the construction of chiral C-C and C-X bonds

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Pd-catalyzed asymmetric allylic substitution is a powerful and sustainable method for preparing chiral compounds.^[1] However, most catalysts are still only tested in benchmark substrates, eluding challenging ones that would yield to more appealing compounds. Our group has taken advantage of the adaptability of biaryl phosphite-based ligands to overcome the substrate specificity and low nucleophile scope in the this process.^[1-3] Here we present our recent finding in the design of two catalyst libraries, which present the advantages of been synthesized in a few steps from unexpensive starting materials and are solid and stable to air and therefore easy to handle. Improving the approaches reported to date, they present a broad substrate and nucleophile scope.^[4,5] Excellent enantioselectivities has been achieved for a broad range of linear (including challenging unsymmetrical di- and monosubstituted) and cyclic substrates with different electronic and steric properties, using many C-, N- and O-nucleophiles (70 compounds in total).^[4,5] Furthermore, the combination of computational (DFT) and NMR spectroscopy studies of the key Pd-complexes provide an explanation on the origin of the enantioselectivity. Finally, the application of these catalysts for the preparation chiral (poly)carbo- and heterocyclic compounds, with multiple stereocenters, will be demonstrated by the use of straightforward sequences of allylic substitution and either ring-closing metathesis or Pauson-Khand reactions.^[4,5]

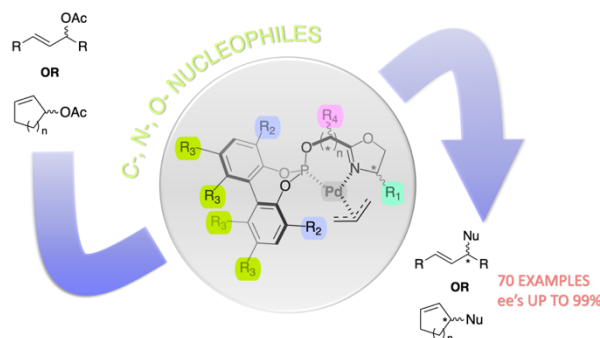


Fig 1. Formation of C-C and C-X chiral bonds with biaryl phosphite-containing Pd catalysts.

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DFT guided ligand design for iridium catalyzed asymmetric hydrogenation. Filling the gap by in silico optimization

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The metal catalysed asymmetric hydrogenation is one of the most powerful tools for the preparation of enantioenriched compounds due to its perfect atom economy.^[1] Despite it has been a deeply studied reaction, a specific ligand design is required for each substrate class.^[1] In this communication we show the feasibility of in silico optimization of Ir/P,S-catalysts for the asymmetric hydrogenation of broad and diverse type of challenging olefins.^[2]

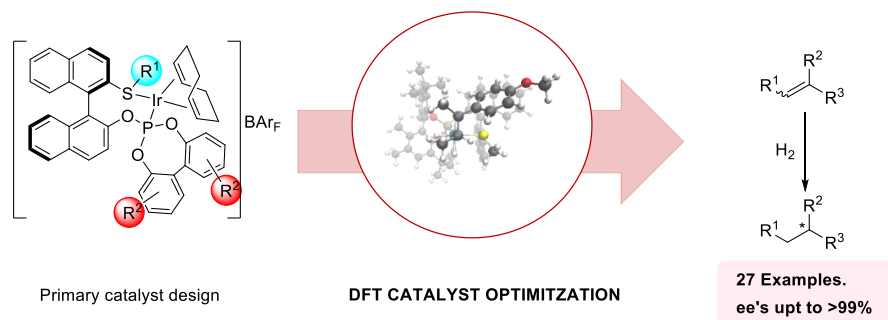


Figure 1. Catalyst design, optimization and application in asymmetric hydrogenation.

DFT calculations showed that the bulkiness of the thioether has a major role to direct the olefin coordination, thus overcoming very common face selectivity issues and controlling the relative position of the axial hydride and the hydrogen. DFTs also showed that the chirality of the biphenyl phosphite needs to be controlled to maximize the energy gap between the most stable TSs leading to opposite enantiomers. We therefore discovered an Ir-P,S catalysts, which contains an cyclohexyl thioether group and an S-biphenyl phosphite group, as the most enantioselective for reduction of a range of challenging unfunctionalized olefins and with relevant poorly coordinative groups, regardless of the type of functional groups or their coordination abilities. Appealingly, further modifications on the thioether groups and the biaryl phosphite moiety also allowed the highly enantioselective hydrogenation of olefins with different geometry patterns, such as α,β -unsaturated lactones and lactams, 1,1'-disubstituted enol phosphinates and cyclic β -enamides, present in relevant products (e.g. rotigotine, alnesporine, etc).

To sum up we show the usefulness of an in silico-based catalyst optimization for the discovery of an efficient Ir-P,S catalyst family, whose application in asymmetric catalysis was discarded because early studies failed.

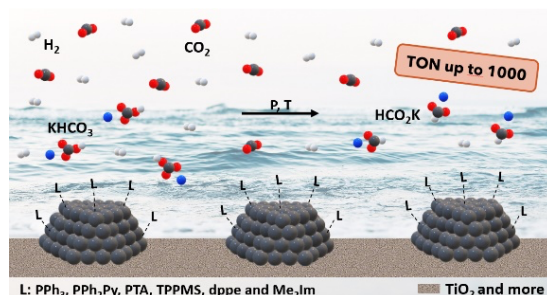
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New supported phosphine-stabilized palladium nanocatalysts for the hydrogenation of CO₂ into formate

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Recently, interest has grown both in reducing the emissions of CO₂ and its use as a source of C1 for the synthesis of high-added value compounds.^[1] One of these products is formate, which can be obtained by hydrogenation of CO₂ in a basic medium.^[2] This is a promising system in terms of the valorization of CO₂ and its potential utilization as hydrogen storage.

In this work, a series of heterogeneous palladium catalysts have been developed. The synthesis of the nanoparticles has been carried out by the organometallic method,^[3] using ligands and supports of different nature for their stabilization. Indeed, the aim was to modify the surface of these nanoparticles both at a morphological/size level and at an electronic level through their interaction with the stabilizer and the support. These catalysts were characterized by several techniques and have been evaluated for the hydrogenation of CO₂ to formate catalysis with promising results. However, after catalysis, agglomeration of our nanoparticles has been observed. This problem has been solved by making modifications to the support. Modifiers with different elements (P, Si)^{[4], [5]} have been used to deposit them by condensation with the acid centers of TiO₂. Likewise, the influence of adding an amine at the end of the alkyl chain has been seen in some cases and when using ILs^[6] the influence of anions of different nature was studied.

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Propane dehydrogenation over small platinum clusters supported on g-C₃N₄

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Platinum, with high density of electronic states close to the Fermi level is one of the most suitable catalysts for propane dehydrogenation (PDH), an attractive approach for the production of propylene also hydrogen.^[1] However, it always suffers from low alkene selectivity and rapid deactivation due to coke formation.^[1] Fortunately, it has been proven that both drawbacks could be avoided by appropriate supports,^[2] anchoring single atom catalysis or small clusters.^[3,4,5] On this basis, we present a theoretical study on the PDH mechanism catalysed by small platinum clusters supported on novel g-C₃N₄ surfaces, shown in **Figure 1**,^[5,6] paying attention to the effects of platinum size for PDH.

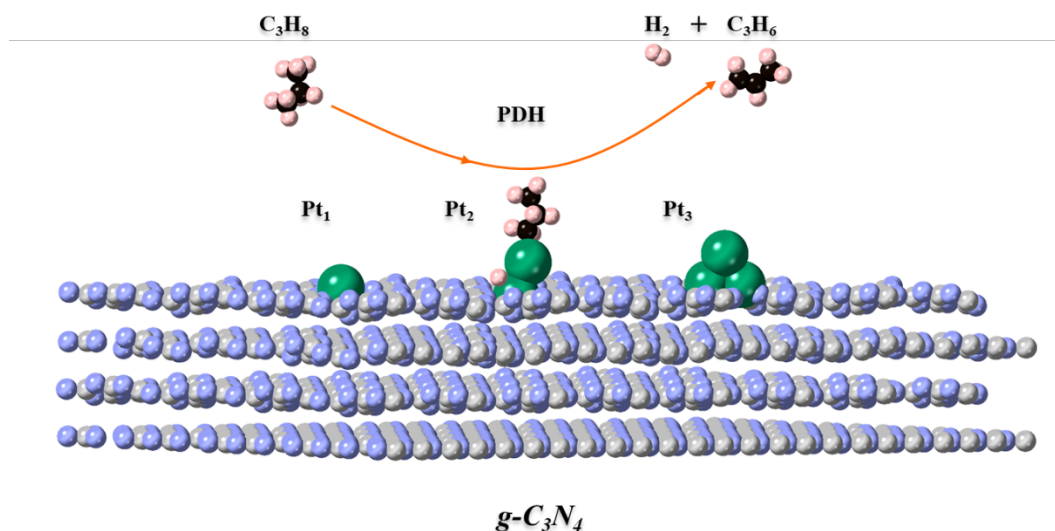


Figure 1. Comparison of propane dehydrogenation catalyzed by small Pt clusters anchored on g-C₃N₄.

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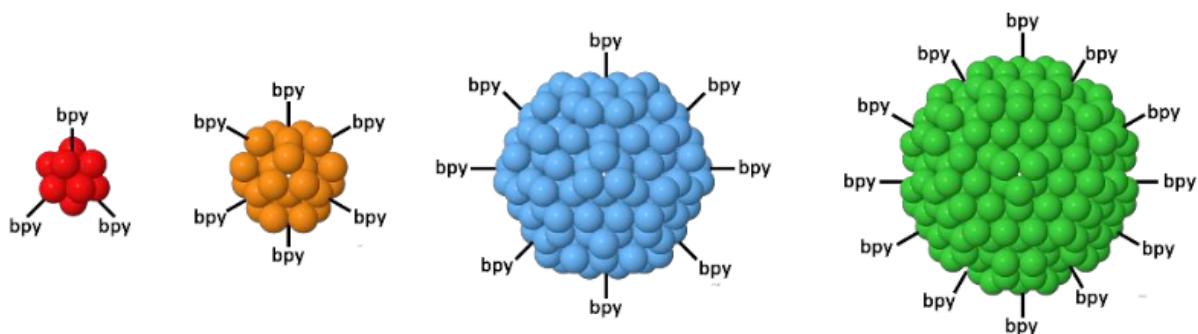
Is size all that matters? A discussion on the fine-tuning of metallic nanoparticles

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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 such as a large number of active sites and enhanced stability, while also displaying a certain degree of tuneability.^[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, these ligands can have an effect on the physicochemical properties of the NPs. The presence of certain species on the surface of the NPs can be used to control their size and tune their active sites, enhancing their catalytic performance. One good example can be found in Ru NPs stabilised with 4-phenylpyridine (4PP). Our group showed that the presence of the 4PP ligand on these NPs shifts the Ru-H bond energy to an optimal value, therefore increasing their catalytic performance towards the hydrogen evolution reaction (HER).^[3] Inspired by this work, we decided to test the effect of 2,2'-bipyridine (bpy) on Ru NPs. Herein we present various systems consisting of Ru NPs stabilised with different amounts of bpy. It was found that there is an inverse relationship between the amount of bpy used and the size of the resulting nanoparticles *i.e.*, the more equivalents of ligand added, the smaller the nanoparticles and vice versa. These differences in size also translate into large differences in their catalytic performances towards HER being the smallest system the worst catalyst and the biggest one the best. This behaviour can seem counterintuitive, although it can be justified by the coordination of the bpy ligand on the surface of the NPs and its effect on the active sites of these catalysts.



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A new Ir-P,N catalyst design to solve the asymmetric hydrogenation of challenging alkenes

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Metal-catalyzed asymmetric hydrogenation is a powerful and sustainable method for preparing chiral compounds due to its perfect atom economy.^[1] However, most catalysts are only tested in benchmark substrates, eluding challenging ones that would yield to more appealing compounds, such as exocyclic olefins with a benzofused five/six-membered ring motif, whose hydrogenation products are present in pharmaceutical natural products and key bioactive drug intermediates (Figure 1).

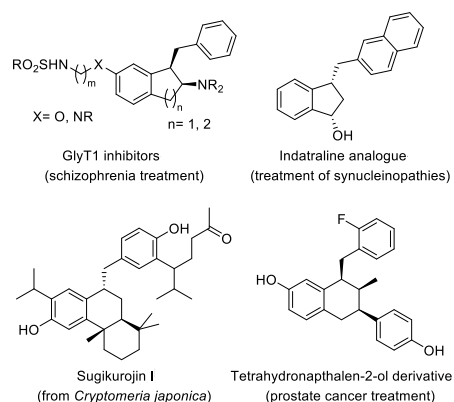


Figure 1.

Compared to the considerable number of reports about the reduction of unfunctionalized acyclic and endocyclic olefins, the reduction of unfunctionalized exocyclic olefins is underdeveloped. Only the Ir/In-BiphPHOX catalyst have reported a high catalytic performance in a range of exocyclic benzofused five-membered olefins (93-98% ee).^[2] However, the enantioselectivity was lower in the reduction of the parent benzofused six-membered olefin (75% ee). Additionally, the reaction required an additive and a specific solvent (*o*-xylene), moving away from the commonly used solvents in Ir-catalyzed asymmetric hydrogenation. The difficulty in the reduction of this type of benzofused five/six-membered olefins is even more evident if we consider that PHOX, which are the most successful ligands for Ir-catalyzed hydrogenation, did not work. Herein, we present a new and simple chiral phosphine-triazole ligand for the asymmetric Ir-catalyzed hydrogenation of exocyclic benzofused alkenes.^[3] Overcoming previous limitations, the new catalytic system can successfully hydrogenate a series of exocyclic olefins bearing a benzofused five- and six-membered ring motif (ee's up to 99%). The catalyst tolerates well the presence of several substituents and substitution patterns at both aromatic rings. Mechanistic studies explain the origin of this exceptional high catalytic performance.

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Stereoselective multi-component allylic alkylation enabled by dual photoredox/Ni catalysis

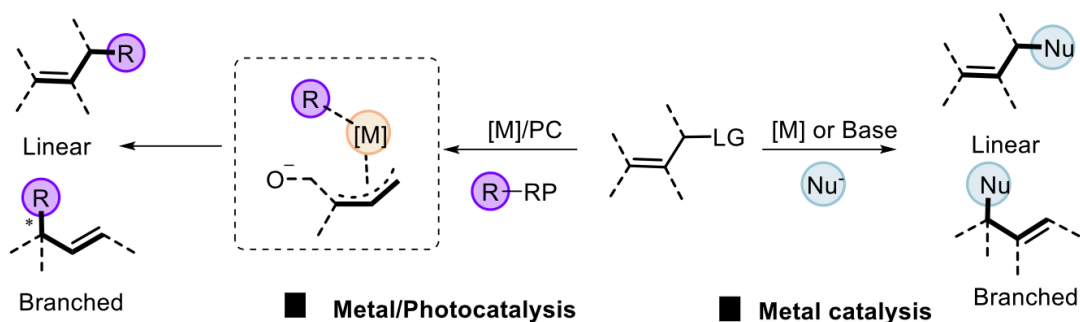
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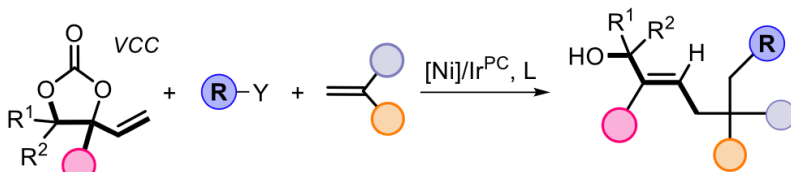
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A rare regio- and stereoselective three-component allylic alkylation enabled by dual Ni/photoredox catalysis has been developed. Our approach allows for rapid access to multi-functional allylic alcohols with congested/functional stereocenters from a wide range of allylic precursors, vinyl compounds and primary, secondary and tertiary alkyl radicals. This new three-component, photo-mediated catalytic process expands the use of vinyl cyclic carbonates affording a variety of elaborative stereo-defined building blocks with excellent synthetic potential.^{[1][2]}

(a). Existing strategies for allylic alkylation



(b) This work: dual photoredox/Ni catalyzed stereoselective 3CR



Excellent regio- and stereocontrol
41 examples, E/Z typically >95:5
Elaborate quaternary carbon centers
Use of 1°, 2° and 3° radicals
Extendable to other allylic substrates

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1a REUNIÓ DE QUÍMICA INORGÀNICA I ORGANOMETÀL·LICA de la SCQ



Understanding polyoxometalates as water oxidation catalysts through iron vs. cobalt reactivity

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Cobalt polyoxometalates (Co-POMs) have emerged as promising water oxidation catalysts (WOCs), with the added advantage of their molecular nature despite being metal oxide fragments.^[1-2] In comparison with metal oxides, that do not offer well-defined active surfaces, POMs have a controlled, discrete structure that allows for precise correlations between experiment and computational analyses. Thus, beyond highly active WOCs, POMs are also model systems to gain deeper mechanistic understanding on the oxygen evolution reaction (OER). The tetracobalt Weakley sandwich $[\text{Co}^{\text{II}}_4(\text{H}_2\text{O})_2(\text{B}-\alpha\text{-PW}_9\text{O}_{34})_2]^{10-}$ (**Co₄-WS**) has been one of the most extensively studied.^[3] We have compared its activity with that of the iron analogue $[\text{Fe}^{\text{III}}_4(\text{H}_2\text{O})_2(\text{B}-\alpha\text{-PW}_9\text{O}_{34})_2]^{6-}$ (**Fe₄-WS**) looking for the electronic effects determining their activity. Furthermore, the effect of POM nuclearity was also investigated by comparison with the iron- and cobalt-monosubstituted Keggin clusters.

Electrocatalytic experiments employing solid state electrodes containing the POMs and the corresponding computational calculations demonstrate that Co^{II}-POMs display better WOC activity than the Fe^{III} derivatives. In good agreement with the experimental data, computational methods, including pK_a values, confirm that the resting state for Fe-POMs in neutral media corresponds to the **S₁** (Fe^{III}-OH) species. Overall, the proposed reaction mechanism for **Fe₄-WS** is analogous to that found for **Co₄-WS**, despite their electronic differences. The potential limiting step is a proton-coupled electron transfer event yielding the active **S₂** (Fe^{IV}=O) species, which receives a water nucleophilic attack to form the O-O bond. The latter has activation energies slightly higher than those computed for the Co-POMs, in good agreement with experimental observations. These results provide new insights for the accurate understanding of the structure-reactivity relationships of polyoxometalates in particular, and of metal oxides in general, which are of utmost importance for the development of new bottom-up synthetic approaches to design efficient, robust and non-expensive earth-abundant water oxidation catalysts.^[4]

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Cianuro complexos de Fe(II) amb grups azo solubles en aigua: estudi mecanístic de la seva isomerització tèrmica *cis-trans*

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L'estudi de les propietats fotoquímiques de l'azobenzè i els seus derivats ha estat, i és, una àrea de recerca molt activa.^[1] El canvi de geometria que implica el procés d'isomerització entre les formes *cis* i *trans* pot orientar les molècules de manera adequada per realitzar una determinada funció, dona lloc a canvis en les propietats espectroscòpiques, o desplaça un substituent que pot bloquejar o no l'activitat de la molècula. La complexació de lligands derivats de l'azobenzè a centres metàl·lics, obre la possibilitat de modular el mecanisme (rotacional o inversional) d'aquest procés d'isomerització.^[2]

S'han dut a terme estudis cinètico-mecanístics del procés tèrmic d'isomerització *cis-trans* per a un conjunt de nous compostos derivats de l'azobenzè que contenen grups isocianuro, cianuro o piridina terminals. Ja que aquests compostos són capaços de coordinar-se a centres metàl·lics, s'ha estudiat el mecanisme de la mateixa isomerització espontània, per als complexos resultants de la coordinació a fragments pentacianuroferrat(II).

La comparació dels paràmetres d'activació tèrmics i bàrics determinats per als lligands i per als corresponents complexos, ha permès conèixer en detall la influència de la coordinació en el mecanisme del procés.

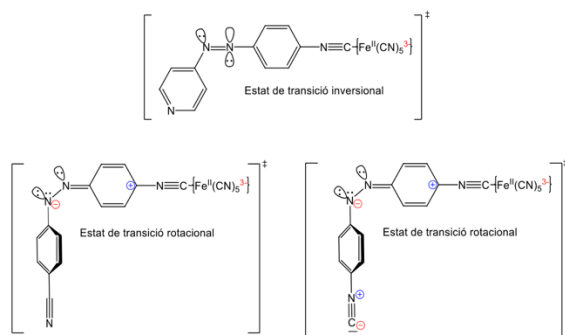
Cal destacar que la presència de grups donadors terminals en els compostos de Fe(II) sintetitzats els fa susceptibles de ser utilitzats com a blocs de construcció d'espècies de major nuclearitat amb una interessant activitat fotoquímica.^[3]

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Kinetic-mechanistic studies on the lability of Cu(II)-carbon bonds: homo- or heterolysis?

M. A. Gonzalez, ¹ M. Martinez, ^{2,3} P. V. Bernhardt¹

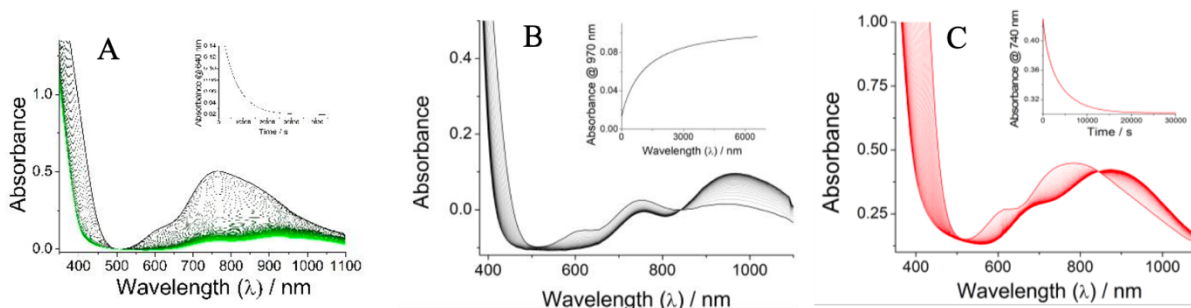
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Organocopper(II) reagents are the unexplored front of copper catalysis. Despite being proposed as reactive intermediates formed from radical addition to a Cu(I) species, we still do not have a clear picture of the stability and reactivity of the Cu(II)-C bond. Two pathways can be considered for the cleavage of a Cu(II)-C bond: homolysis, and heterolysis. We recently showed how organocopper(II) reagents can react with alkenes via radical addition, which corresponds to a homolytic pathway.

We have studied the decomposition of the [Cu^{II}LR]⁺ (L = Me6tren, R = CH₂CN) complex in the absence and presence of an initiator (RX, X = Cl, Br). In the absence of initiator, a first-order reaction is observed, which corresponds to the homolysis process (Spectra A). However, when an excess of initiator is present, we observe the formation of [Cu^{II}LBr] via a second-order reaction, which corresponds to the activation of [Cu^IL]⁺ with R-X (Spectra B). The alternative decomposition pathway is heterolysis, although conventional heterolysis does not take place, a protonolysis reaction involving the heterolytic cleavage of Cu(II)-C by an acidic substrate such as water, is possible (Spectra C).



In this study, we examine the different pathways of Cu(II)-C bond cleavage and determine via kinetics the thermal (ΔH^\ddagger , ΔS^\ddagger) and pressure activation parameters (ΔV^\ddagger) of the processes. This has allowed us to better understand the nature of the Cu(II)-C bond, as well as the nature of the transition state of the reaction. We hope that by knowing how this bond reacts, new catalytic cycles for the unexplored organocopper(II) reagents take place.

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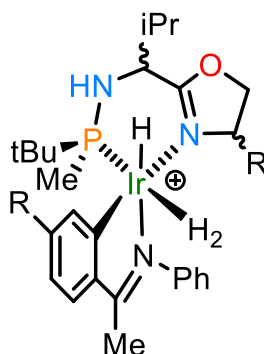
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Cyclometallated iridium catalysts for the asymmetric hydrogenation of imines

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MaxPHOX Iridacycle

We previously reported the asymmetric hydrogenation of *N*-alkyl imines using MaxPHOX iridacycles^[1], which was generated in-situ by reacting Ir-MaxPHOX catalyst with acetophenone *N*-phenyl imine in presence of hydrogen. This was the first catalytic system to attain high enantioselectivity (up to 94% ee) in this type of transformation. Following the density functional theory calculations that allowed us the rationalization of the stereochemical course of the reaction, we have synthesized several novel additives that further improved the enantioselectivity of this transformation (up to 97% ee). Evaluation of the substrate scope showed that both *N*-methyl imines and *N*-alkyl imines were tolerated and reduced with excellent enantioselectivity. This catalytic system also showed enhanced selectivity in the asymmetric hydrogenation of *N*-aryl imines (up to 98% ee).

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Three-component Suzuki-Miyaura/allylic substitution: a regioselective approach to 2-aryl allyl sulfones

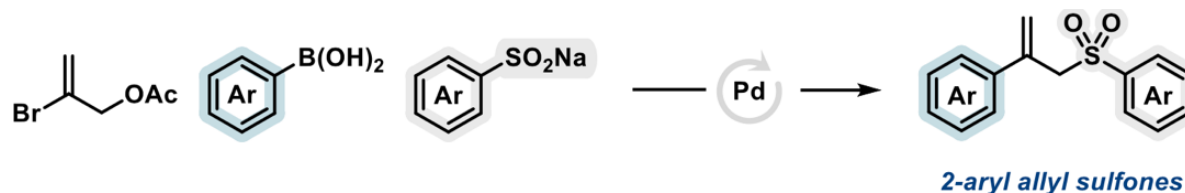
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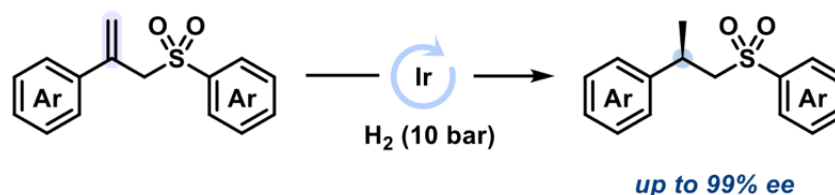
The synthesis of chiral sulfones has been widely used mainly due to the versatility of this functional group.^[1] Regarding asymmetric and catalytic transformations, several groups have synthesized and hydrogenated vinylic sulfones by using ruthenium, rhodium, or iridium complexes.^[2]

Most reported substrates were internal alkenes (2-aryl-2-methyl vinyl sulfones) that often encounter *E/Z*-selectivity issues in their preparation steps and may be hard to separate. To overcome this, a three-component Pd-catalysed synthesis of terminal 2-aryl allyl sulfones has been developed. This novel one-pot synthesis is regioselective and allows functionalization both at the aryl and sulfonyl moieties with good to excellent yields (65-90%), avoiding the selectivity issues (Scheme 1).



Scheme 1. Regioselective preparation of terminal 2-aryl allyl sulfones.

The aforementioned allylic sulfones were subsequently hydrogenated employing the commercially available UbaPHOX iridium complex, affording chiral β -methyl sulfones with up to 99% ee (Scheme 2). The screening conditions, the mechanism and the scope of both reactions as well as some synthetic applications will be reported in the present communication.



Scheme 2. Ir-catalysed asymmetric hydrogenation of 2-aryl allyl sulfones.

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Mechanistic insights into the oxidation of Cp*Co(III) species with F⁺ oxidants

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Over the past few years, Cp*Co(III) catalysts have shown their tremendous potential in directed C–H functionalization reactions, especially involving electrophiles as coupling partners. ^[1] In sharp contrast, methodologies based on the coupling with nucleophiles remain extremely scarce. ^[2] Contrary to previous mechanistic proposals, our group exposed the existence of oxidatively induced C–SCF₃ reductive eliminations (ORE), via high-valent Cp*Co species, triggered under chemical (AgSCF₃ or Mn(OAc)₃·2H₂O) or electrochemical conditions. ^[3] In this work, we explored the reactivity of weakly coordinated cobaltacycles ^[4] with other kinds of oxidants, widely used in catalysis, F⁺ oxidants. In this case, we focused our attention on the oxidation step of the reaction and investigated its mechanism experimentally and computationally.

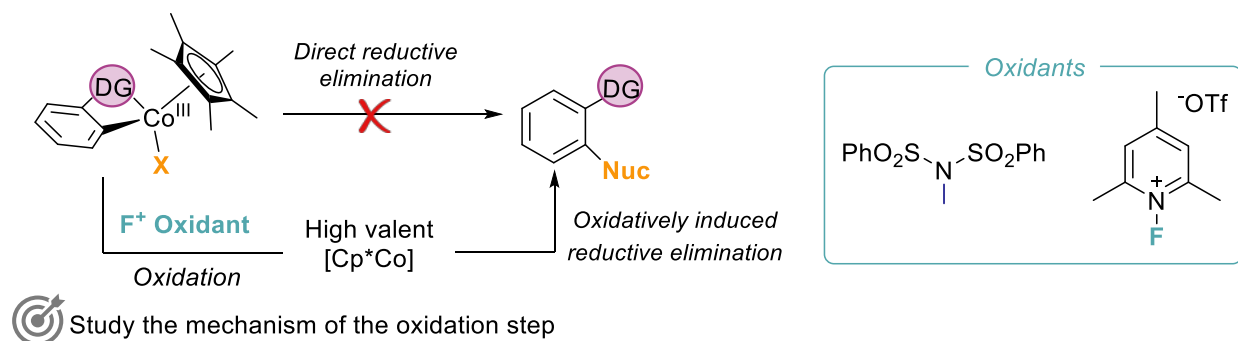


Figure 1. Mechanistic study on the oxidation of Cp*Co species by F⁺ oxidants

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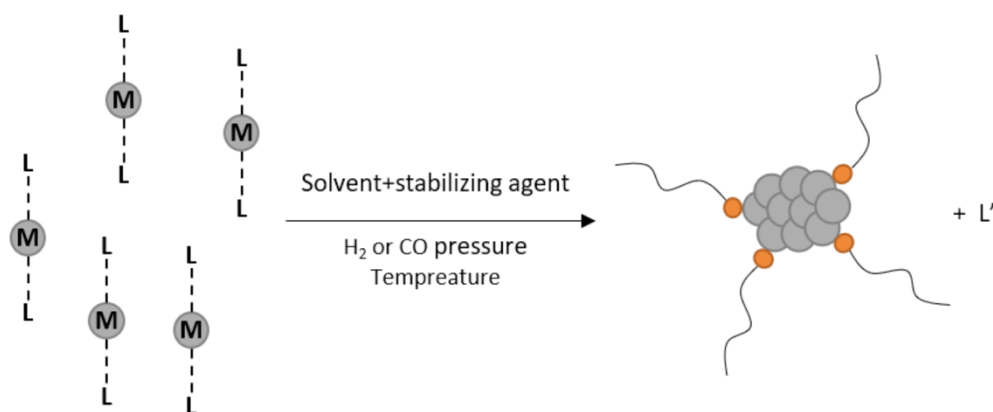
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Tuning nanoparticles for artificial photosynthesis applications

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There are several well-known ways to synthesise nanoparticles, from physical methods as milling to chemical methods as salt reduction.^[1] From all these methods, there is a bottom-up approach that offers significant advantages compared to all other methodologies and has gained importance in the last decades: the organometallic approach. This way of synthesising nanoparticles consists of decomposing an organometallic precursor under mild conditions of temperature and pressure and allows to control the surface chemical environment of the nanoparticles.^[2] The control of the chemical species on the surface of the final material is of critical importance to unravel the role of ligands and ions in catalysis applications for nanoparticles. That is the reason why the organometallic approach is an ideal method to study the role of organic ligands on the surface of metallic nanoparticles to tune their catalytic properties and performance.^{[3],[4]} In the present communication an experimental case of such synthetic method together with its catalytic application in artificial photosynthesis is presented, showing the particular advantages of the organometallic approach.



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Switchable MOP solubility through surface chemistry: engineering molecular self- sorting systems

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Metal-organic polyhedra (MOPs) represent the ultimate miniaturization of a metal-organic material with intrinsic porosity as they can be conceptualized as the isolation of a sub-5 nm single cavity of an extended metal-organic framework.^[1] Moreover, the combination of their discrete nature and nano-sized scale endows them with properties tied to macromolecules, such as solubility and stoichiometric reactivity, or ultrasmall nanoparticles, as densely functionalized and highly reactive surfaces.^[2] This unique entanglement of properties opens up the possibility to post-synthetically modify their properties in solution with stoichiometric control through ionic exchange, organic covalent reactions or supramolecular chemistry, both orthogonally and synergistically.^[3]

Here we show how the role of these abovementioned properties gives rise to the possibility to modulate intrinsic physicochemical molecular properties such as solubility. MOPs solubility can be post-synthetically modulated through simple protonation/deprotonation and ionic exchange reactions and this behavior can be exploited to design phase transfer systems.^[4] We will show how this control over the MOP solubility can be coupled with the MOP coordination capabilities to undergo molecular transport and separation processes of regioisomeric mixtures in which the MOP governs the solubility of a molecule coordinatively bounded to the MOP surface.^[5] Moreover, we will discuss about the possibility of using such control of the solubility not only in solution, but also in heterogeneous conditions by using the MOP as a coordinatively capture agent to remove organic micropollutants from water by pH-controlled precipitation.^[6]

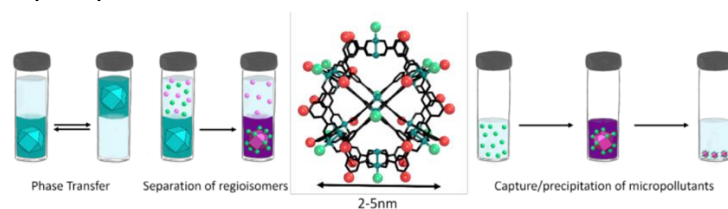


Figure 1. Schematic representation of a MOP (centre) and examples of self-sorting systems based on its tunable solubility (left and right).

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Polimerització covalent de caixes moleculars poroses: síntesi, funcionalització i aplicacions

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Recentment, els poliedres metal·lòrgànics (MOPs) estan emergent com a potents blocs de construcció supramolecular per a la síntesi de xarxes poroses esteses complexes^[1]. No obstant, en la majoria de casos els MOPs es polimeritzen mitjançant enllaços de coordinació amb lligands addicionals, la qual cosa fa que els materials resultants presentin propietats mecàniques modestes i tinguin tots els seus centres metàl·lics saturats. En aquesta conferència presentaré la polimerització de MOPs mitjançant química covalent. Com a punt de partida fem servir un MOP de rodi funcionalitzat amb 24 grups amina a la seva superfície^[2]. La reactivitat de les amines permet polimeritzar aquest MOP amb aldehids via la formació d'enllaços imina. Aquesta polimerització dona lloc a gels que un cop activats mitjançant CO₂ supercrític deriven en aerogels porosos tal i com demostren les mesures d'adsorció de gasos. L'aerogel obtingut és robust i estable inclús sota immersió en diferents solvents, com ara l'aigua. La novetat del nostre material radica en la possibilitat de post-funcionalitzar-lo a través de química de coordinació en les posicions axials lliures dels àtoms de rodi que formen el MOP, permetent així modificar les propietats macroscòpiques de la xarxa estesa (polaritat, càrrega, etc...). Així doncs, hem aprofitat el caràcter versàtil i la estabilitat dels nostres aerogels per a desenvolupar nous adsorbents modulars per a la captura de contaminants en aigua.

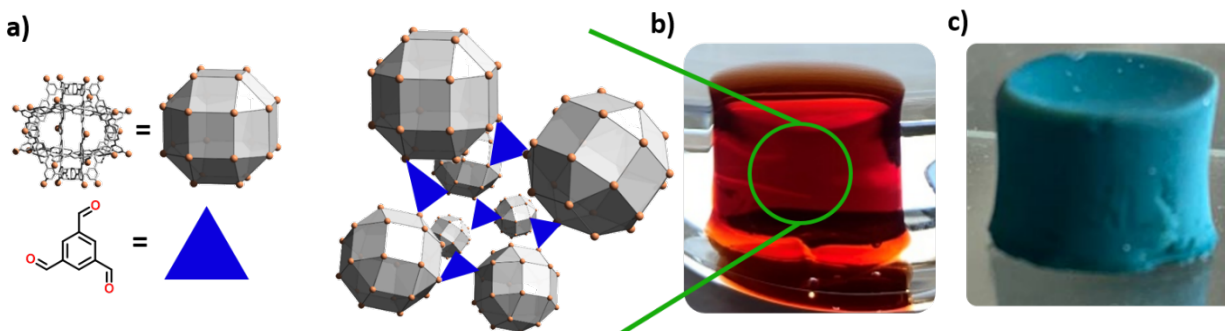


Figura 1 a) Esquema de la polimerització covalent de MOPS per donar lloc a b) gels i c) aerogels.

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L'efecte plantilla de l'anió SiF_6^{2-} i els ponts d'hidrogen: L'aliança perfecta per aconseguir la formació exclusiva de nous sistemes de coordinació heterolèptics

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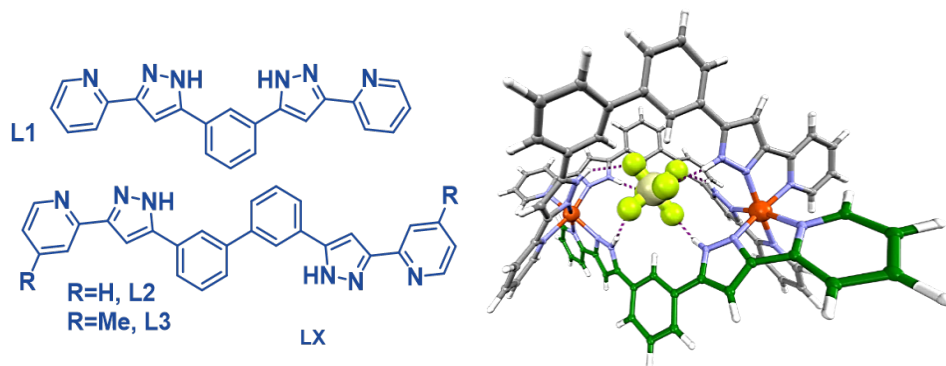
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Inspirats per la natura, busquem el disseny i la síntesi eficaç de fragments orgànics capaços de produir nous assemblatges moleculars que incorporen diverses funcions que poden interactuar de manera sinèrgica o ser abordades per estímuls externs.

La versatilitat dels nous lligands orgànics bis-(pirazol-piridil), permet la síntesi de diversos nous helicats de triple cadena que encapsulen espècies aniòniques com ClO_4^- , SiF_6^{2-} , $[\text{Cr}(\text{Oxalat})_3]^{3-}$, $[\text{Fe}(\text{Oxalat})_3]^{3-}$, entre d'altres.

L'encapsulació de SiF_6^{2-} mostra un efecte de plantilla evident que guia la reacció per formar exclusivament l'helicat heterolèptic amb fórmula $(\text{SiF}_6@[\text{M}(\text{L1})(\text{LX})_2])(\text{PF}_6)_2$ (on $\text{M} = \text{Ni}(\text{II}), \text{Fe}(\text{II})$ o $\text{Co}(\text{II})$). La influència de la relació de L1/LX s'ha estudiat contra la naturalesa de les espècies encapsulades, i aquesta relació no afecta l'estequiometria del complex esmentat anteriorment.

Aquesta nova família de sistemes moleculars amfitrió-convidat pot oferir diferents propietats, segons els centres metàl·lics implicats i la naturalesa de l'espècie encapsulada. A més a més, aquest sistema ofereix un assemblatge únic que permet la coordinació de qubits adreçables de manera independent, degut als diferents entorns de coordinació dels metalls.



Lligands orgànics utilitzats a la síntesi (esquerra) dels nous assemblatges heterolèptics formats per l'efecte plantilla de l'anió SiF_6^{2-} : $\text{SiF}_6@[\text{M}(\text{L1})(\text{L2})_2]^{2-}$; $\text{SiF}_6@[\text{M}(\text{L1})(\text{L3})_2]^{2-}$ (dreta)

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Synthesis of Ni(II) helicates for the chemical tuning of spin clock transitions

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Exploiting quantum bits and quantum gates to develop new functional tools and devices is one of the main current challenges in quantum computing (QC). Among their different physical realizations, magnetic metal-organic complexes are a very promising option. Magnetic molecules are so far hampered by the rapid loss of quantum information, a process known as decoherence, which is mainly induced by magnetic noise. Combining good isolation from noise with the ability to externally control the molecular spin states and their mutual interactions is one of the main current challenges in QC research. A possible approach is to deal with superposition states that form at level anti-crossings, also known as clock transitions. Quantum tunneling between opposite orientations of non-Kramers spins generates these level anti-crossings, which possess an excellent stability against magnetic field fluctuations [1].

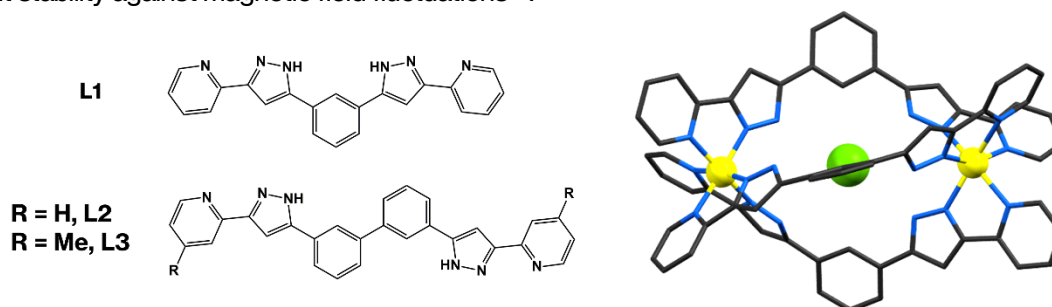


Figure 1. Structures of L1, L2 and L3 (left), and the homoleptic $(Cl@[Ni_2(L1)_3])^{3+}$ (right). Color code: yellow, Ni; green, Cl; blue, N; black, C. H atoms are omitted for clarity.

Considering that sizable quantum tunneling splitting has been shown to exist between the two lowest electron spin levels of mononuclear Ni(II) complexes with an octahedral geometry [2], here we report the synthesis of different triple-stranded Ni(II) dinuclear helicates, with the internal cavity occupied by different guests. With the correct ligand design, metallo-helicates can selectively encapsule guest species within them, offering a valuable option to modulate the functional properties of their complexes [3,4]. We have been exploiting bis-pyrazolopyridine type ligands L1, L2, or L3 (Fig. 1, left). The volume of the central cavity depends on the choice of spacer between the coordinating pockets; with ligand L1, halide ion guests, X, are trapped (X = Cl, Br). Ligands L2 and L3, with a longer spacer, allow the incorporation of a bigger guest. By the modification of the chemical environment, is possible to tune the quantum tunneling splitting. The only nickel isotope with a nonzero nuclear spin (^{61}Ni , $I = 3/2$) has a close negligible natural abundance of 1.14%. So, with its $S = 1$ ground state, Ni(II) provides a realization of the simplest non-Kramers system, with just three magnetic levels ($m_s = 0$ and ± 1) [3]. For all these reasons, we prepared several dinuclear octahedral Ni(II) complexes using bis-pyrazolopyridine type ligands to obtain homoleptic (Fig. 1, right) and heteroleptic Ni(II) helicates.

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Design of functional inorganic 2D materials *via* molecular engineering

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Succeeding Graphene, *Inorganic 2D Materials* (i2DMs) – viz. Germanane (2D-Ge) derivatives, Transition-Metal Carbides (MXenes), Inorganic Micromotors, etc. – have attracted great attention since most of their physicochemical features can be entirely tuned by modulating the nature of the surface substituent ^[1]. Although very interesting from a scientific point of view, a main bottleneck can be clearly identified: the lack of Functional i2DMs for task-specific applications. Consequently, devising versatile, robust and eco-friendly synthetic approaches to customize them with the desired architectonic is a must to advance in the field of Materials Chemistry.

In this regard, Molecular Engineering is currently leading the global “Fourth Industrial Revolution” – also called as Industry 4.0, described as the convergence of digital technologies with breakthroughs in Materials Science, Chemistry and Biology to progress in the deep digital transformation – through the use of molecular-level science to supply “intelligent” materials and devices with entirely new and programmable capabilities for people and Machines^[2]. In particular, Molecular Engineering provides integrative protocols which allow to manipulate the properties of materials on-demand by simply tailoring the nature of the implanted molecular constituent.

Consequently, general synthetic chemical strategies are proposed for expanding the library of i2DMs by implanting molecular fingerprints, resulting in Functional i2DM derivatives with unprecedented characteristics, making possible their implementation in yet unexplored tasks otherwise inaccessible for the pristine i2DM counterparts. As a proof of illustration, **Figure 1** shows the functionalization of 2D-Ti₃C₂T_x MXene with responsive molecules (*i.e.*, amino acids), making possible to translate the main molecular characteristics of amino acids (e.g., chirality, supramolecular recognition, fluorescence and pH response) to the i2DM^[3].

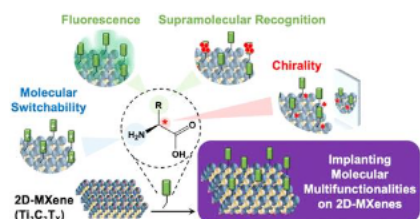


Figure 1. Illustration of anchoring active molecular moieties upon i2DMs for the development of Functional i2DMs. As a proof-of-concept, an amino acid has been anchored upon 2D-Ti₃C₂T_x MXene, resulting in a multifunctional material.

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Disseny de compostos dinuclears de lantànid per portes lògiques quàntiques

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La cerca de sistemes físics per implementar bits quàntics (*quantum bits, qubits*) i portes lògiques quàntiques (*quantum gates, qugates*) és un dels reptes més importants per la realització de la computació quàntica. En aquest sentit, l'espín electrònic derivat de molècules magnètiques és considerat com un dels candidats més prometedors, tenint en compte la flexibilitat del seu disseny, la fàcil manipulació i la possibilitat de produir aquest material a gran escala.^[1] Els compostos amb ions lantànid (Ln) són particularment atractius, ja que cada ió pot ser emprat com a *qubit* (gràcies als dos nivells de l'estat fonamental) o com a *qudit* (sistema quàntic d-dimensional) si l'estat de més baixa energia té més de dos nivells (**Figura 1**). Amb aquest objectiu en ment, hem dissenyat compostos dinuclears homo- i heterometàl·lics de lantànid [LnLn'], utilitzant un lligand asimètric capaç d'incorporar de manera selectiva cada ió en entorns de coordinació diferents.^[2,3] La puresa i selectivitat dels sistemes ha estat confirmada per mesures espectromètriques i cristal·logràfiques. Estudis magnètics i de ressonància paramagnètica electrònica de diferents anàlegs han demostrat que els ions Ln d'aquesta arquitectura molecular compleixen els requisits per ser utilitzats com a qubits o *qudits*, podent dur a terme de manera satisfactòria operacions lògiques quàntiques.

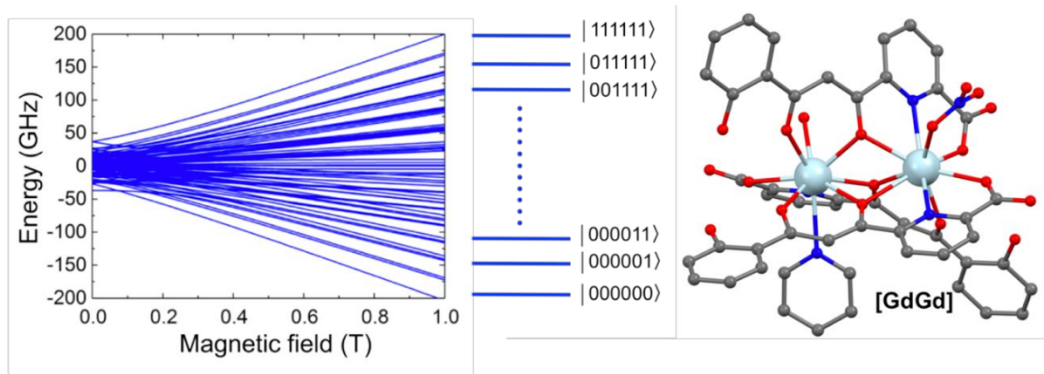


Figura 1. Diagrama de nivells energètics de l'anàleg [GdGd] i estructura molecular del compost.

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Highly selective heterometallic [LnLn'Ln] molecules as 3-qubit quantum gates

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Molecular complexes containing lanthanide ions are promising candidates to embed quantum bits (qubits) for quantum computing based on the coherent manipulation of the molecular spin. Our group has discovered a coordination scaffold hosting three Ln(III) ions using two β -diketone ligands, H₂LA and H₂LB, containing two types of chelating pockets.^[1,2] The mixture with two Ln(III) salts form a family of trinuclear heterometallic complexes with formula [Ln₂Ln'(LA)(LB)(py)(H₂O)₂](NO₃) (Figure 1a). Mass spectrometry experiments evidence the selectivity, robustness and stability of the [LnLn'Ln] disposition, which have been further confirmed by DFT calculations.^[3] Magnetization and calorimetric measurements prove its potential to perform a 3-qubit quantum gate while pulsed EPR experiments suggest that all relevant spin states can be coherently manipulated (Figure 1b,c).

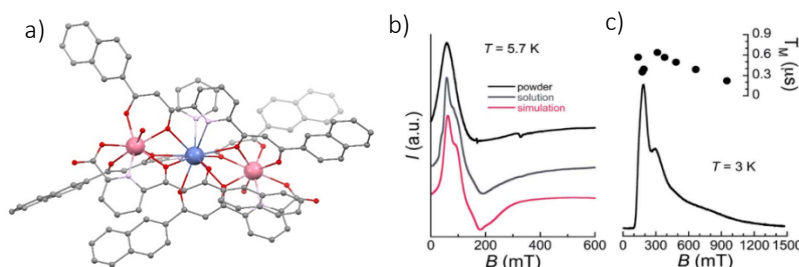


Figure 1. a) Representation of the molecular structure of [Ln₂Ln'(LA)(LB)(py)(H₂O)₂]⁺. b) Continuous-wave EPR spectra for bulk polycrystalline powder, a frozen solution and the simulation of the latter. c) Echo-detected field-swept EPR spectrum of a frozen solution at 3 K.

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1a REUNIÓ DE QUÍMICA INORGÀNICA I ORGANOMETÀL·LICA de la SCQ



Light-driven hydrogen evolution using Ni, Cu and Pt nanoparticles supported on carbon nitride and covalent triazine-frameworks

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In the present energetic context, the production of hydrogen from water triggered by sunlight is regarded as a promising technology to obtain this gas in a sustainable way. Many efforts are in progress to find the suitable photocatalyst to carry out the hydrogen evolution reaction (HER). Among them, covalent triazine-based frameworks (CTF) and graphitic carbon nitrides (g-C₃N₄) - two classes of polymeric materials - show promising performances [1,2]. Nevertheless, the presence of a metallic co-catalyst is usually required to facilitate the reaction. Although platinum nanoparticles (Pt NPs) are the most used benchmark co-catalyst for HER, its high cost and scarcity has prompted the search for alternative non-noble metals such as Ni and Cu.

Therefore, herein we report a family of metallic nanoparticles, MNPs, (Cu, Ni, Pt) supported on CTF and g-C₃N₄ prepared by the organometallic approach^[3]. This synthetic method, which consists in the decomposition of an organometallic precursor under mild conditions (room temperature and 3 bar of H₂), allows to obtain monodisperse NPs of narrow size distribution and controllable surface environment.

The resultant materials were tested towards photocatalytic HER in the presence of TEOA (10% V/V) as sacrificial hole-scavenger using as irradiation source LEDs (430 nm maximum emission) and/or a solar simulator (300 W Xe lamp). The materials were characterized by several techniques (TEM, IR, UV-vis, XRD, XPS, ICP, electrochemical) to obtain a correlation between the material structure and the photocatalytic activity. Moreover, clarification will be given on the effect of the metallic NPs on both supports, and how this influences the HER performance.

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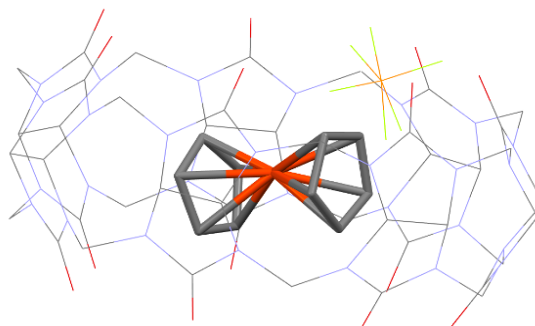
Millora dels temps de relaxació de imants unimoleculars

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El magnetisme molecular és un camp multidisciplinari que estudia el comportament magnètic de les entitats moleculars. Per això, preparar molècules que actuïn com a imants i siguin capaços de retenir la magnetització en absència de camp magnètic resulta de gran interès. Aquestes molècules es denominen imants unimoleculars (SMM)^[1,2] i podrien tenir un paper rellevant en aplicacions tecnològiques ja que són capaços de combinar-se en materials multifuncionals amb altres propietats moleculars d'interès, com les fotoquímiques o les conductives.^[3] A més, les molècules magnètiques amb llargs temps de relaxació d'espín són candidates potencials per a actuar com qubits en els ordinadors quàntics. Els SMM tenen una orientació preferent de l'espín. Quan s'aplica un camp magnètic extern s'alineen i si se suprimeix aquest camp, l'espín roman un període en aquesta direcció (temps de coherència) a causa de l'anisotropia intrínseca de la molècula.^[4] La relaxació de l'espín pot ocórrer per diversos mecanismes de relaxació: Orbach, Raman, directe, mode local i túnel quàntic de magnetització (QTM).

El ferricini és una molècula de espín baix ($S=1/2$), que presenta una considerable anisotropia magnètica a causa de l'estat fonamental E_{2g} , causat per una ocupació non-Aufbau dels orbitals que és gens habitual. Aquest metal·locè relaxa el seu espín ràpidament a camp zero a través del QTM.^[5] Existeixen diverses estratègies per a intentar disminuir-ho i tenir temps de coherència més llargs. La més important consisteix a disminuir les interaccions dipolars que ho afavoreixen mitjançant i) mitjançant dilució magnètica incloent un catió diamagnètic, ii) fent les mesures en solució o iii) encapsulant la molècula en una espècie que actuï com a amfitrió. També es poden combinar les tres. En aquest treball encapsulem el SMM en una molècula diamagnètica amb la finalitat d'aïllar la molècula per a reduir les interaccions dipolars i canviar l'espectre vibracional.



Il·lustració 1. Encapsulació del ferricini en un curcubit[7]uril.

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Dearomatizative *syn*-dihydroxylation of arenes

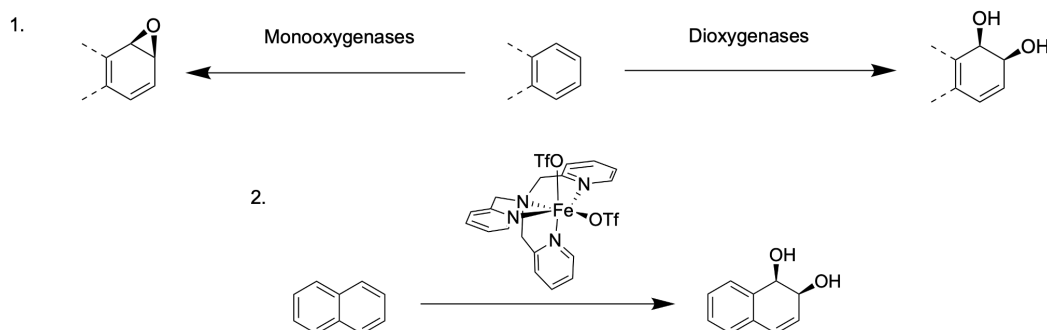
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The abundance of arenes in nature makes them very interesting substrates in organic synthesis. Through their dearomatizative oxidative reactions, they can be easily converted into very elaborated molecules, containing multiple stereogenic centers with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



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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1a REUNIÓ DE QUÍMICA INORGÀNICA I ORGANOMETÀ-LICA de la SCQ

Societat Catalana de Química

C-H Bonds as functional groups. simultaneous generation of multiple stereocenters by enantioselective hydroxylation at unactivated tertiary C-H bonds

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Given the ubiquity of chiral oxygenated moieties in natural and bioactive products, there is a growing interest in developing efficient strategies to achieve them in enantioselective manner. Due to the high fraction of C(sp³)-H bonds in available feedstock's, enantioselective C-H oxidation carries considerable appeal in this context. However, enantioselective C-H oxidation is particularly challenging because it requires highly reactive oxidizing species capable of cleaving strong non activated C-H bonds while discriminating between enantiotopic sites. This reactivity has remained inaccessible to contemporary oxidation methods and remains limited to enzymes. Bioinspired non-porphyrinic Fe and Mn complexes with linear aminopyridine ligands have emerged as powerful catalysts for site-selective C-H oxidations.^[1] These catalysts activate H₂O₂, a waste-free oxidant, in an enzyme-like manner, to generate an electrophilic high-valent metal-oxo species within a chiral ligand framework, opening the possibility to engage in enantioselective C-H oxidations.^[2,3]

In this contribution, we will present the first example of non-enzymatic enantioselective hydroxylation of non-activated C-H bonds using Mn bioinspired catalysts. A highly efficient and selective catalytic system for C-H hydroxylation was designed, which provides the alcohol as a single product with high yields and enantioselectivities. The reaction exhibits a high functional group tolerance, which includes esters, amides, ketones and nitriles, among others. In all cases, chiral alcohol products were obtained in good yields and excellent enantioselectivities, up to 98% ee. Further functionalization of the obtained oxidized products demonstrates the potential of this methodology for the construction of a range of chiral compounds. Moreover, the principles of catalysis design presented in this work constitute a solid platform for further development of stereoselective C-H hydroxylation reactions.

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Synthesis and reactivity of organometallic nickel complexes relevant in carbon-carbon and carbon-heteroatom bond formation reactions

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Transition metal catalyzed carbon-carbon and carbon-heteroatom bond formation reactions are very relevant transformations in organic chemistry. Although noble metal-based systems are often used as catalysts for C-C and C-heteroatom bond forming reactions, first-row transition metal catalysis is an attractive alternative^[1]. In the case of nickel catalysis, Ni⁰, Ni^I and Ni^{II} species were historically considered as the key intermediates for these transformations. However, recent studies show that high-valent Ni^{III} and Ni^{IV} species can also play an important role in the formation of new C-C and C-heteroatom bonds^[2,3].

In 2022, our group reported the synthesis and spectroscopic characterization of three new Ni^{II}, Ni^{III} and Ni^{IV} organometallic species supported by the tetradentate N-based macrocyclic ligand PyNMe₃ (Figure 1a)^[4]. Furthermore, the Ni^{II} compound was isolated and its reactivity with two electron O-based oxidants was tested, showing a preference for the formation of the C-C coupling products over the C-O coupling ones (Figure 1b)^[4]. On the other hand, despite the Ni^{III} compound was also isolated, its reactivity was not tested. Thus, we are currently working on the reactivity of the Ni^{III} complex with different nucleophiles to test its capacity to form new C-heteroatom bonds (Figure 1c).

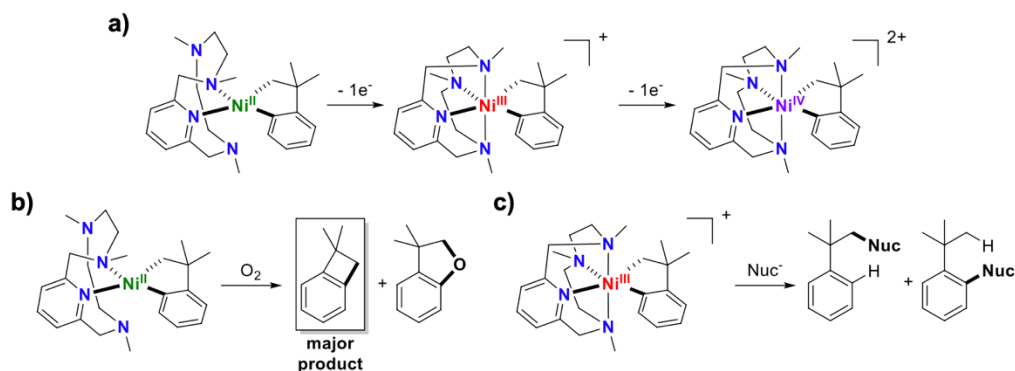


Figure 1. a) Stepwise oxidation from Ni^{II} to Ni^{III} and Ni^{IV}. b) Ni^{II} reactivity with O-based two electron oxidants. c) Possible reactivity of Ni^{III} towards nucleophiles.

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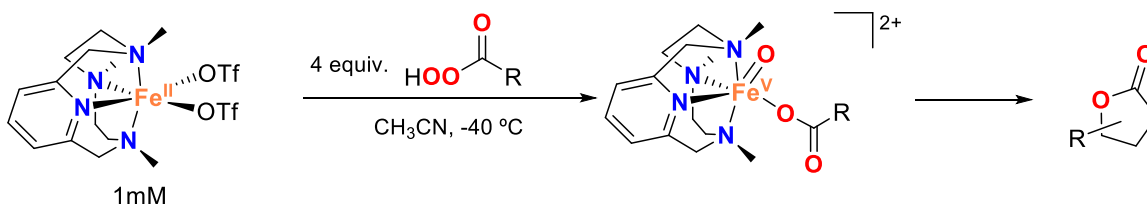
Exploring the intramolecular chemistry of iron(V)-oxo-carboxylato species

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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, $[\text{Fe}^{\text{V}}(\text{O})(\text{OC}(\text{O})\text{R})(\text{PyNMe}_3)]^{2+}$, 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 $[\text{Fe}^{\text{V}}(\text{O})(\text{OC}(\text{O})\text{R})(\text{PyNMe}_3)]^{2+}$ species by reaction of $[\text{Fe}^{\text{II}}(\text{PyNMe}_3)(\text{OTf})_2]$ with different peracids at -40°C in acetonitrile followed by γ -lactone formation.

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1a REUNIÓ DE QUÍMICA INORGÀNICA I ORGANOMETÀL·LICA de la SCQ



Carbene transfer reactions catalyzed by an iron/lithium dual system

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Functionalization of C-H bonds via carbene insertion is a reaction that finds wide synthetic utility.^[1,2] Traditionally, most of the carbene transfer reactions have been based on the use of precious metals as catalysts. Especially, carbene transfer using rhodium(II) complexes is widely developed, achieving outstanding yields and enantiomeric excesses.^[3] However, the high cost, and an increasing limited availability of precious metals have focused research towards their substitution by other more sustainable metals or complexes. Thus, iron becomes a potentially interesting alternative, since it is abundant, biocompatible and environmentally benign.^[4]

In our previous work, the electrophilic catalyst $[\text{Fe}(\text{Fpda})(\text{THF})]_2$ (Fpda=N,N'-bis(pentafluorophenyl)-o-phenylenediamide) in combination with the Lewis acid $\text{Li}[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ as co-catalyst, proved to be able to functionalize highly stable C(sp³)-H bonds in insertion reactions with good yields and high regioselectivities. Moreover, the catalytic system exhibited excellent yields, similar to those of rhodium catalysts, in the cyclopropanation of external and internal aliphatic alkenes under mild reaction conditions.^[5,6]

Building on this precedent, our current efforts are directed to obtain a deeper understanding of this elaborated system. We also aim to identify new iron-based catalysts capable of performing carbene transfer reactions, such as cyclopropanations and C-H insertions, via metallocarbene intermediates.

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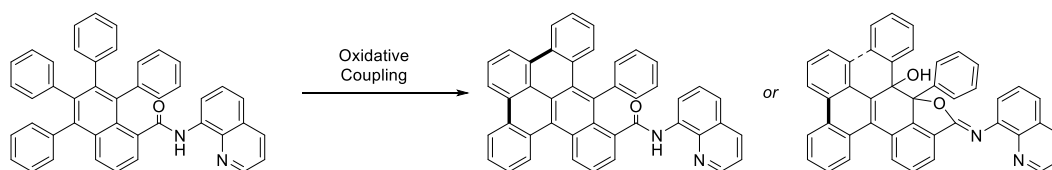
Development of a new protocol towards the synthesis of nanographene-like compounds via aromatic homologation catalysis

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In the recent years, polycyclic aromatic hydrocarbons (PAHs) compounds such as nanographenes and graphene nanoribbons (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 research topic of interest^[1,2]. Recently, our group reported a Ni-catalyzed system to activate selectively C_{sp2}-F strong bonds, using 8-aminoquinoline as directing group and different alkynes as non-activate coupling partners. The methodology reported forms the aromatic homologation and the alkyne monoannulation product in a chemodivergent manner using internal alkynes^[3,4]. In this work, we report the synthesis of nanographene-like compounds via oxidative coupling using the aromatic homologation as starting substrate, which in turn is obtained via Ni-catalyzed C_{sp2}-OMe functionalization strategy (Scheme 1).



Scheme 1. Oxidative Coupling for the bottom-up synthesis of nanographene-like compounds.

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Orthogonal regioselective bis-functionalization of C₆₀ by Diels-Alder reaction via avant-garde supramolecular mask strategy

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Fullerenes are carbon molecules with a spherical-like shape. As such, their functionalization is not region-controlled and renders mixtures of regioisomers, not amenable for applications.^[1] In this regard, only easily accessible mono-functionalized fullerenes are used as electron transport layers in solar cells (SC) devices. Pure regioisomers of poly-adducts are envisioned as good alternative to achieve boosting the efficiency of SC. For this reason, there is a great interest in developing new strategies for synthesizing C₆₀ derivatives with multiple addends in a pure regioisomeric way.

Here, we present a strategy using a tetragonal prismatic supramolecular nanocapsule as a supramolecular mask,^[2,3] that directs the Diels-Alder 4+2 cycloaddition reaction on fullerene C₆₀ towards pure bis-adduct isomers in a tunable fashion. The unprecedented *trans-1* bis-adduct has been obtained in excellent relative yields by using pentacene as the diene of the reaction, while *equatorial* bis-adduct has been achieved in a regioisomerically pure way using anthracene as the diene.^[4] These differences in regioselectivity have been studied using computational tools, such as Molecular Dynamics simulations and Frontier Molecular Orbitals analysis, to fully understand the behavior of these host-guest complexes. Moreover, combined Diels-Alder and Bingel cyclopropanation render tris- and hexakis-hetero adducts as pure isomers.

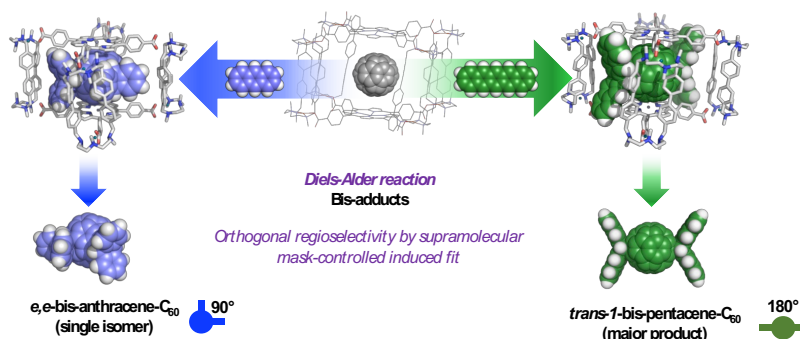


Figure 1. Schematic representation of both host-guest complexes obtained by means of orthogonal Diels-Alder functionalization directed by supramolecular-mask strategy.

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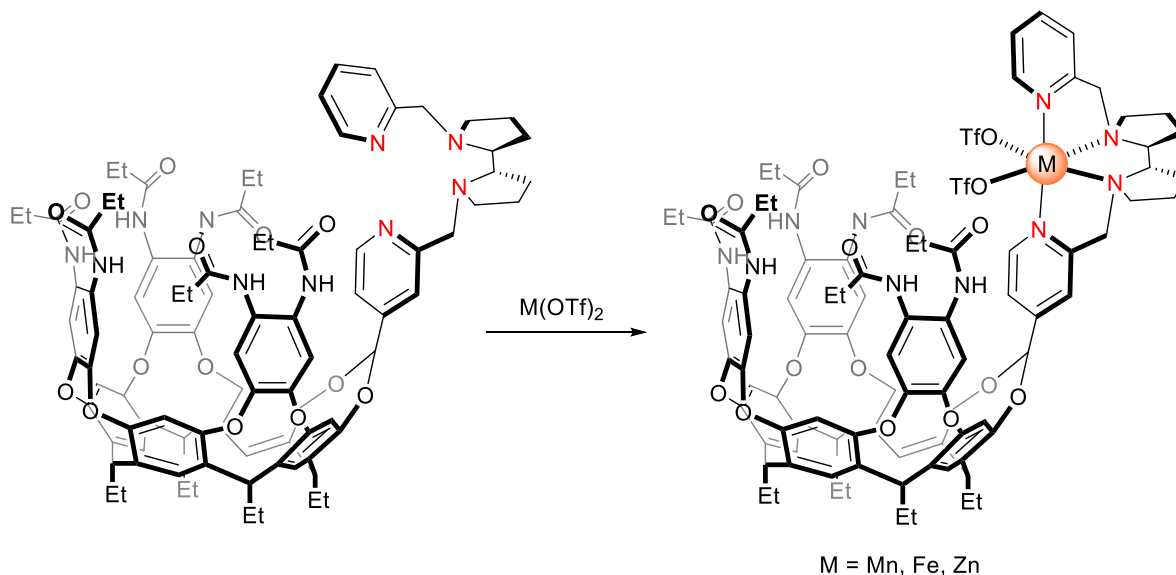
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Biologically inspired C–H hydroxylation catalysis with metallocavitand

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Direct functionalization of unactivated sp³ C–H bonds represents a powerful synthetic tool to construct and diversify molecules. However, due to the presence of multiple C–H bonds with similar bond energy in most organic molecules, precise control of site-selectivity in C–H functionalization remains an arduous task. Instead, secondary coordination sphere from the enzymatic system offers different kinds of subtle interactions for recognizing and pre-organizing the substrates for the selectivity control. Herein, we present a supramolecular approach for the preparation of metallocavitand (M = Mn(II), Fe(II) and Zn(II)) based on a resorcinarene scaffold and functionalization of the tetradentate bis(pyridyl)pyrrolidine (pdp) ligand (Scheme 1). The pdp ligand is connected with acetal bridge in its *para* substituted pyridine position instead of *meta* position from our previous work in order to orientate the metal center closer to the cavity of the cavitand.[1] The cavitand unit is used as receptor for pre-organizing substrates in unique conformations by means of hydrophobic forces. Thus, it reproduces some key features of enzymes in order achieve selectivity control in C–H hydroxylation. The resulting Mn(II)-Metallocavitand complex was tested to be competent in oxidation of unactivated sp³ C–H bonds with hydrogen peroxide under mild condition.



Scheme 1. Preparation of the metallocavitand (M = Mn(II), Fe(II) and Zn(II)) in this work.

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Regioselective bis-functionalization of fullerene C₇₀ via supramolecular masks

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Isomer-pure poly-functionalized fullerenes are required to boost the development of fullerene chemistry in any field, specifically in solar cell design^[1]. Developing new synthetic strategies capable to restrict the regioisomer formation is a challenge, especially for C₇₀, less abundant than C₆₀, and with 8 distinct bonds at which mono-functionalization may occur, leading to a complicate mixture of multiple adducts when functionalized.

In this work we show the regioselective synthesis of bis-C₇₀-adducts upon Bingel cyclopropanation using supramolecular nanocapsules as masks^[2]. In order to deep into the subtle mask-mediated regiofunctionalization, a tetragonal prismatic nanocapsule (C₇₀@(Pd-pp)Cage) and a three shell Matryoshka complex ^[2] (C₇₀@[10]cycloparaphenylene@(Pd-pTp)Cage) have been explored; additionally a series of malonates differing in bulkiness have been tested. Strikingly, a single pure regio-isomer (2 o'clock) of the Bingel bis-adduct of C₇₀ is obtained by using the dibenzyl bromomalonate and the three shell Matryoshka complex, preventing the poly-functionalization and achieving a 100% regioselectivity. Molecular Dynamics simulation have help in rationalizing the experimental results showing that the high regioselectivity is due to the conformation of the 2 o'clock regio-isomer inside the Matryoshka complex.

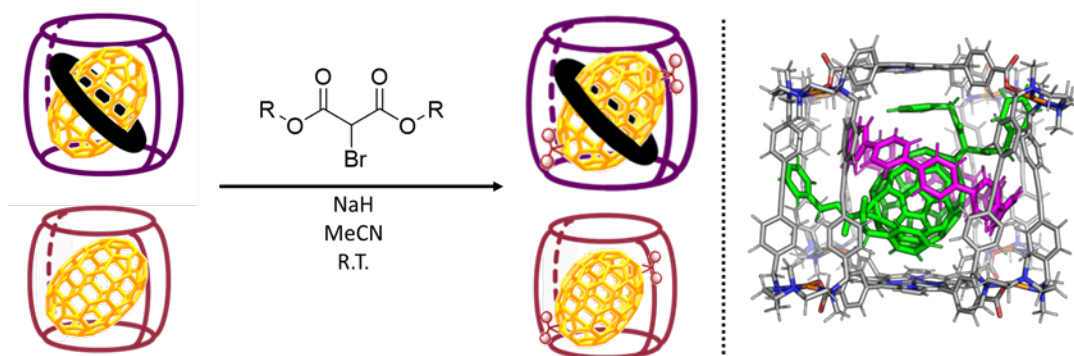


Figure 1. Bingel cyclopropanation of C₇₀ using supramolecular nanocapsules and Matryoshkas as masks. MD Simulation of the (2 o'clock) bis-adduct inside the Matryoshka complex.

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Molecular and hybrid materials based on metallocarboranes

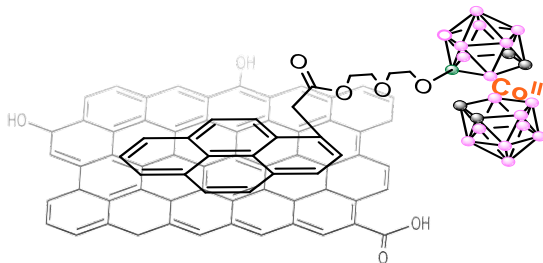
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The design of new catalysts to improve the activity and selectivity of the chemical processes and, at the same time, be compatible with the environment, is challenging. Photoredox catalysis is the right way to mimic nature in efficiency and sustainability^[1]. From the perspective of sustainability and industrial applicability, grafting of homogeneous catalysts on solid support, is a good approach^[2]. Graphene and derivatives, are conjugated systems, with high conductivity and electron mobility, favoring charge separation and electron transport^[3]. Then homogeneous systems supported on graphene, can facilitate the photogenerated electron transfer, leading to an enhance of the photocatalytic activity.

Recently, we have also demonstrated that cobaltabis (dicarbollide), [1]- and derivatives represent efficient homogeneous photoredox catalysts for oxidation processes in water, through Single Electron Transfer processes (SET)^[4]. We prepare polyaromatic hydrocarbons bonded to COSANE and the corresponding heterogeneous catalysts supported on GO in which, the molecular catalyst, is firmly bound to the support by non-bonding interactions. Photocatalytic oxidation processes have been studied using these materials.



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Preparation of carbons with different morphologies from xylose obtained from almond shells: carbon microspheres and ordered mesoporous carbons

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The preparation of carbon materials with different morphologies is becoming an excellent contribution for the valorisation of lignocellulose, the most abundant renewable biomass [1]. Thus, the obtention of spherical carbons and the so-called ordered mesoporous carbons (OMC) is of interest because they can be used as catalytic supports or, after-functionalization, as catalysts [2, 3]. In this work, microspherical carbons and OMC were prepared from commercial xylose and from xylose extracted from lignocellulosic wastes, almond shells, provided by Cooperativa Unió Nuts, Reus.

Carbon microspheres were obtained by hydrothermal treatment with microwaves at 180 °C for 15 or 60 min in acid medium (1 % v/v H₂SO₄.) Comparative experiment with conventional heating did not produce any solid even adding acid medium at the same preparation conditions. Interestingly, when using the xylose extract obtained from almond shells, small carbon microspheres between 1-3 μm were observed by SEM (Figure 1a).

OMCs were prepared mixing the carbon precursor, commercial xylose or xylose extract, and SBA-15 template in a ratio of 6:1 in an acid medium assisted with ultrasounds. Then, the solids were carbonized under N₂ at 650 °C for 2 h. The SBA-15 elimination was performed with NaOH at 90 °C for 24 h. OMC samples presented the 100, 110 and 200-diffraction peaks, confirming the hexagonal inverse structure of SBA-15. TEM micrography allowed us to observe the ordered mesoporous channels of the OMCs (Figure 1b). Also, OMCs exhibited isotherms type IV corresponding to mesoporous materials, high surface BET areas (575-675 m²/g) and high C content (≥ 90 %).

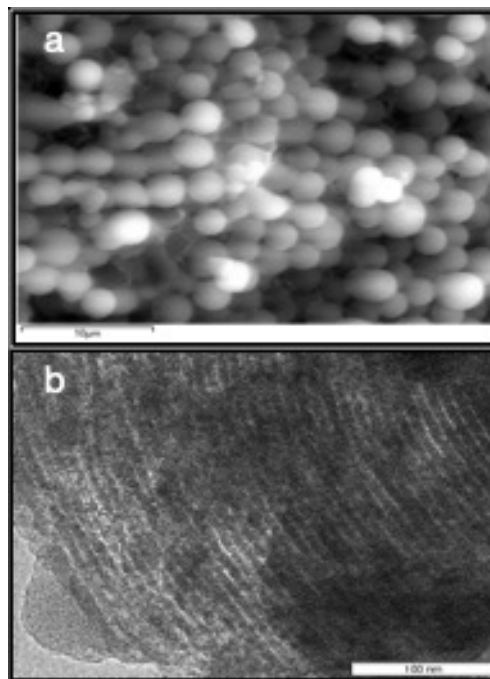


Figure 1. a) SEM image of carbon microspheres and b) TEM image of OMC, both from xylose extract (almond shells).

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Catalitzadors de Ni suportats en carbons mesoporosos ordenats, obtinguts a partir de lignina procedent de biomassa, per a la hidroxidrogenació de guaiacol

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Un procés interessant per a la valorització de residus de biomassa lignocel·lulòsica és la preparació de carbons amb porositat jerarquitzada, anomenats carbons mesoporosos ordenats (CMO), utilitzant plantilles com el SBA-15 [1]. Aquests materials són potencials suports catalítics degut a la seva no toxicitat, degradabilitat i elevada àrea superficial [1]. D'altra banda, una reacció rellevant per a reduir la dependència dels derivats de petroli en el transport és la hidroxidrogenació (HDO) catalítica de lignina per a produir hidrocarburs. Per a estudiar aquesta complexa reacció es fan servir compostos model com el guaiacol que dona lloc a metoxiciclohexanol (MCH), ciclohexanol i ciclohexà com a principals productes quan la HDO es porta a terme a temperatures per sota de 200 °C [2].

En aquest treball s'han preparat i caracteritzat catalitzadors de Ni suportats en CMOs, obtinguts a partir de la fracció de lignina de la closca d'ametlla (Cooperativa Unió Nuts, Reus) amb SBA-15 com a plantilla, per a ser provats en l'HDO de guaiacol. Fig. 1 mostra els principals resultats.

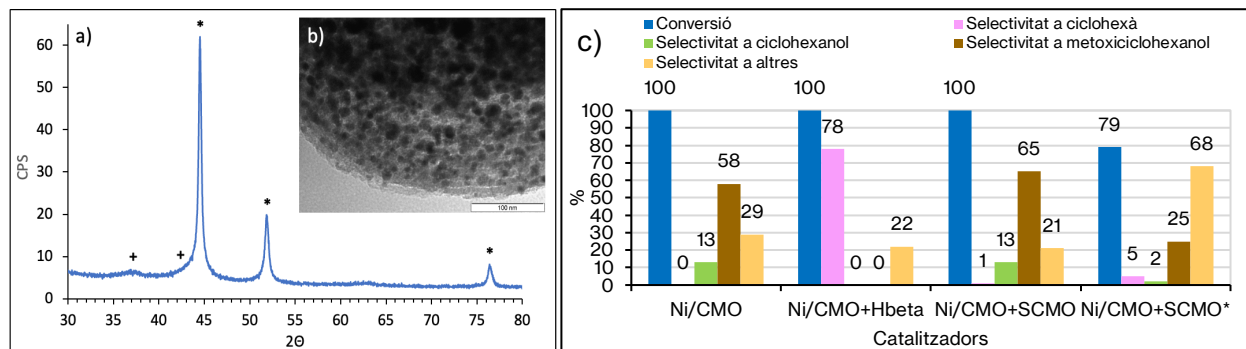


Figura 1. a) Difractograma + NiO i * Ni; b) Micrografia TEM del catalitzador Ni/CMO; c) Resultats catalítics, condicions: 180 °C, 30 bars H₂, 1 h, quantitat: 100 mg Ni/CMO (+ 100 mg H-Beta o 100 o 300* mg SCMO).

DRX, fisisorció de N₂ i TEM van confirmar l'estructura hexagonal dels CMOs preparats a partir de lignina i la presència dels canals mesoporosos ordenats. El catalitzador Ni/CMO, preparat per impregnació d'un CMO (785 m²/g) amb nitrat de níquel (28 % Ni) i calcinat a 450 °C, conté un 90 % de Ni reduït (Fig.1a) demostrant el paper reductor del CMO. TEM va mostrar la bona dispersió de nanopartícules de Ni (10-30 nm) a l'OMC (Fig. 1b). Aquest catalitzador va donar total conversió i selectivitats del 58 % a MCH i 13 % a ciclohexanol (Fig. 1c). Es van afegir centres àcids de Brønsted mitjançant mescla física de H-Beta o CMO sulfonat (SCMO) amb Ni/CMO. La presència de H-Beta va permetre obtenir ciclohexà en un 78 % a conversió total (Fig. 1c) mentre l'addició de SCMO va donar un màxim de 5 % de ciclohexà confirmant l'efecte del nombre i força dels centres àcids a la reacció.

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