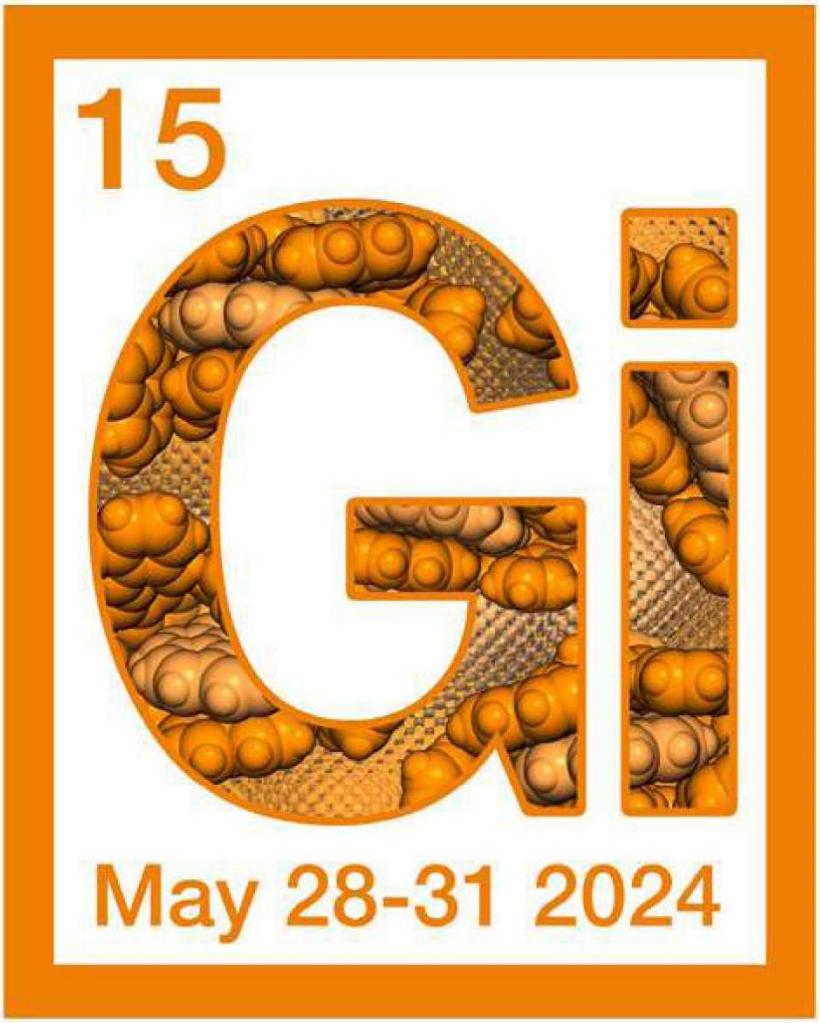



# Abstract's Book

# Welcome letter

Dear colleagues,

On behalf of the organizing committee, it is our pleasure to invite you to the Girona Seminar, and the corresponding Young Researchers Symposium, that will take place in the city of Girona, Catalonia (Spain). The meetings will be held from May 28th to May 31st 2024 at the "La Mercè" Auditorium.

Since 1993, the Institute of Computational Chemistry and Catalysis (IQCC) has been organizing this biannual conference. Early editions were focused on theoretical chemistry, which changed in 2006 when for every seminar a different research topic related to the IQCC interests was chosen. In the last two editions of the Girona Seminar (2018 and 2022) the subthemes were "Transition-Metal Reactivity by Design" and "Biocatalysis". For the next edition in 2024, the topic will be "Supramolecular Chemistry".

The Girona Seminar has an outstanding reputation for excellence and highly engaged discussion, and it has become a focal point for scientists at the forefront of chemistry to present and discuss their latest developments. The meeting also aims at promoting new collaborations and it brings together young and senior scientists in a beautiful environment and in an informal and friendly atmosphere.

In order to put special emphasis on the research of young researchers, prior to the main meeting there will be a one-day Young Researchers Symposium. This symposium will be organized for, and by, PhD students in order to showcase their results, and we encourage all participants of the Girona Seminar to also attend this symposium.

We hope to count on your participation to contribute to this meeting.

Best regards,

**The Organizing Committee**

# Organizing and Scientific Committee

**Agustí Lledó**
Associate Professor
Universitat de Girona

**Xavi Ribas**
Professor
Universitat de Girona

**Silvia Osuna**
ICREA Research Professor
Universitat de Girona

**Anna Pla**
Associate Professor
Universitat de Girona

# Young Researchers Symposium

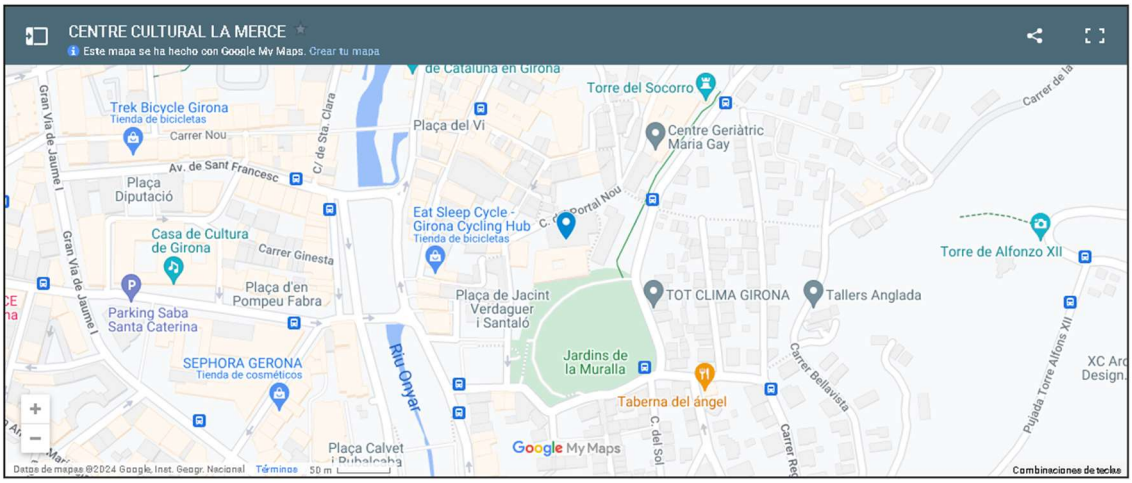
**Albert Artigas**
IQCC Research postdocs
Universitat de Girona

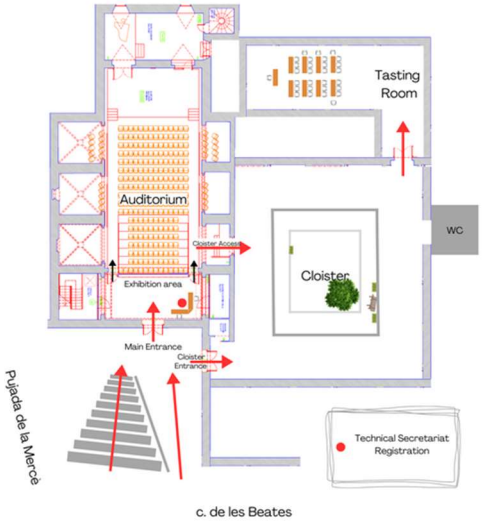
**Carles Fuertes**
IQCC Research postdocs
Universitat de Girona

# Venue

Girona Seminar 2024 will be held in Girona at the **Auditori of Centre Cultural la Mercè**, located in the city centre.

Address: Pujada de la Mercè, 12, 17004 Girona



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## May 28th, 2024

| | |
|---|---|
| **10:45** | **Opening Ceremony** |
| 11:00 | Computational Analysis Of C(Sp)-C(Sp) Bond Oxidative Addition To Macrocyclic Pincer Complexes - **N. Roig** |
| 11:15 | Selective Host-Guest Interactions in Aryl-Extended Calix[4]pyrrole Nanocages: A Computational Study - **E. Garcia** |
| 11:30 | Enhancing Catalysis and Selectivity through the Dynamic Control of Confined Spaces: Insights from Enzymatic to Synthetic Catalyst Systems - **G. Casadevall** |
| | **coffee break** |
| 12:15 | Non-Templated Assembly of Five-Membered Pd5L10 Rings - **L. Neukirch** |
| 12:30 | Metal-Organic Polyhedra As Porous Molecular Nanoparticles - **L. Hernández-López** |
| 12:45 | Regio-Functionalization Of Fullerenes By Diels-Alder Reaction Via Supramolecular Mask Strategy - **T. Pèlachs** |
| | **lunch** |
| 14:30 | Binding Of Aliphatic Diformamides By An Octa-Imine Bis-Calix[4]Pyrrole Cage: Thermodynamic And Kinetic Characterization - **Y. Li** |
| 14:45 | Terpene Cyclization Inside An Asymmetric Cavitand - **R. López** |
| 15:00 | New Electrically And Optically Active Molecular Materials Characterized By Synchrotron Circular Dichroism - **G Pancotti** |
| 15:15 | Transformation and self-sorting in azulene-based coordination cages - **A. Walther** |
| | **coffee break** |
| 15:45 | Interlocked Chromophores: Design And Synthesis - **G. Cutillas** |
| 16:00 | Novel Interlocked Organocatalysts Based On Hydrogen-Bond Donors - **J. Puigcerver** |
| 16:15 | BODIPY-functionalized silicon oxide microchips for intracellular glutathione (GSH) sensing - **S. Bagherpour** |
| 16:30 | Designing A Surfactant Trap Using Molecular Cages - **M. Pérez** |
| 16:45 | **Round Table** |
| 17:15 | **Closing Ceremony** |

15

## May 29th, 2024

| | |
|---|---|
| 8:45 | **Opening Ceremony** |
| 9:00 | Mechanically Chiral Molecules: Synthesis and Applications - **Steve Goldup** (Keynote Speaker) |
| 9:30 | Neutral Metallocontainers For Anion Recognition - **D. Van Craen** |
| 9:50 | Polymorph Transitions In Supramolecular Polymers - **B Soberats** |
| 10:10 | Flow Chemistry As A Tool For Supramolecular Research - **Anna Slater** (Keynote Speaker) |
| | **10:40 - coffee break** |
| 11:10 | Supramolecular Control: Strategic Uses of Carbon Nanohoops, Fluorinated Cyclohexanes and Organophosphates - **Max von Delius** (Keynote Speaker) |
| 11:40 | Supramolecular Peptide-Based Materials As Optical Waveguides Components- **A.M. García Fernández** |
| 12:00 | Controlling Self-Sorting In Dynamic Assembly: Stimuli-Responsive Multi-Cage Systems - **E. Benchimol** |
| 12:20 | Molecular Wires & Nanorings - **Harry Anderson** (Plenary Speaker) |
| | **13:10 - lunch** |
| 15:10 | Acceleration of Cycloaddition Reactions by Inclusion in a [4+2] Octaimine BiSCAlix[4]Pyrrole CaGe - **Pablo Ballester** (Keynote Speaker) |
| 15:40 | Regioswitchable Bingel Bis-Functionalization Of Fullerene C70 Via Supramolecular Masks - **V. Iannace** |
| 16:00 | Short Peptides As Versatile Building-Blocks For Multicomponent Supramolecular Materials - **B. Escuder** |
| 16:20 | Clip-off Chemistry: Synthesis by Bond Cleavage - **Daniel Maspoch** (Plenary Speaker) |
| 17:10 | **Poster Session** |

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## May 30th, 2024

9:00 Old macrocycles doing new tricks - unexpected modes of interactions of resorcinarenes - **Agnieszka Szumna** (Keynote Speaker)

9:30 Self-Assembled Nanotubes Based On Amidinium-Carboxylate Interactions In Water - **F. Aparicio**

9:50 Regulated Transfer Of Chemical Information Using Stimuli-Responsive Squaramides - **L. Martínez Crespo**

10:10 Supramolecular machinery for disequilibrating azobenzenes - **Rafal Klajn** (Plenary Speaker)

**11:00 - coffee break**

11:30 Carbon Nanotubes, 2D Materials, and Single-molecule Supramolecular Chemistry. A Multidimensional Approach to Nanochemistry- **Emilio Pérez** (K. Speaker)

12:00 Remote Amino Acid Recognition Enables Effective Hydrogen Peroxide At A Manganese Oxidation Catalyst - **L. Vicens**

12:20 Chemical Fueling Of Dynamic Covalent Networks Features Endergonic Adaptation - **S. Al Shehimy**

12:40 Supramolecular Chemistry Guiding Cell-Chip Interactions - **M. Lluisa Pérez Garcia** (Plenary Speaker)

**13:30 - lunch**

15:00 **Social Events**

City Tour: 14:30 - 16:00 → 1st group
16:00 - 17:30 → 2nd group
17:30 - 19:00 → 3rd group

Tastings: 16:00 - 17:30 → Ratafia
17:30 - 19:00 → Wines

May 28-31 2024

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## May 31th, 2024

| | |
|---|---|
| 9:00 | Molecules in Metal Boxes - **Jonathan Nitschke** (Plenary Speaker) |
| 9:50 | Computational/Experimental Symbiosis in the Design of Supramolecular Peptide Architectures - **I. Sasseli** |
| 10:10 | Kinetic Control Of Supramolecular Systems Through Dynamic Covalent Chemistry Of Tetrazines - **R. Carrillo** |
| 10:30 | Modulation Of Fe(Iv) Oxo Reactivity Via Supramolecular Recognition - **G. Olivo** |

**10:40 - coffee break**

| | |
|---|---|
| 11:20 | Computational Modelling of Supramolecular Metallo-Organic Cages: Challenges and Opportunities - **Fernanda Duarte** (Keynote Speaker) |
| 11:50 | Novel Advances in Mechanical Bond-Controlled Reactions in [2]Rotaxanes - **J. Berná** |
| 12:10 | Quantification of Carboxylate-π Interactions in Water - **M. Petroselli** |
| 12:30 | Catalysis inside supramolecular capsules: From terpene cyclizations to β-selective glycosylations - **Konrad Tiefenbacher** (Plenary Speaker) |

**13:20 - lunch**

| | |
|---|---|
| 15:20 | TowArds funtional SElf-assembled α,γ-cyclic peptides - **Juan Granja** (Keynote Speaker) |
| 15:50 | Unravelling The Real-Time Dynamics Of Hydrogen-Bonding Molecular Shuttles - **G. Tobajas** |
| 16:10 | Origin of Rate Enhancement by Metallocages: A Molecular Description - **G. Ujaque** |
| 16:30 | Host-Guest Chemistry Within Smart Porphyrin Cages - **F. Guijarro** |
| 16:50 | Peptide-BASED self-assembled AND stimuli-responsive systems - **Elena Pazos** (Keynote Speaker) |
| 17:20 | **Closing Ceremony** |

20:30 *Gala Dinner*

May 28-31 2024

# Program

**Plenary**

Anderson, Harry L.
Klajn, Rafal
Maspoch, Daniel
Nitschke, Jonathan R.
Pérez-Garcia, Lluïsa
Tiefenbacher, Konrad

**Keynote**

Ballester, Pablo
Duarte, Fernanda
Granja, Juan R.
Goldup, Stephen M.
Pazos, Elena
Perez, Emilio
Slater, Anna G.
Szumna, Agnieszka
von Delius, Max

**Oral communications**

Al Sheshimi, Shaymaa
Aparicio, Fátima
Bagherpour, Saman (YRS)
Benchimol, Elie
Berná, J.
Carrillo, Romen
Casadevall, Guillem (YRS)
Cutillas-Font, Guillermo (YRS)
Escuder, Beatriu
García, A. M.
García-Padilla, Eduardo (YRS)
Guijarro, Fernando G.
Hernández-López, Laura (YRS)
Iannace, Valentina
Li, Yifan (YRS)
López, Ricard (YRS)
Martínez-Crespo, Luis
Neukirch, Laura (YRS)
Olivo, Giorgio
Pancotti, Giulia (YRS)
Pèlachs, Tània (YRS)
Pérez-Ferreiro, María (YRS)

Petroselli, Manuel
Puigcerver, Julio (YRS)
Roig, Nil (YRS)
Sasselli, Iván R.
Soberats, Bartolome
Tobajas-Curiel, Gloria
Ujaque, Gregori
Van Craen, David
Vicens, Laia
Walther, Alexandre (YRS)

**Poster**

Ahsan, Faiza
Artigas, Albert
Berga, Cristina
Bhaskaran, Athul Santha
Bonachea, Mario
Call, Arnau
Capdevila, Lorena
Christou, Christos
Diack, Y.
Esteve, Ferran
Esteve-Nebot, Lorenzo
Fuertes-Espinosa, Carles
Hebenbrok, Lars
Kalarikkal, Malavika G.
La Manna, Martina
Lopatina, Yaroslava
Luizaga, Jonnely
Marchi-Luciano, Hugo
Martínez-Cuezva, Alberto
Monreal-Corona, Roger
Ocklenburg, David
Ortiz-Garcia, Thalia
Rieu, Tangui
Sabrià, Clara
Sala, Judith
Sethuraman, Muthuramalingam
Sight, Misthi
Skorynia, A.
Solà, Miquel
Valdés, Hugo
Vila-Siles, Guillem

# Plenary speakers

15 Girona Seminar
May 29-31 2024

# MOLECULAR WIRES & NANORINGS

Harry L. Anderson

*Oxford University, Department of Chemistry, Oxford OX1 3TA, United Kingdom*
*e-mail: harry.anderson@chem.ox.ac.uk*

Porphyrins are versatile redox-active building blocks for the construction of molecular wires and their small reorganization energies lead to low barriers for charge transport.[1,2] For example, the linear porphyrin octamer shown in Fig. 1a was connected across a graphene nanogap to give a single-molecule transistor displaying coherent transport.[1] On the other hand, coherent transport in the butadiyne-linked 12-porphyrin nanoring (Fig. 1b) was demonstrated by its global aromatic ring currents.[2] Recent work on π-conjugated porphyrin arrays will be presented.

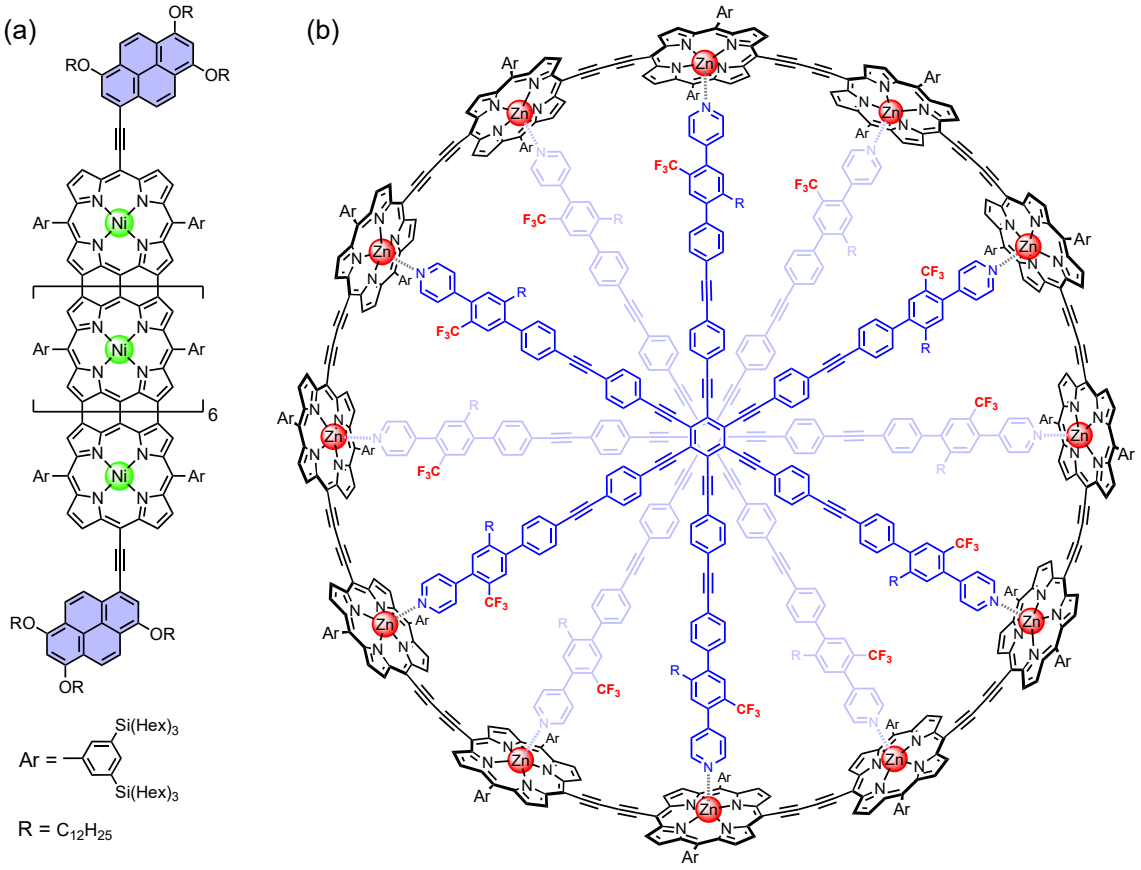


Figure 1. (a) A porphyrin octamer nanoribbon used as a single-molecule transistor,[1] and (b) a 12-porphyrin nanoring displaying global aromatic ring currents.[2]

**References**
1) Chen, Z., et al. *J. Am. Chem. Soc.* **2023**, *145*, 15265–15274.
2) Rickhaus, M., et al. *Nat. Chem.* **2020**, *12*, 236–241.

# SUPRAMOLECULAR MACHINERY FOR DISEQUILIBRATING AZOBENZENES

Rafal Klajn *

*Addresses list: Institute of Science and Technology Austria (ISTA), 3400 Klosterneuburg, Austria*
*e-mail: rafal@ist.ac.at*

DisEquilibration by Sensitization under Confinement (DESC) is a supramolecular approach to isomerize photoswitchable molecules from the stable state to the metastable state using visible light of the desired wavelength (including red light). In this talk, I will show that a combination a coordination cage and a visible-light sensitizer can act together to selectively bind and sensitize the *E* isomer of various azobenzenes and other azo switches.[1] Upon switching to the metastable *Z* isomer the azoarene loses its affinity to—and is expelled from—the cage which can then convert additional copies of *E* into *Z*. In this way the cage·sensitizer complex acts as a light-driven supramolecular machine converting light energy into chemical energy in the form of out-of-equilibrium photostationary states that cannot be accessed directly using visible light.

**References**

1) J. Gemen, J. R. Church, T.-P. Ruoko, N. Durandin, M. J. Białek, M. Weißenfels, M. Feller, M. Kazes, M. Odaybat, V. A. Borin, R. Kalepu, Y. Diskin-Posner, D. Oron, M. J. Fuchter, A. Priimagi, I. Schapiro, R. Klajn, *Science* **2023**, *381*, 1357

Plenary speaker

# CLIP-OFF CHEMISTRY: SYNTHESIS BY BOND CLEAVAGE

Daniel Maspoch

*Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology Campus UAB, Bellaterra, 08193 Barcelona (Spain); Departament de Química, Facultat de Ciències, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain; ICREA Pg. Lluís Companys 23, 08010 Barcelona (Spain), daniel.maspoch@icn2.cat*

Historically, innovations in synthetic methods and reactions have changed the way scientists think about designing and synthesizing materials and molecules. Indeed, novel synthetic methods not only unlock access to previously unattainable structures, but also inspire new concepts as to how we design and build materials to address global social, economic and industrial needs. In this talk, I will present the concept of bond breaking as a new synthetic methodology that we have named Clip-off Chemistry. Unlike most state-of-the-art synthetic approaches, which use bottom-up strategies to link atoms and molecules through the formation of new bonds, Clip-off Chemistry is based instead on the selective cleavage of existing bonds in molecules and materials, providing precise spatial control over bond cleavage. Therefore, Clip-off Chemistry represents a new synthetic methodology, whereby the programmed selective disassembly affords new molecules and materials. This disassembly occurs at the molecular level through a chemical reaction; in a first approach, through ozonolysis, a gas/solid reaction that enables cutting of constituent organic molecular building blocks or linkers via direct cleavage of their alkene bonds. In this talk, I will show the principles of Clip-off Chemistry and the first examples of structures and molecules synthesized through controlled bond fission in reticular materials (ie. MOFs, macrocycles and cages).

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# MOLECULES IN METAL BOXES

Jonathan R. Nitschke

*Yusuf Hamied Department of Chemistry, University of Cambridge, UK*
*e-mail:jrn34@cam.ac.uk*

Simple organic subcomponents can come together around metal-ion templates to produce intricate hollow capsules,[1] which can bind guest molecules selectively. This talk will describe the design and uses of some of these three-dimensional architectures, a few of which are shown in Figure 1 below, along with the use of the same construction principles to produce interlocked structures – catenanes[2] and knots[3] – and double-helical metallopolymers with potentially useful optoelectronic properties.[4]

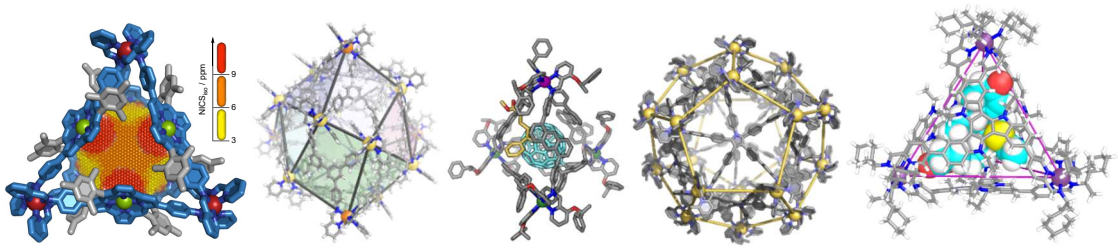



**Figure 1.** From left to right: an antiaromatic-walled cage;[5] a capsule isomorphous to ferritin;[6] a capsule capable of stereoselectively functionalizing fullerenes,[7] a dodecahedral capsule with enough interior volume to house a small protein,[8] and a capsule that discriminates between and selectively binds steroids.[9]

**References**

[1] D. Zhang, T. K. Ronson, J. R. Nitschke, *Acc. Chem. Res.* **2018**, *51*, 2423-2436.
[2] C. S. Wood, T. K. Ronson, A. M. Belenguer, J. J. Holstein, J. R. Nitschke, *Nature Chem.* **2015**, *7*, 354-358.
[3] J. P. Carpenter, C. T. McTernan, J. L. Greenfield, R. Lavendomme, T. K. Ronson, J. R. Nitschke, *Chem* **2021**, *7*, 1534-1543.
[4] J. L. Greenfield, D. Di Nuzzo, E. W. Evans, S. P. Senanayak, S. Schott, J. T. Deacon, A. Peugeot, W. K. Myers, H. Sirringhaus, R. H. Friend, J. R. Nitschke, *Adv. Mater.* **2021**, *33*, 2100403.
[5] M. Yamashina, Y. Tanaka, R. Lavendomme, T. K. Ronson, M. Pittelkow, J. R. Nitschke, *Nature* **2019**, *574*, 511-515.
[6] J. A. Davies, T. K. Ronson, J. R. Nitschke, *Chem* **2022**, *8*, 1099-1106.
[7] Z. F. Lu, T. K. Ronson, A. W. Heard, S. Feldmann, N. Vanthuyne, A. Martinez, J. R. Nitschke, *Nature Chem.* **2023**, *15*, 405-412.
[8] K. Wu, T. K. Ronson, P. Su, Z. Chen, L. Goh, A. W. Heard, X. Li, F. Klautzsch, C. A. Schalley, M. Vinković, J. R. Nitschke, *Nature Synth.* **2023**, *2*, 789-797.
[9] G. Li, T. K. Ronson, R. Lavendomme, Z. Huang, C. Fuertes-Espinosa, D. Zhang, J. R. Nitschke, *Chem* **2023**, *9*, 1549-1561.

15 Girona Seminar May 29-31 2024

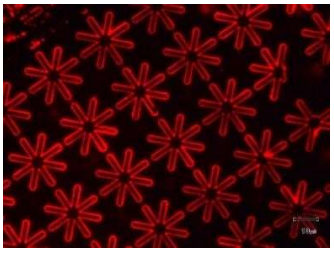
# SUPRAMOLECULAR CHEMISTRY GUIDING CELL-CHIP INTERACTIONS

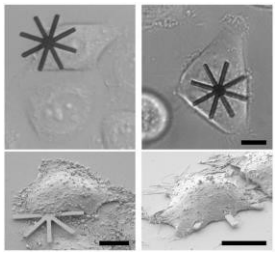
Lluïsa Pérez-García

*Departament de Farmacologia, Toxicologia i Química Terapèutica, Facultat de Farmàcia i Ciències de l'Alimentació, Universitat de Barcelona, Avda. Joan XXIII 27-31, 08028 Barcelona, Spain.*

*Institut de Nanociència i Nanotecnologia UB (IN2UB), Universitat de Barcelona, Spain e-mail: mlperez@ub.edu*

Cell adhesion, internalization, and intracellular actuation are crucial in medicinal chemistry and pharmacology, enabling precise diagnosis and treatment at the cellular level. Molecular recognition is at the core of all those biological interactions and governs target-directed pharmacological therapeutic strategies.[1] More recently, a great deal of attention has been devoted to study the interaction of biological entities with nanostructured materials, which has led to advances in the field of Nanomedicine.[2] However, the interface between micromaterials and living cells is not so well understood.[3] Over the years, our group has worked on the functionalization of silicon-based microchips, with the objective of developing new tools to interact with living cells. In the talk, some examples of this interaction will be described, such as those directed to individual cell tagging or intracellular sensing, revealing the supramolecular nature of the cell-microchip interaction,[4] and pushing the design of new intracellular sensors and actuators.





1) C. Bissantz, B. Kuhn, M. Stahl, J. Med. Chem. 2010, 53, 5061–5084; DOI: 10.1021/jm100112j.
2) C. Domingues, A. Santos, C. Alvarez-Lorenzo, A. Concheiro, I. Jarak, F. Veiga, I. Barbosa, M. Dourado, A. Figueiras, ACS Nano 2022, 16, 9994–10041; DOI: 10.1021/acsnano.2c00128
3) V. B. Juska, G. Maxwell, P. Estrela, M. E. Pemble, A. O'Riordan, Biosensors and Bioelectronics 2023, 237, 115503; DOI: https://doi.org/10.1016/j.bios.2023.115503
4) M. I. Arjona, M. Duch, A. Hernández-Pinto, P. Vázquez, J. P. Agusil, R. Gómez-Martínez, M. Redondo-Horcajo, E. Amirthalingam, L. Pérez-García, T. Suárez, J. A. Plaza, Adv. Mater. 2022, 2109581; DOI: 10.1002/adma.202109581.

Acknowledgement: This work was supported with funds from the Spanish Government Grant PID2020-115663GB- C32 funded by MCIN/AEI/10.13039/501100011033. We also thank AGAUR (Generalitat de Catalunya) for a grant to consolidated research groups 2021 SGR 01085.

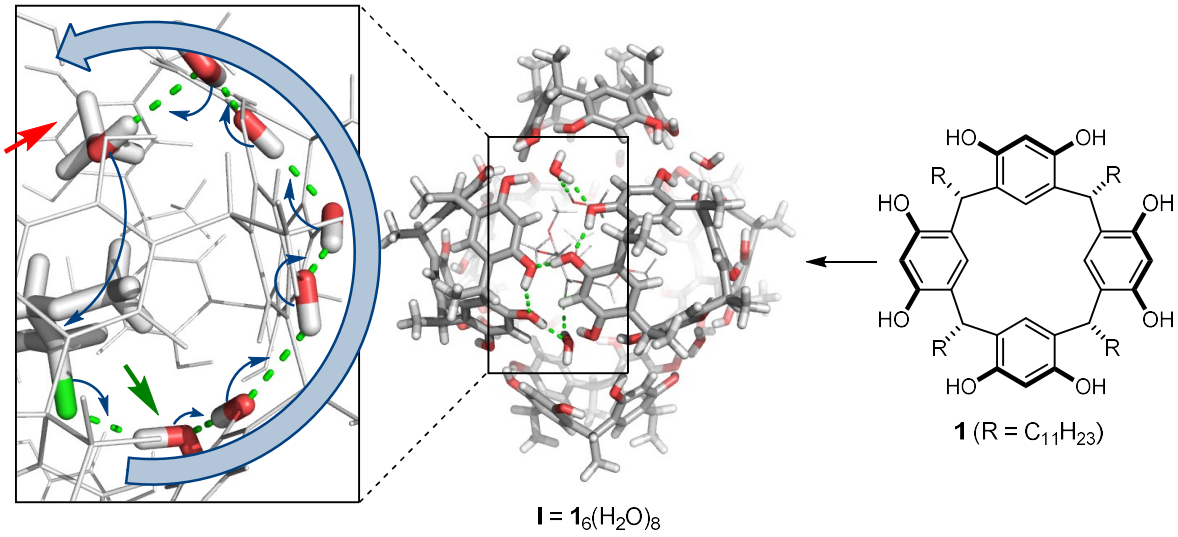
Plenary speaker

# CATALYSIS INSIDE SUPRAMOLECULAR CAPSULES: FROM TERPENE CYCLIZATIONS TO B-SELECTIVE GLYCOSYLATIONS

Konrad Tiefenbacher[a,b]

[a] *Department of Chemistry, University of Basel, Mattenstrasse 24a, CH-4058 Basel, Switzerland.*
[b] *Department of Biosystems Science and Engineering, ETH Zurich, Mattenstrasse 26, CH-4058 Basel, Switzerland.*
*E-mail: konrad.tiefenbacher@unibas.ch*

My group is interested in exploring catalysis inside supramolecular containers. Our main focus has been the hexameric resorcin[4]arene capsule (see below), originally reported by the Atwood group.[1] It has served us as a reliable catalyst for a variety of acid-catalyzed cationic reactions ranging from simple acetal hydrolysis to more complex iminium catalysis and terpene cyclizations. Investigations revealed that related molecular capsules are not competent in these reactions. The most recent results concerning terpene cyclizations will be presented. [2,3] Furthermore, very recently published, as well as unpublished, results concerning stereoselective glycosylations inside the hexameric resorcin[4]arene capsule will be discussed. [4] An unusual proton wire mechanism is likely at work (see below).




**I** = **1**$_6$($H_2O$)$_8$ **1** (R = $C_{11}H_{23}$)

**References**
1) L. R. MacGillivray, J. L. Atwood *Nature* **1997**, *389*, 469.
2) L.-D. Syntrivanis, I. Némethová, D. Schmid, S. Levi, A. Prescimone, F. Bissegger, D. T. Major, K. Tiefenbacher *J. Am. Chem. Soc.* **2020**, *142*, 5894.
3) I. Némethová, D. Schmid, K. Tiefenbacher *Angew. Chem. Int. Ed.* **2023**, *accepted.*
4) T-R. Li, F. Huck, GM. Piccini, K. Tiefenbacher *Nat. Chem.* **2022**, *14*, 985.

# Keynote speakers

# ACCELERATION OF CYCLOADDITION REACTIONS BY INCLUSION IN A [4+2] OCTAIMINE BISCALIX[4]PYRROLE CAGE

Pablo Ballester

*ICREA, Passeig Lluís Companys, 23, 08010-Barcelona, Spain*
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The azide-alkyne Huisgen 1,3-dipolar cycloaddition was accelerated in the cavity of a cucurbit[6]uril[1] and a self-assembled dimeric capsule derived from a resorcin[4]arene cavitand.[2] In both cases, the regioselectivity of the reaction was also altered providing exclusively the 1,4-cycloaddition isomer. In this presentation, I will describe the self-assembly of a [4+2] octa-imine capsule based on calix[4]pyrrole and its application as a supramolecular reaction vessels.[3,4] I will show that the dynamic covalent capsule promotes the cycloaddition reaction between two pyridine-*N*-oxide derivatives properly functionalized with azide and ethynyl groups at their *para*-positions. The reactants are bound in the polar capsule's cavity by establishing mainly hydrogen bonding interactions between the oxygen atom of the pyridine *N*-oxides and the pyrrole NHs of the calix[4]pyrrole hemispheres. The formed hetero-ternary complex results in a constrained convergence of the *p*-pyridyl substituents favoring their reaction and the exclusive formation of the 1,4-isomer. I will also report on: a) the measured changes in reaction rates using different conditions and b) the calculation of the rate constant of the reaction taking place inside the capsule and c) its comparison with that in the bulk solution and in other molecular vessels scaffolds.

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Keynote speaker

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# COMPUTATIONAL MODELLING OF SUPRAMOLECULAR METALLO-ORGANIC CAGES: CHALLENGES AND OPPORTUNITIES

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Nature demonstrates how simple molecular building blocks can self-organize to create systems with enhanced or entirely novel functionalities. This phenomenon has inspired chemists to replicate such behaviour using simpler assemblies. Among supramolecular structures, metallo-organic assemblies stand out for their versatility, modularity, and synthetic simplicity. Metal-ligand interactions enable the formation of supramolecular structures not easily achievable through traditional covalent chemistry and find applications in separation, transport, delivery, and catalysis. However, the process of identifying the appropriate building block for a specific application remains a time-consuming and primarily trial-and-error endeavour.[1]

This talk will discuss current challenges and opportunities in the field and our ongoing efforts to establish systematic and widely accessible protocols to advance supramolecular modelling, with a focus on elucidating the key features that make these assemblies effective catalysts. We will illustrate how combined molecular modelling and experimental work has enabled us to gain insights into the factors governing selectivity and catalytic activity in Diels-Alder and Michael addition reactions within supramolecular [Pd2L4]4+ cages, helping to guide future designs.[2] Furthermore, we will outline the methodology developments that have enabled us to automate the characterisation of these systems and streamline laborious computational modelling.[3]

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Keynote speaker

# TOWARDS FUNTIONAL SELF-ASSEMBLED α,γ-CYCLIC PEPTIDES

Juan R. Granja, Victoria López-Corbalán, Ezequiel Mondragón, Alberto Fuertes, Manuel Amorín

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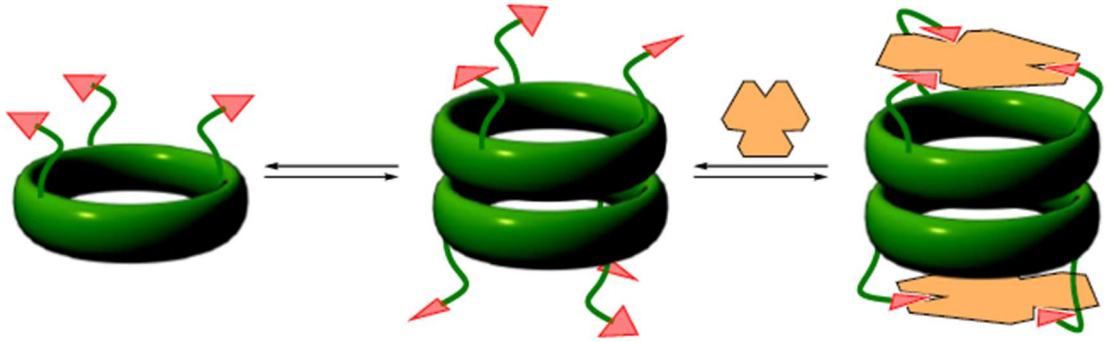
Self-assembled α,γ-cyclic peptides are powerful tools for the supramolecular construction of certain types of structures with precise control of shape, dimensions and properties.[1] In recent years, our group has been able to develop a variety of functional supramolecular materials based on this type of compounds; whose properties range from molecular tweezers[2] or capsules[3] to ion transporters.[4]

In this communication we will describe our latest findings in the developing of functional supramolecular receptors in which the synthetic design of basic components, their dynamism and competition between molecular recognition and self-assembly, play a determinant role.



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Keynote speaker

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# MECHANICALLY CHIRAL MOLECULES: SYNTHESIS AND APPLICATIONS

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Interlocked molecules can display forms of stereochemistry that do not rely on classical covalent stereogenic units, including many examples that have yet to be realised in chemical form.[i] We have pioneered the use of a "small" macrocycle[ii,iii] mediated active template[iv] reaction in combination with covalent chiral auxiliaries in order to allow the synthesis of mechanically planar chiral rotaxanes[v,vi,vii] and chiral catenanes (Figure 1),[viii] as well as discovering new forms of mechanical stereochemistry.[ix,x,xi,xii] In this lecture I will describe our recent efforts to improve access to these intriguing molecules, and their applications in enantioselective sensing and catalysis.[xiii]

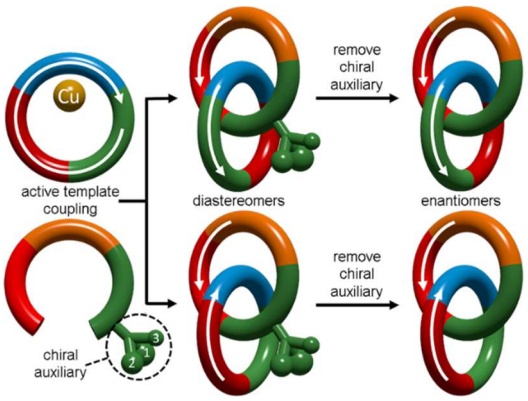


**Figure 1**. Schematic representation of our auxiliary approach to a topologically chiral catenane.

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# PEPTIDE-BASED SELF-ASSEMBLED AND STIMULI-RESPONSIVE SYSTEMS

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Peptides and proteins are natural polymers that perform a myriad of functions in biological systems. Among others, they play an important role as structural and signaling molecules thanks to their self-assembling and molecular recognition capabilities. Moreover, these biopolymers offer the greatest structural and functional versatility, combined with synthetic simplicity, and intrinsic biocompatibility and biodegradability. Consequently, it is not surprising that these polymers have been widely used for the development of new drugs,[1] biosensors,[2] or even for designing a large range of nanomaterials.[3]

Over the last years, our group has focused on the use of peptide platforms as the basis for the design of different conjugates with potential biomedical applications.[4]-[7]. In this lecture, our latest achievements in the application of peptide-conjugates to obtain self-assembled or stimuli-responsive systems will be presented.


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# CARBON NANOTUBES, 2D MATERIALS, AND SINGLE-MOLECULE SUPRAMOLECULAR CHEMISTRY. A MULTIDIMENSIONAL APPROACH TO NANOCHEMISTRY

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Our research group is interested in three main lines: 1) the modification of carbon nanotubes through mechanical bonding, 2) the chemistry of 2D materials, and 3) supramolecular chemistry at the level of single molecules. In this seminar, I will present a brief summary of each of the lines, with a broad introduction to the concepts that will be addressed.

I will first discuss the characteristics of the mechanical bond that make it appealing for SWNTs. I will then describe the potential advantages of making mechanically-interlocked derivatives of SWNTs (MINTs), as compared to covalent or classic supramolecular derivatives of SWNTs,[1] and go on to explain our approach for the synthesis of MINTs.[2,3] Finally, I will illustrate with examples how the making of MINTs can contribute to modifying the surface properties of SWNTs,[4] modulating their electronic properties,[5] and linking them to functional molecular fragments.[6,7]

In the 2D materials field, I will describe the covalent grafting of 2H-MoS2 flakes on graphene monolayers embedded in field-effect transistors.[8] A bifunctional molecule was used that features a maleimide and a diazonium functional group, known to connect to sulfide- and carbon-based materials, respectively. MoS2 flakes were first exfoliated, functionalized by reaction with the maleimide moieties, then anchored to graphene through the diazonium groups. This approach enabled the simultaneous functionalization of several devices. The electronic properties of the resulting heterostructure are shown to be dominated by the MoS2–graphene molecular interface.

I will also discuss the journey that has led to these results, including the development of a “click” chemistry reaction for transition metal-dichalcogenides,[9-11] and insights into the covalent patterning of graphene.[12-14]

Finally, I will describe our endeavors to study supramolecular systems at the single-molecule level, using optical tweezers.[15] In particular I will focus on the study of H-bonded molecular shuttles.[16]

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Keynote speaker

# FLOW CHEMISTRY AS A TOOL FOR SUPRAMOLECULAR RESEARCH

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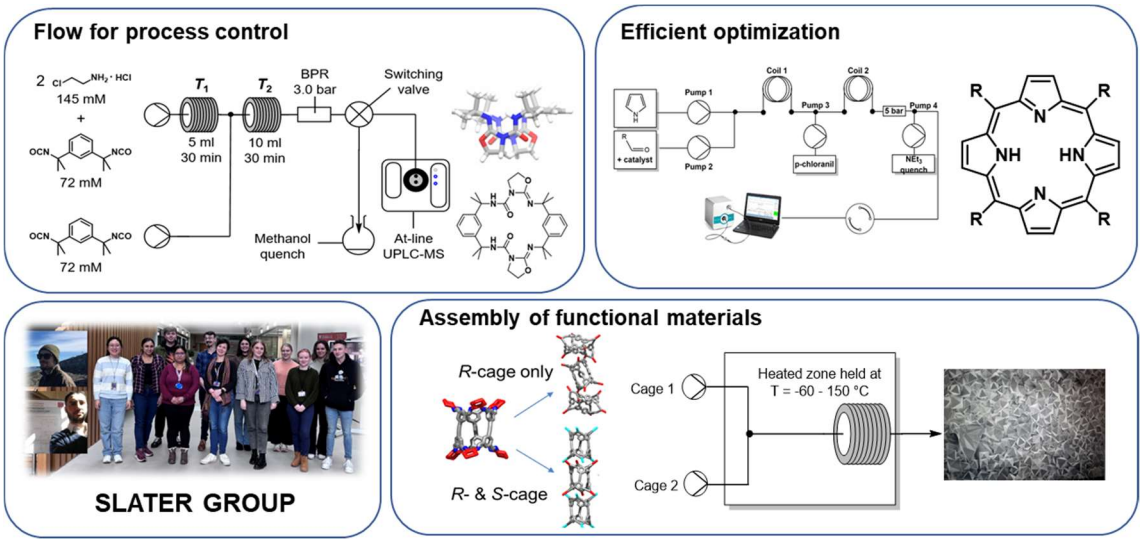
The design and application of supramolecular materials and complexes is continually evolving, but their synthesis and scale-up is still challenging. When dealing with reversible, multi-component chemical processes that exploit weak interactions, reaction conditions can have a significant effect on yield and selectivity. Insufficiently controlled reaction conditions ultimately impact reproducibility, scalability, and sustainability of supramolecular processes, limiting understanding as well as translation activities.

In this talk, I will present continuous flow chemistry as a tool that can alleviate these challenges, and that supramolecular chemistry is particularly well-suited to benefit from.[1][2] By describing case studies of organic cage,[3] macrocycle,[4][5] and molecular knot synthesis,[6] and the continuous crystallisation of organic materials,[7][8] I will illustrate the steps taken and the available benefits. Finally, I will briefly present an outlook on future perspectives for the field, including opportunities in non-thermal plasma,[9][10] automation and autonomous optimization.

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Keynote speaker

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# OLD MACROCYCLES DOING NEW TRICKS – UNEXPECTED MODES OF INTERACTIONS OF RESORCINARENES

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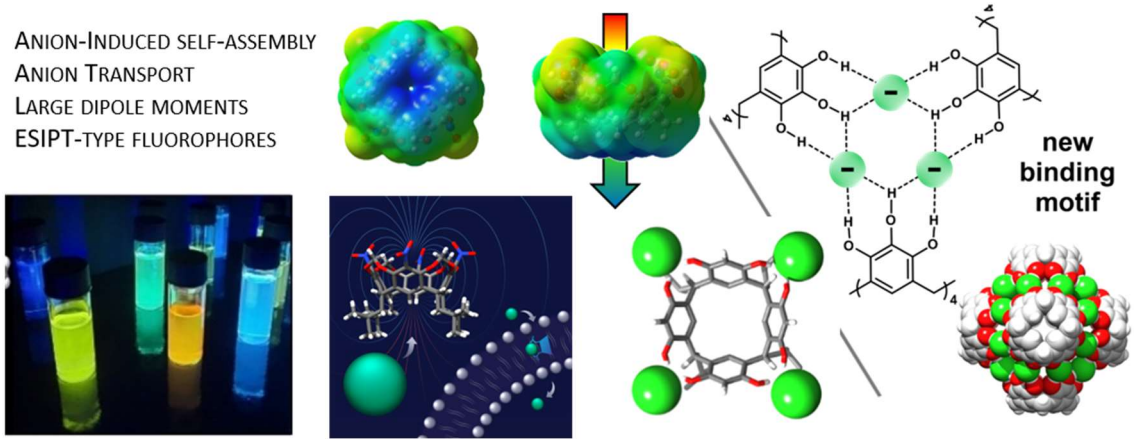
Resorcinarenes have been known for more than half a century and are nowadays considered the classics of supramolecular chemistry. Numerous supramolecular receptors have been synthesised by functionalization of their upper or lower rim, and spectacular self-assembly into hexameric capsules has been demonstrated with even more spectacular catalytic properties. After many years of extensive studies, it seems that these macrocycles have no mysteries. However, our recent studies demonstrated several new properties and interaction models that have not been known before. In particular:

- strong interactions with anions leading to the formation of capsular species; [1,2]
- unique properties of the lower rim cavity (not previously used for recognition) originating from large dipole moments leading to anion transporters through the membranes; [3]
- construction of large Stokes shift fluorescent receptors through unique double ESIPT mechanisms [4]

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Keynote speaker

# SUPRAMOLECULAR CONTROL: STRATEGIC USES OF CARBON NANOHOOPS, FLUORINATED CYCLOHEXANES AND ORGANOPHOSPHATES

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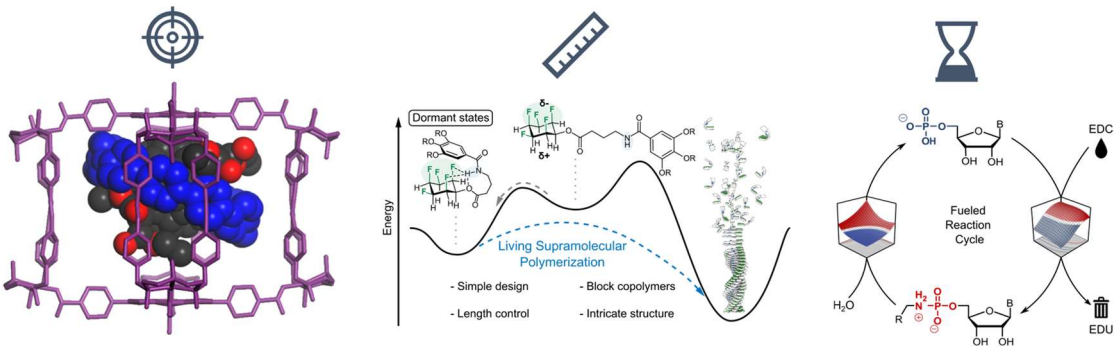
In this talk, I will present recent work by our group on the use of supramolecular chemistry to address challenges in synthesis, materials science and systems chemistry.

In collaboration with the Ribas lab, we achieved control over the **selectivity** of fullerene bis-addition reactions by encapsulating $C_{60}$ in a three-shell complex ("Russian Doll"). Thanks to the combined template effects of a self-assembled cage and nanohoop [10]CPP,[1] the $C_{60}$ *trans-3* bis-adduct (Fig. left) was obtained with ideal chemo-, itero- and regioselectivity,[2] which has recently also enabled the synthesis of unprecedented $C_{60}$/[10]CPP [2]catenanes.[3] Control over the **length** of self-assembled nanofibers was achieved by the living supramolecular polymerization of *all-cis* fluorinated cyclohexanes (Fig. centre)[4] and control over the persistence of supramolecular assemblies over **time** was achieved in chemically-fuelled phosphoramidate[5] and acylphosphate[6] systems (Fig. right).

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Keynote speaker

# Oral communication

15 Girona Seminar May 29-31 2024

# CHEMICAL FUELING OF DYNAMIC COVALENT NETWORKS FEATURES ENDERGONIC ADAPTATION

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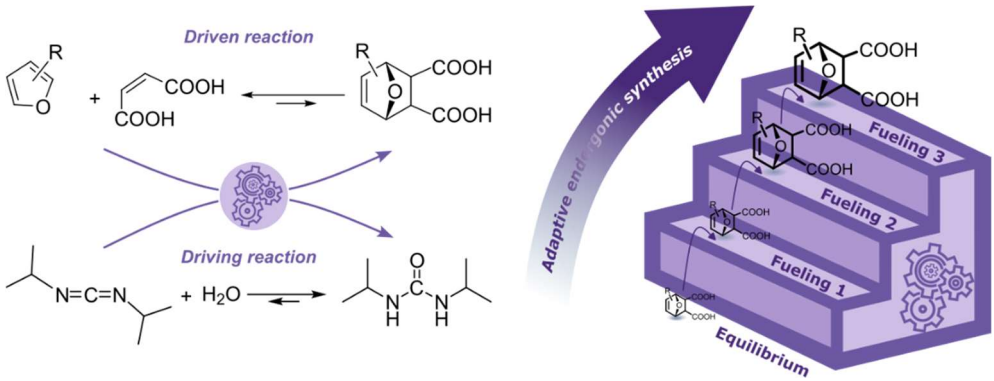
The principles of molecular machines can be exploited for purposes different than motion. Indeed, suitably engineered chemical reaction networks can, for example, harvest energy to afford the formation of high-energy species.[1],[2] This process is possible by coupling an exergonic energy-providing reaction, a *driving reaction*, to an orthogonal energy-demanding one, a *driven reaction (see scheme)*. The latter can absorb energy and shift the distribution of the reaction components away from equilibrium. Leveraging these principles is one of the hallmarks of living organisms.[2]
In this contribution, I will discuss our recent efforts in driving chemical reactions away from equilibrium to realize adaptive behaviors[4] – including the most recent unpublished results. In particular, I will discuss how we could use the acid-catalyzed exergonic carbodiimide hydration[3] to drive otherwise inefficient Diels-Alder reactions: a process which proved efficient for the endergonic accumulation of several adducts. We further leveraged this strategy to accumulate progressively higher amounts of the target compounds upon sequential carbodiimide additions correlated in time. Such an adaptive behavior is reminiscent of the Venus fly trap carnivorous plant, which can capture its prey only if tapped repetitively in a short time frame, as a result of a progressive accumulation of charges.
Mastering endergonic processes has far-reaching implications in energy harvesting, transduction, and exploitation. In this particular case, our findings illustrate how endergonic processes can contribute to the transition from responsive to adaptive systems.[5]

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Oral communication

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# SELF-ASSEMBLED NANOTUBES BASED ON AMIDINIUM-CARBOXYLATE INTERACTIONS IN WATER.

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Nature has shown its own capacity to form self-assembled tubular systems with specific functions, like tube-forming proteins including tubulin or aquaporin. Inspired in these biological systems, our project aims to establish a versatile, and reliable strategy based on non-covalent interactions which allows the formation of discrete tubular systems[1] in an aqueous medium through the stacking of discrete supramolecular macrocycles.[2], [3] We have designed and synthesized two π-conjugated and symmetric semicircular fragments equipped with two carboxylate (Cn.m) and two amidinium (An.m) functional groups at the edges, respectively (Figure 1). Cyclic dimers are formed due to the high complementarity and association strength of these functional groups through an amidinium-carboxylate "salt-bridge".[3] Finally, the formation of self-assembled nanotubes with pores of different size and/or diameter in water is achieved by π-π stacking between these cyclic dimers.

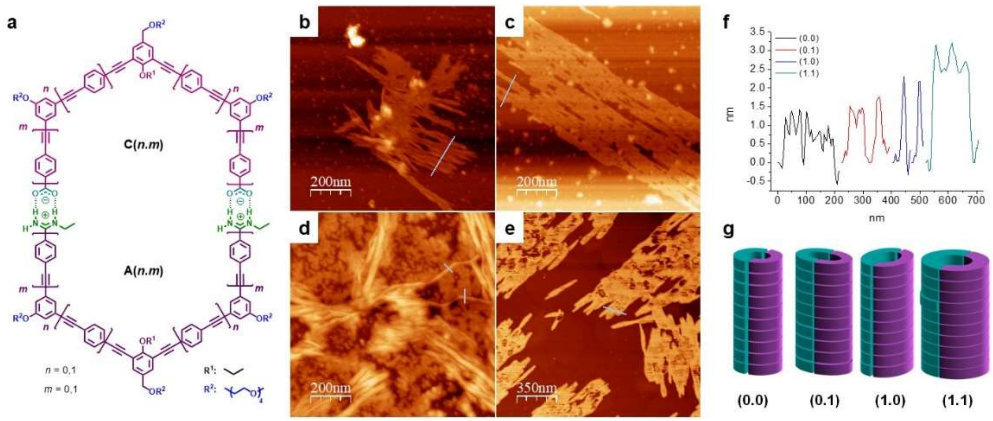


Fig. 1. General chemical structure (a), AFM images of nanotubes formed by (b) **C(0.0):A(0.0)**, (c) **C(0.1):A(0.1)**, (d) **C(1.0):A(1.0)** and (e) **C(1.1):A(1.1),** comparison of corresponding AFM heights (f) and schematic representation of the nanotubes with different pores (g).

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Oral communication

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# (YRS) BODIPY-functionalized silicon oxide microchips for intracellular glutathione (GSH) sensing

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Self-assembly monolayers (SAMs) are considered a key tool in the surface design of nanolayers for the bioactive coating of biomedical devices[1,2]. Two types of glutathione (GSH) probes based on BODIPY derivatives were synthesized and conjugated to the surface of silicon oxide microchips, which had been functionalized with a linker using self-assembled silane-based monolayers. The sensitivity of functionalized microchips was studied in the GSH solution. The cell internalization of functionalized microchips and their sensitivity to the intracellular GSH were also investigated in HeLa cells.

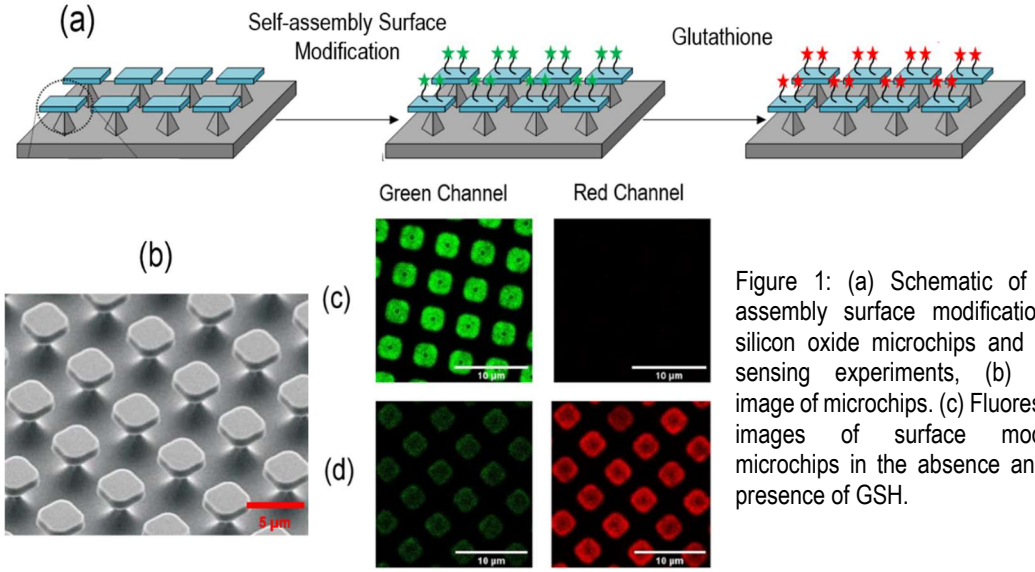


Figure 1: (a) Schematic of self-assembly surface modification of silicon oxide microchips and GSH sensing experiments, (b) SEM image of microchips. (c) Fluorescent images of surface modified microchips in the absence and (d) presence of GSH.

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# CONTROLLING SELF-SORTING IN DYNAMIC ASSEMBLY: STIMULI-RESPONSIVE MULTI-CAGE SYSTEMS

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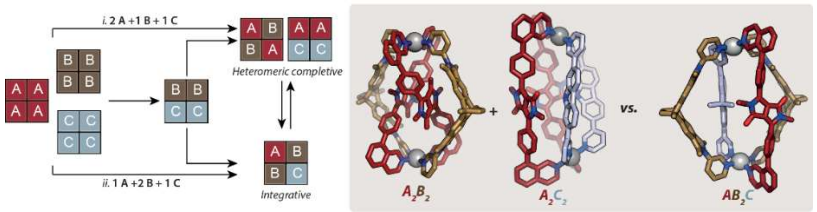
Heteroleptic coordination cages are self-assembled nano-objects composed of multiple organic ligands associating in a discrete assembly through integrative self-sorting. We have recently pushed integrative self-sorting of Pd(II) cages to its limit by bringing four distinct building blocks in a unique $C_s$-symmetrical $Pd_2$**ABCD** architecture. [1] However, while the majority of studies on heteroleptic assembly were aimed at producing a single discrete species in solution, biological systems are composed of a multitude of complex assemblies in mixtures that either act together or perform separate functions. This requires multiple non-covalent assemblies to coexist under the same set of conditions and in an orthogonal fashion. Mimicking such a level of complexity has proven to be one of the most difficult tasks in supramolecular chemistry, in particular in dynamic equilibria. We report the first example of "heteromeric completive" self-sorting in coordination cage systems. [2] Two heteroleptic assemblies coexist in solution, forming a *population*, and the system can be controlled by means of ligand stoichiometry. Furthermore, it is possible to switch between either a $Pd_2$**AB**$_2$**C** heteroleptic cage through strict integrative sorting assembly or a discrete mixture of two architectures $Pd_2$**A**$_2$**B**$_2$ and $Pd_2$**A**$_2$**C**$_2$. Eventually, using multicomponent systems where several assemblies coexist independently can be exploited to transfer specific information from one assembly to another through stimuli responsiveness. This allowed us to observe the emergence of system-like functions in cage populations.

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# NOVEL ADVANCES IN MECHANICAL BOND-CONTROLLED REACTIONS IN [2]ROTAXANES

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Enzymes are highly efficient natural catalysts that drive numerous biochemical reactions with precise specificity, facilitated by their well-defined active sites.[1] The molecular architecture of [2]rotaxanes allows for modifications in their interlocked components, crucially maintaining the mechanical bond that significantly influences the reactivity of the threaded functionalities.[2] Typically, the macrocycle's shielding effect reduces reactivity but also provides a confined space for controlled chemical reactions. Our recent research has highlighted a new function of the mechanical bond in promoting and controlling the stereochemistry of intramolecular cyclizations. For example, benzylfumaramide threads in [2]rotaxanes react with a base to produce interlocked trans-β-lactams.[3,4] This method has been also extended, in different manners, to produce enantioenriched 2-azetidinones.[4] Additionally, the mechanical interlocking of glutaconamides is key to their selective oxidation to β,γ-unsaturated α-ketoamides which undergo light-driven cyclizations to produce hydroxy-2-azetidinones or oxazolidinones (Fig. 1).[5] The mechanical bond's capacity to control complex reactions offers a high level of precision in synthetic chemistry.

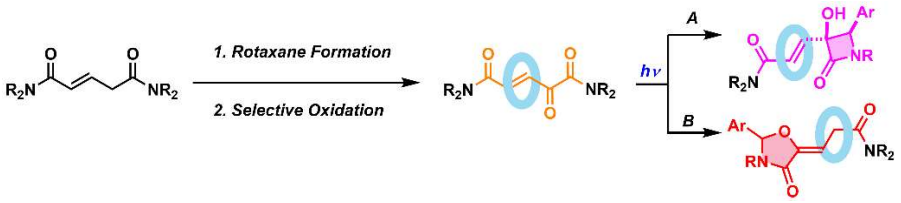


Figure 1

*This work is supported by MICIN/AEI/10.13039/501100011033 (Project PID2020-113686GB-I00) and Fundacion Seneca-CARM (Project 21907/PI/22).*

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15 Girona Seminar
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# KINETIC CONTROL OF SUPRAMOLECULAR SYSTEMS THROUGH DYNAMIC COVALENT CHEMISTRY OF TETRAZINES

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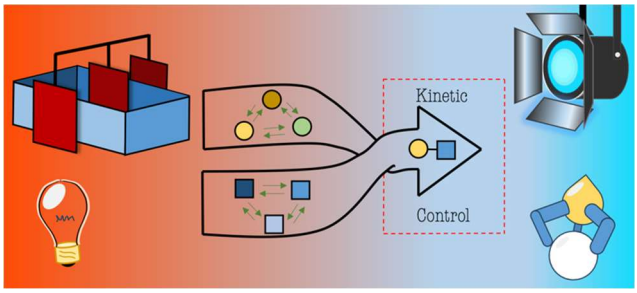
Dynamic Covalent Chemistry (DCvC) has become a powerful tool for supramolecular chemistry, particularly to generate sophisticated hosts such as macrocycles and cages, and also due to its ability to generate complexity as libraries of compounds.[1] DCvC is based on reversible covalent chemistry, and therefore, the components of a library can interconvert by exchanging building blocks within such library, constituting a dynamic molecular network, in which the composition is traditionally governed by thermodynamics. DCvC is rarely combined with irreversible reactions except for those occasions in which cancelling the dynamics, to isolate stable compounds, is the objective. And yet, the combination of complexity generated by dynamic libraries, with an eventual simplification or manipulation by kinetically controlled process, offers an optimal pathway to mimic the intricate chemical schemes of biological systems.[2] Herein we have taken advantage of the dynamic nucleophilic substitution of tetrazines,[3][4][5] to generate supramolecular systems and to kinetically control them: A stable molecular system with specific host-guest and fluorescence properties, can be irreversibly transformed by the right stimulus into a completely different system, and concomitantly, the original properties are cancelled, and new ones emerged.[6]

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15 Girona Seminar
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# (YRS) ENHANCING CATALYSIS AND SELECTIVITY THROUGH THE DYNAMIC CONTROL OF CONFINED SPACES: INSIGHTS FROM ENZYMATIC TO SYNTHETIC CATALYST SYSTEMS

Guillem Casadevall[a*], Andrea Palone[a,b], Colin Pierce[d], Sergi Ruiz-Barragan[a], Arnau Call[a], Javier Iglesias-Fernández[a], Romas J. Kazlauskas[d], Massimo Bietti[b], Miquel Costas[a], Sílvia Osuna[a,c*]

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Understanding and engineering function directly from the single static picture of the confined space of catalytic entities, ranging from enzymes to metal-based catalysts, is not straightforward. To comprehend the catalytic function requires the evaluation of the several chemical steps along the catalytic itinerary, but also the exploration of the ensemble of thermally accessible conformations that catalysts adopt in solution. The importance of dynamics has been successfully demonstrated in enzyme engineering, in which mutations in positions located far away from the confined active site pocket have a significant impact on the catalytic activity.[1]

In this study, we developed a computational approach based on merging insights from the evolution of enzymatic functions with advanced computational modeling of synthetic catalysts to evaluate how microenvironments within catalytic sites need to be altered to achieve significant enhancements in catalysis. We investigate the transformation of the active site in the *Hevea brasiliensis* hydroxynitrile lyase (*Hb*HNL) enzyme to recapture its lost ancestral esterase activity and design a new variant with higher esterase activities than a natural esterase.[2] We evaluate how the network of complementary weak non-covalent interactions governs enantioselectivity in a conformationally rich biomimetic oxidation manganese catalyst.[3] Our work not only promotes a deeper understanding of the structural determinants of catalytic behavior but also contributes to the design of catalysts with optimized selectivity and efficiency.

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# (YRS) INTERLOCKED CHROMOPHORES: DESIGN AND SYNTHESIS

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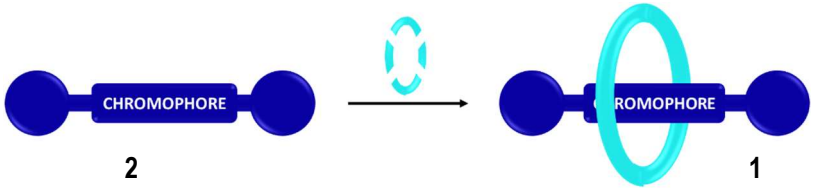
Organic dyes, like cyanines, phthalocyanines, escuaraines, or porphyrin derivatives, are widely used pigments in various commercial products. These substances have important qualities, especially in in vivo fluorescence imaging.[1] Additionally, they play essential roles in semiconductor materials, textiles, solar cells, and paints.[2] However, these organic pigments face two main challenges: a) they are susceptible to chemical and photochemical degradation due to their high reactivity, and b) they tend to aggregate, reducing their solubility in common solvents and causing changes in color.[2] Therefore, it is crucial to create new variations of these compounds to improve their stability, solubility, and optical properties.

The idea of supramolecular encapsulation is a smart way to improve the characteristics of chromophores.[2] Basically, when we put chromophores inside a macrocycle to make a rotaxane or pseudo-rotaxane structure, it gives them a protective shield, making them more stable and preventing them from self-aggregation. Taking inspiration from this idea, we synthesized a set of rotaxanes (**1**) where we included specific chromophores along the thread (**2**). This method ensures that the chromophores remain within the macrocycle, protected from outside influences or sticking together. In this presentation, we share the process of making a new group of benzylic amide rotaxanes [3,4] with integrated chromophores along the threads and explore their properties.

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# SHORT PEPTIDES AS VERSATILE BUILDING-BLOCKS FOR MULTICOMPONENT SUPRAMOLECULAR MATERIALS

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Short peptides have been revealed as fascinating materials that, despite their low molecular weight, are able to mimic structural and functional features of their bigger counterparts, peptides and proteins.[1] In particular, very simple self-assembling peptides have been shown to produce a diversity of nanostructures as a result of pathway-dependent aggregation mechanisms.[2] On the other hand, amino acid side chains contain diverse functional groups which can play an important role not only for structural but also for functional abilities of those materials.[3]

Here we will present the rich self-assembly behavior of short peptides as single component aggregates and hydrogels as well as a part of functional multicomponent materials.

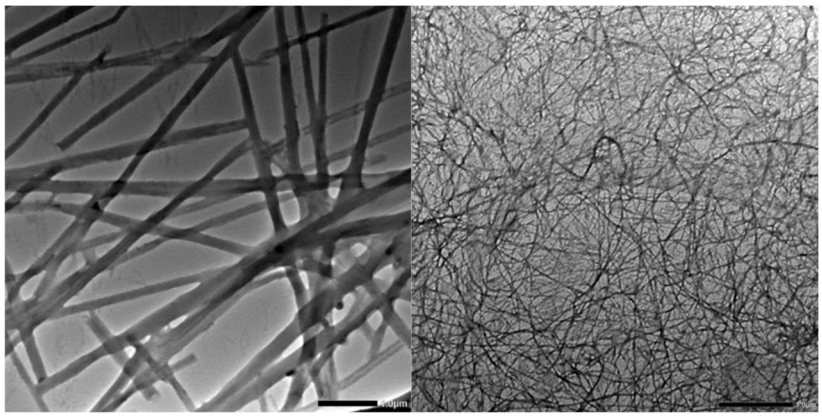

Figure 1. Co-existing morphologies found for a self-assembling dipeptide.

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# SUPRAMOLECULAR PEPTIDE-BASED MATERIALS AS OPTICAL WAVEGUIDES COMPONENTS

Garcia, A.M.;* Garcia-Romero, J.A.; Mejias, S.H.; Prieto, P; Saggiomo, V.; Velders, A.H.; Soriano, M.L.; Ruiz-Díez, V.; Cabanillas-González, J.;* Gomez. M.V.*

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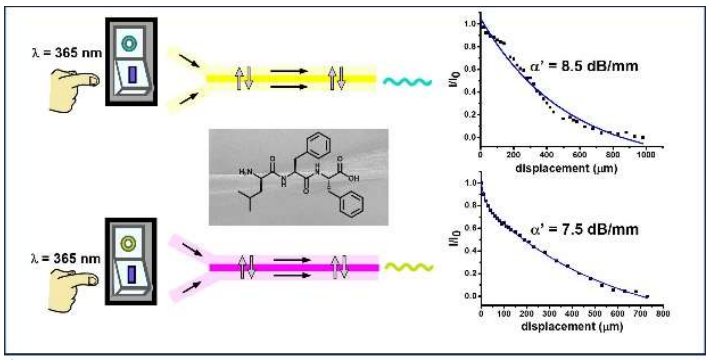
Soft photonic elements with optical waveguiding capabilities, particularly biocompatible hydrogels, have emerged as indispensable components in optical techniques for medical diagnosis and phototherapy.[1] However, the exploration of supramolecular hydrogels based on peptides remains limited. Only robust crystals derived from short peptides that show optical waveguiding capabilities have been reported so far.[2] Short peptide assemblies offer advantages as their ease of preparation, biocompatibility and functional flexibility.

In this study, we present a microfluidic-assisted approach for the formation of heterochiral short peptide hydrogels with active optical waveguiding properties. By incorporating two distinct dyes, Thioflavin T and Rhodamine B, into the hydrogel structure, we achieved enhanced optical performance with emission in diverse spectral regions. Thanks to our microfluidic platform, we systematically explored various parameters-, including peptide concentration, dye type and concentration, and flow rate, with remarkable efficiency and minimal reagent consumption.[3] Overall, by harnessing the unique properties of supramolecular peptide-based materials and using microfluidic technology for rapid optimization, this work the way for the development of innovative optical materials with broad applicability in biomedical diagnostics, phototherapy, and beyond.

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# (YRS) SELECTIVE HOST-GUEST INTERACTIONS IN ARYL-EXTENDED CALIX[4]PYRROLE NANOCAGES: A COMPUTATIONAL STUDY

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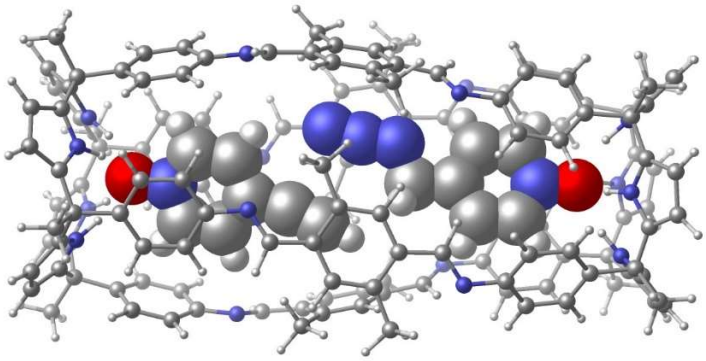
Aryl-extended calix[4]pyrroles have been extensively studied as a supramolecular scaffold to bind neutral and charged guests, with many potential applications.[1] There has been an interest in expanding these systems to imine-based nanocages, which could encapsulate suitable guests and display different properties and conformational distributions from those in solution.[2] Analogous imine cages were explored experimentally to accelerate the (3+2) Huisgen cycloaddition of a terminal azide with a terminal alkyne, however, showing preferential encapsulation to one of the substrates and thus limiting its potential development as a catalyst. Such reactions in supramolecular settings have been successfully modelled in the past with a DFT approach.[3]



In view of these results, we have approached this system through conformational analysis and DFT calculations so as to reproduce the experimental observations, explain the origin of the encapsulation selectivity and ultimately endeavour to propose strategies to optimise the nanocage design.

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Oral communication

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# HOST-GUEST CHEMISTRY WITHIN SMART PORPHYRIN CAGES

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***Keywords:*** *host-guest chemistry, metalloporphyrin cages, supramolecular receptors*

Over the last decades, there has been a huge trend to recreate natural processes as a key model in the design of new molecular systems capable of mimicking the behavior and performance of enzymes.[1] It is well-known that porphyrin derivatives are currently used in natural processes for light harvesting, electron and energy transfer reactions, catalysis, or as oxygen transporters. In addition, their chemical, optical and electronic properties can be easily modulated by changes in the aromatic core.[2] In the last few years, the design of molecular cages based on porphyrins in the host structure opens several attractive opportunities:[3] define the molecular cavity, stabilize π-conjugated guest molecules inside these cavities and coordinate with different ligands within the cage through its metalated form.

The present communication highlights our recent studies on the preparation of novel and simple porphyrin cages assembled by imine bonds under thermodynamic control. Their adaptable cavity is able to accommodate a wide variety of ditopic nitrogen ligands (Figure 1). Unexpectedly, the cage is an exceptional host for $C_{60}$ as well.

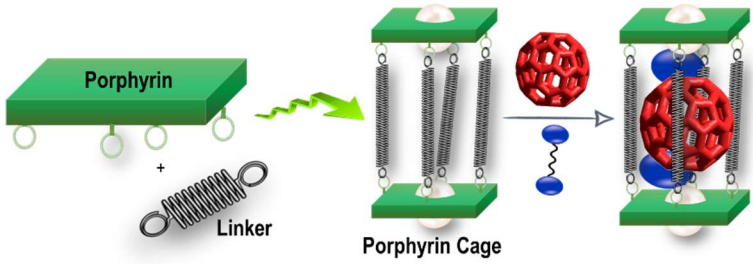


***Figure 1****. General scheme of our novel porphyrin cages showing Host-Guest Chemistry.*

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# (YRS) METAL-ORGANIC POLYHEDRA AS POROUS MOLECULAR NANOPARTICLES

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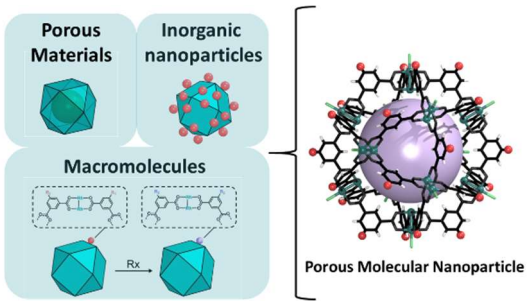
Metal-Organic Polyhedra (MOPs) represent the ultimate strategy to downsize hybrid porous materials below 5 nm.[1] The combination of their intrinsic structural features endows them with properties akin to macromolecules, such as solubility and stochiometric reactivity, and ultrasmall nanoparticles, with densely functionalized and highly reactive surfaces. Additionally, they exhibit characteristics of reticular porous materials, including porosity and tunable cavity size. We have harnessed this unique entanglement of properties to develop Rh(II)-based MOPs as porous molecular nanoscopic platforms or "porous molecular nanoparticles" which can be functionalized through covalent and coordination chemistry.[2] By leveraging a synergistic use of these two orthogonal surface reactivities, we targeted specific properties and applications, such as tunable solubility, bio-functionalization and molecular transport/separation. [3-6]

In addition, we demonstrated how precise knowledge on the position and number of reactive groups decorating the surface of the Rh(II)-based MOPs can be used to control the polymerization degree. Such synthetic control allows us to obtain plethora of new MOP-based complex architectures as soft or crystalline extended structures [7] as well as giant oligomeric porous materials.

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Oral communication

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# REGIOSWITCHABLE BINGEL BIS-FUNCTIONALIZATION OF FULLERENE $C_{70}$ VIA SUPRAMOLECULAR MASKS

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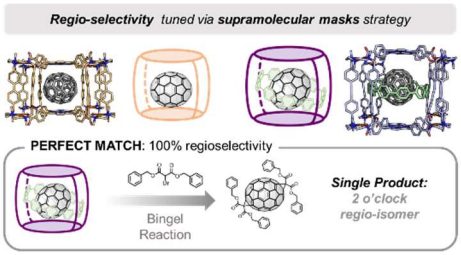
Isomer-pure functionalized fullerenes are required to boost the development of fullerene chemistry in any field, but their multiple functionalization renders a mixture of regio isomers that are very difficult to purify by chromatography. For the specific case of $C_{70}$, its non-spherical geometry makes its regioselective functionalization more challenging than that of spherical $C_{60}$. In this work, the supramolecular mask approach is applied for the first time to $C_{70}$, which is encapsulated in two different nanocapsules to achieve the Bingel bis-cyclopropanation at α-bonds of opposite poles. Based on the tetragonal prismatic geometry imposed by the smaller supramolecular mask tested[1], the obtained major bis-adduct is completely reversed (major 5 o'clock) compared to bare $C_{70}$ functionalization (major 2 o'clock). Moreover, by further restricting the accessibility of $C_{70}$ using a three-shell Matryoshka mask[2] and dibenzyl-bromo malonate, a single regiospecific 2 o'clock bis-isomer is obtained[3], owing to the perfect complementarity of the mask and the addend steric properties. The outcome of the reactions is fully explained at the molecular level utilizing a thorough molecular dynamics (MD) study of the accessibility of the α-bonds to produce the different bis-adducts.

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Oral communication

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# (YRS) BINDING OF ALIPHATIC DIFORMAMIDES BY AN OCTA-IMINE BIS-CALIX[4]PYRROLE CAGE: THERMODYNAMIC AND KINETIC CHARACTERIZATION.

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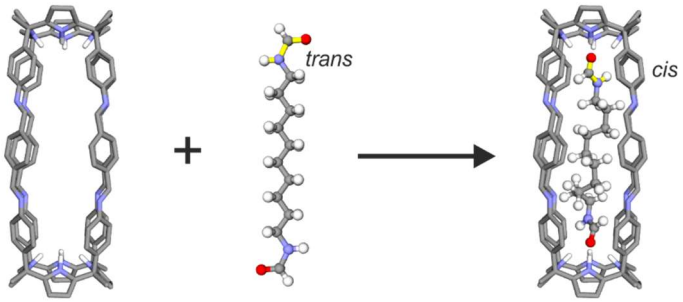
In contrast to rigid guests, flexible guests can adopt unusual conformations to fit and optimize the interactions with natural and synthetic host cavities.[1,2] Herein, we describe the formation of inclusion complexes between a homologous series of aliphatic diformamides having a different number of methylene units (n = 5-11) separating the two formamide ends and a molecular octa-imine bis-calix[4]pyrrole cage in a mixture of organic solvents. Diformamides can exist in solution as a mixture of three isomers: the most abundant *trans,trans*-, the *cis,trans*- and the least abundant *cis,cis*- isomer. The size and shape limitations of the octa-imine cage forces diformamide guests to adopt folded conformations, having at least one of their terminal formamides ends in *cis*-conformation. We report two semi-stable conformations of the guests in the isomeric inclusion complexes that interconverted with time from *cis,trans* to the corresponding *cis,cis*-analogues. The interconversion processes of the semi-stable states *cis,trans*- into the thermodynamically more stable *cis,cis*- form of the inclusion complex are slow on the human time scale (i.e. hours). Using kinetic $^1$H NMR spectroscopy we determined the energy barrier for the *cis,trans*- to *cis,cis*-interconversion process (23.5 kcal·mol$^{-1}$) and that of a guest exchange process between two different diformamides (27.1 kcal·mol$^{-1}$). The derived results suggest that the interconversion of *cis,trans*-isomer into the *cis,cis*-analogue occurs through an isomerization process inside the cage.

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# (YRS) TERPENE CYCLIZATION INSIDE AN ASYMMETRIC CAVITAND

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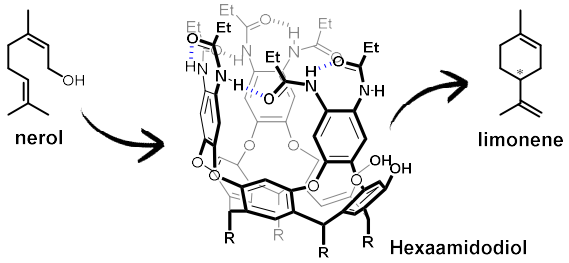
In nature, the synthesis of intricate terpene natural products involves the Tail-to-Head Terpene (THT) cyclization process, transforming simple, acyclic starting materials. This cationic reaction cascade is particularly facilitated within complex enzyme pockets, where cationic intermediates and transition states find effective stabilization.[1] In contrast, performing the same reaction in solution proves challenging to control, often resulting in the generation of various acyclic byproducts. Recent advancements utilize supramolecular pockets to mimic enzymatic terpene cyclization, showing success in selectively producing cyclic products from unfunctionalized acyclic terpenes. Notably, the hexameric resorcin[4]arene self-assembly capsule efficiently catalyzes the cyclization of geraniol, nerol, and linalool with trace amounts of HCl, yielding α-terpinene or eucalyptol as major products within 72 hours.[2] Given the potential for obtaining over 10 different cyclic monoterpenes, the quest for new supramolecular hosts persists. Our approach involves cavitands, covalent rigid structures with enforced permanent cavities, due to their characteristic dynamism and narrow pocket. Additionally, the functionalization of cavitands is more straightforward. Orchestrating the later functionalization, we employ the well-known hexaamidodiol,[3] the parent intermediate to asymmetric cavitands – cavitands with three self-folding walls to maintain the cavity and a fourth wall with distinct functionality. The hexaamidodiol cavitand bears two unprotected phenolic moieties that resemble those of the hexameric capsule. Notably, the narrow pocket of the cavitand can exclusively accommodate nerol, and the use of HCl co-catalyst allows the terpene cyclization, yielding limonene as the major product. Control experiments involving cavity blocking or using the symmetric octaamido-cavitand (without phenol groups) result in minimal reactivity.

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# REGULATED TRANSFER OF CHEMICAL INFORMATION USING STIMULI-RESPONSIVE SQUARAMIDES

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In this work we describe two squaramide-based (Fig. 1a) molecular systems able to transfer chemical information on the nm scale and that can be controlled by different stimuli. The first system is formed by an oligo(phenylene-ethynylene) rigid rod connected to a hydrogen-bonding array formed by multiple squaramides interacting in a head-to-tail mode (Fig 1a).[1] The squaramide units show all the same orientation related to the rigid rod, and when a change in orientation is induced in one squaramide, it is relayed across the intramolecular network to the other end of the structure (Fig 1b). A terminal director can transform the chemical information of acid-base reactions into conformational information which is then transferred across 2 nm. The relay could also respond to pulses of a chemical fuel, leading to the first example of an artificial system relaying conformational information under out-of-equilibrium conditions. The second system consists on a series of squaramide-based transmembrane anion transporters that responds to light.[2] We have first studied the photochemical transformation of the active compound, which produces inactive residues. Next, we have used fluorescence assays to study anion transport inhibition upon *in situ* irradiation of the compound incorporated into the membranes of liposomes (Fig 1c). Thus, the transported chloride (the chemical signal) is received by the encapsulated fluorophore, a communication process that can be regulated with a second signal; the light.

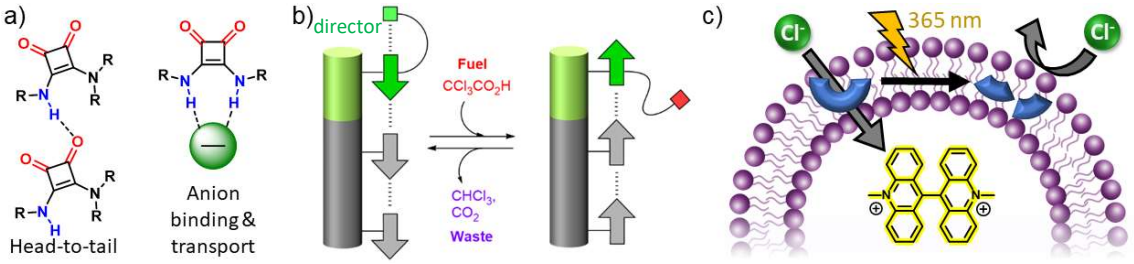


Fig 1. a) Self-assembly and binding properties of squaramides. b) Fuel-responsive molecular communication relay. c) Light-triggered deactivation of an anion carrier studied with lucigenin.

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# (YRS) NON-TEMPLATED ASSEMBLY OF FIVE-MEMBERED PD5L10 RINGS

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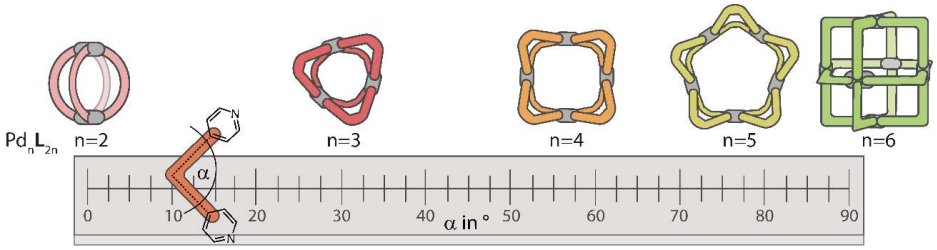
A variety of coordination assemblies $Pd_nL_{2n}$ has been reported by combining bis-monodentate organic ligands and Pd(II) cations. The shape and size of the assemblies depends, among other factors, on the geometry of the ligand employed. Regarding low-nuclearity assemblies (n≤6), most examples possess the nuclearities 2, 3, 4, or 6 and for each of these nuclearities, different topologies can be accessed. Concerning homoleptic pentanuclear assemblies, however, only one example relying on anion templation had been reported before.

In order to fill this long-standing gap, we investigated the self-assembly of bis-pyridyl ligands with systematically varying binding angles (that is the angle between the two nitrogen donor vectors).[1] This allowed us to obtain a series of coordination rings $Pd_nL_{2n}$ n=3-5, including the first non-templated report of a five-membered $Pd_5L_{10}$ ring. In accordance with Fujita's work on large Pd(II)-mediated spheres, we found that larger ligand bent angles led to assemblies of higher nuclearity.[2] Importantly, the five-membered ring could be assembled in the presence of different counter anions, excluding a templation effect. A decrease in the bent angle by only a few degrees impeded exclusive formation of the pentanuclear assembly, showcasing the importance of the precisely adjusted ligand geometry. Close examination of the X-ray crystal structures of five-membered rings based on ligands with ideal and non-ideal binding angles as well as DFT computational analysis revealed that the preference for distinct nuclearities originates majorly from conformational strain.

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# MODULATION OF FE(IV) OXO REACTIVITY VIA SUPRAMOLECULAR RECOGNITION

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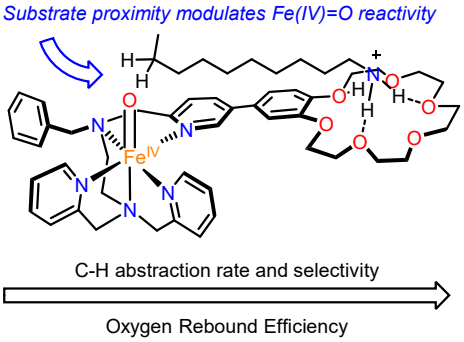
Artificial Fe(IV)=O complexes mimic nonheme Fe oxygenases in the oxidation of C($sp^3$)-H bonds via a Hydrogen Atom Transfer/Hydroxyl Rebound mechanism, but rates, site-selectivity and even hydroxyl rebound efficiency remain lower than enzymatic ones. One of the invoked reasons for such discrepancy is substrate preorganization inside the active site.[1]




In this work, we used a nonheme complex equipped with an 18-crown-6 ether receptor for protonated primary amines[2] to analyze how supramolecular positioning of the substrate modulates the reactivity of a pentadentate Fe(IV)=O complex in biomimetic C-H oxidation.[3] Initially, the enhancement of Hydrogen Atom Transfer rate and selectivity proximity have been quantified and analyzed in terms of Effective Molarity. Then, we observed that the efficiency of Hydroxyl Rebound increases for the methylenic sites favored by recognition, indicating that substrate binding also affects this latter step that is often challenging to replicate in synthetic models. Overall, these observations provide evidence that control of substrate positioning via weak interactions is an effective tool to modulate the reactivity of oxygenases and its models.

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# (YRS) NEW ELECTRICALLY AND OPTICALLY ACTIVE MOLECULAR MATERIALS CHARACTERIZED BY SYNCHROTRON CIRCULAR DICHROISM

Giulia Pancotti,[1] Catherine E. Killalea,[2] Thomas W. Rees,[2] Letizia Liirò-Peluso,[2,3] Sergi Riera-Galindo,[3] Peter H. Beton,[2] Mariano Campoy-Quiles,[1] Giuliano Siligardi,[3] and David B.Amabilino,[1,3]

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Supramolecular chirality, where molecular chirality is transferred to supramolecular structures, is of particular interest for organic photovoltaic devices. Thin films exhibit a close relationship between their supramolecular arrangement and their efficiencies, highlighting the role played by chiral supramolecular arrangement in the physical parameters of the devices.

Additionally, chirality provides the opportunity to employ Circular Dichroism (CD) spectroscopy that have the advantage to be highly sensitive to changes in supramolecular structure, making them uniquely capable of providing valuable insights into the conformational changes that occur in both natural and synthetic materials[1].

The focus of our project is centred on the synthesis of new enantiomerically pure DPP dyes that exhibit high absorbance and excellent photostability. These dyes are intended for use as the active layer in photovoltaic devices, in conjunction with ITIC-4F acceptor. A key objective of our research is to develop an understanding of the relationship between the supramolecular structure of DPPs and their efficiency in electron transfer.

To achieve this goal, we have employed CD studies in the solid state, using the B23 beamline at the Diamond Light Source Synchrotron. This approach involves analysing thin films of chiral materials to obtain a Mueller Matrix Plot (MMP), which enables us to accurately measure the CD spectrum in solid state, without being misled by linear anisotropies, such linear dichroism or linear birefringence[2]. Those techniques allow us to gain a better understanding of the properties of these materials and their potential use in photovoltaic applications.

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# (YRS) REGIO-FUNCTIONALIZATION OF FULLERENES BY DIELS-ALDER REACTION VIA SUPRAMOLECULAR MASK STRATEGY

Tània Pèlachs,[a] Míriam Pujals,[a] Clara Sabrià,[a] Marc Garcia-Borràs,[a] Ferran Feixas[a] and Xavi Ribas[a]

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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 regioisomer, not amenable for applications.[1] In this regard, only easily accessible mono-functionalized fullerenes are used as electron transport layers in solar cells devices. Pure regioisomer of poly-adducts are envisioned as good alternatives to boosting the efficiency of SC. Here, we present a strategy using a tetragonal prismatic nanocapsule as supramolecular mask, [2,3] that directs the Diels-Alder reaction on fullerenes towards pure bis-adducts isomers. For the $C_{60}$, the unprecedent *trans-1* bis-adduct has been obtained by using pentacene as the diene, while the *equatorial* bis-adduct has been achieved in a regioisomerically pure way using anthracene.[4] In the case of the $C_{70}$, the 12 o'clock bis-adduct was obtained using the anthracene, while the 5 o'clock was obtained by using the pentacene as the diene of the reaction.[5] The combination of the use of a supramolecular mask and adjusting the length of the diene, allows the control of the regioselectivity of the bis-Diels-Alder adduct obtained.

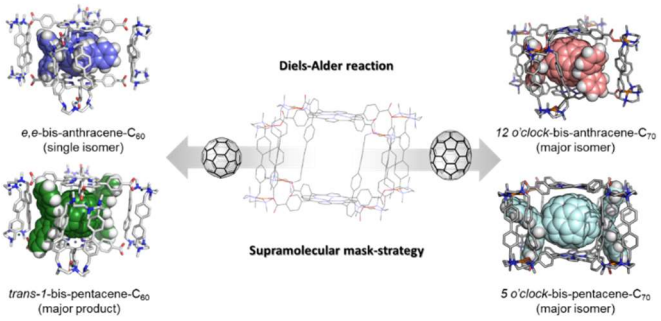


***Figure 1.*** Schematic representation of both host-guest complexes obtained by means of orthogonal Diels-Alder functionalization directed by supramolecular-mask strategy.

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# (YRS) DESIGNING A SURFACTANT TRAP USING MOLECULAR CAGES

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Molecular recognition is ubiquitous in biological processes, and a key factor in plenty technological applications. Molecular cages are a type of discrete synthetic recognition units that possess well-defined inner void spaces where guest molecules can be accommodated.[1,2] Imine condensation has been one of the most fruitful strategies for the synthesis of these type of structures.[3] However, two important disadvantages have difficulted the use of these cages into biological applications, their poor water solubility, and the instability of imine bonds in the presence of water or other nucleophiles, e.g., amine-containing molecules.[4]

In this research, the potential of a double post-assembly modification of imine based structures[5] was explored to: i) increase stability, ii) endow water solubility, and iii) tune the recognition properties. Following the methodology depicted in Figure 1, a functionalized cage demonstrating solubility in both water and phosphate buffer solutions was synthetized. This cage exhibited distinct selectivity towards anionic surfactants, displaying a unique behavior as a template agent for the formation of insoluble anionic micelles, leading to their complete elimination from aqueous media.

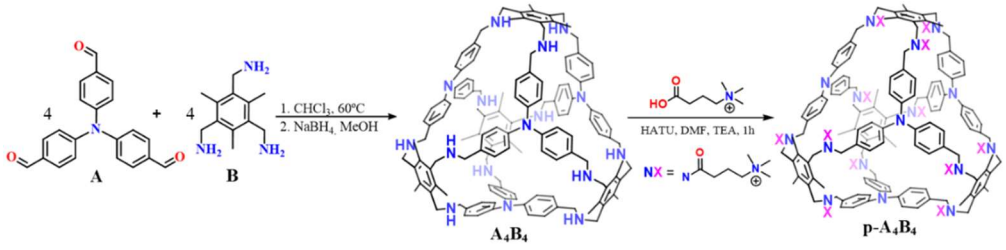


***Figure 1.*** *Followed protocol for the synthesis of the double functionalized cage.*

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# QUANTIFICATION OF CARBOXYLATE-Π INTERACTIONS IN WATER

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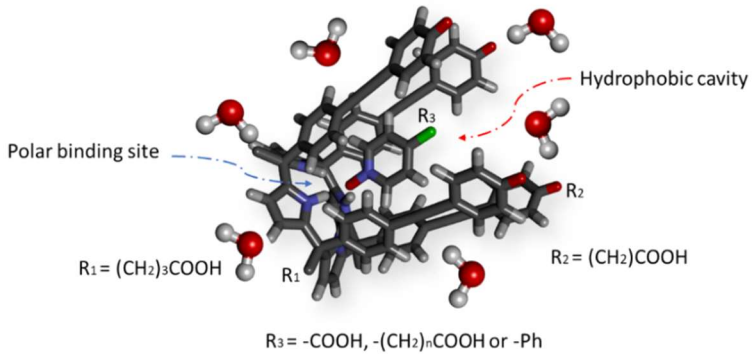
In addition to the complex phenomenon of the hydrophobic effect, electrostatic non-covalent forces, such as hydrogen bonding, and anion and cation-π interactions are also involved in the stabilization of synthetic and biological supramolecular complexes in aqueous medium.[1] In particular, electrostatic interactions involving carboxylate groups buried in the hydrophobic cavities of proteins were largely investigated to their relevance in relation to stability, folding and binding ability.[2] Water-soluble calix[4]pyrrole receptors (C4P) are new physical organic chemistry tools allowing to quantify intermolecular interactions in water. [3,4] Here, we report the synthesis of an unprecedented water-soluble aryl-extended calix[4]pyrrole (AEC4P) functionalized with four carboxylic acids at its lower rim and its super-aryl-extended (SAE) analogue (Figure 1). These C4Ps have been wisely used to build chemical double mutant cycles (DMCs) to quantify non-attractive carboxylate-π interactions, using a series of neutral para-alkyl substituted pyridyl *N*-oxides and their analogues containing a terminal carboxylic group in the alkyl chain in phosphate buffered saline aqueous solution at pH 10.

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Oral communication

# (YRS) NOVEL INTERLOCKED ORGANOCATALYSTS BASED ON HYDROGEN-BOND DONORS

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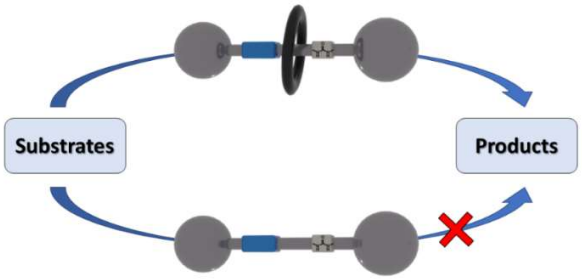
The development of mechanically interlocked molecules has undergone a huge evolution in recent decades.[1] At the same time, the progress of organocatalysis has significantly improved the performance of numerous reactions involving small organic molecules.[2] Our group is combining the special structural features of rotaxanes with the possibilities given by certain catalytic motifs.[3] The present study represents a continuation of our ongoing efforts in this direction.

Herein, we have designed rotaxanes incorporating ureas as catalytic moieties.[4] It is well-known that hydrogen-bond donors such as ureas have broad applications as hydrogen bonding[5] and anion binding[6] catalyst. Through this approach, we have successfully improved the catalytic efficiency of the ureas placed at the thread, by cooperative working with an interlocked tetralactam macrocycle.




**Acknowledgments**: This work is supported by the Spanish Ministry of Science and Innovation (PID2020-113686GB-I00/MCIN/AEI/10.13039/501100-011033) and Fundación Seneca-CARM (Project 21907/PI/22). J. Puigcerver thanks Spanish Ministry of Universities for his pre-doctoral contract (FPU19/05419).

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# (YRS) COMPUTATIONAL ANALYSIS OF C(SP)–C(SP) BOND OXIDATIVE ADDITION TO MACROCYCLIC PINCER COMPLEXES

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As the principal linkages in organic molecules, the chemistry of carbon–carbon bonds is a topic of enduring importance. The strongest carbon–carbon σ-bonds are found in 1,3-diynes, characterised by bond dissociation energies nearly twice that found for ethane, making them exceptionally challenging to cleave by oxidative addition to a transition metal. We have recently developed a means for studying this process which leverages the mechanical bond and involves insertion of a rhodium(I) metal centre into the C(sp)–C(sp) bond of an interlocked 1,3-diyne, with the rhodium(III) product trapped out by reaction with carbon monoxide or hydrogen. [1]

In this contribution we describe the use of classical, static DFT-based calculations and state-of-the-art DFT-based metadynamics simulations[2] to map out and quantify the associated potential energy surface and critically compare it to that of the non-interlocked variant (figure 1). The effect of modifying the 1,3-diyne substituents has also been evaluated computationally in attempt to expand the reaction scope.

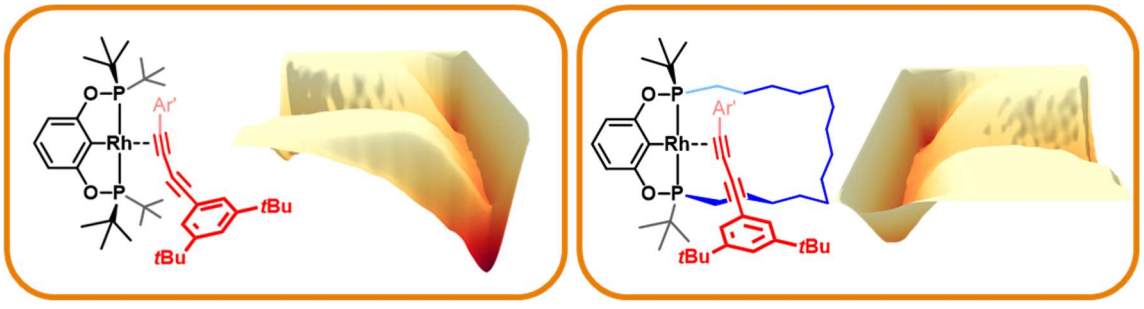


**Figure 1.** Calculated potential energy surfaces for C(sp)–C(sp) bond oxidative addition to acyclic (left) and macrocyclic (right) rhodium (I) complexes.

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# COMPUTATIONAL/EXPERIMENTAL SYMBIOSIS IN THE DESIGN OF SUPRAMOLECULAR PEPTIDE ARCHITECTURES

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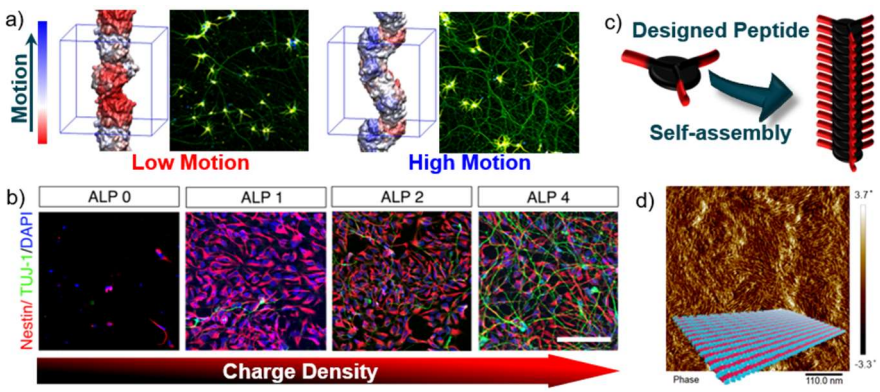
Supramolecular peptide assemblies (SPAs) have emerged in the last few decades as promising materials for bioengineering and nanomedicine due to their versatility and biocompatibility. Specifically, they are revolutionizing the field of artificial extracellular matrices (ECMs) by enhancing cell adhesion, proliferation, maturation, and differentiation. However, designing materials with target properties remains challenging due to the complex connection between the amino acid sequence of SPAs and their structure and bioactivity. The symbiotic combination of experimental and computational methods provides a unique opportunity to elucidate this relationship and deepen our understanding of SPAs.[1,2] This synergy has led to the discovery of molecular motion as a key factor for bioactivity and has facilitated the optimization of materials for spinal cord injury regeneration (Panel a).[3] Currently, our computational/experimental symbiotic approach focuses in two main objectives: 1) understanding how different structural features affect SPA functionality, such as increased bioactivity with higher charge density in the absence of any bioactive sequence (Panel b); and 2) developing innovative architectures to unlock novel material properties. This includes variations in peptide geometry to adjust intermolecular cohesion (Panel c) and the integration of proteins and peptides to create architectures with diverse dimensionality (Panel d). The synergistic integration of experimental and computational methodologies has significantly advanced and refined tools for SPAs, opening new avenues in the realms of bioengineering and nanomedicine.

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Oral communication

# POLYMORPH TRANSITIONS IN SUPRAMOLECULAR POLYMERS

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Recent trends in the field of supramolecular polymers focused on studying pathway complexity,[1] highlighting the importance of the kinetic aspects of supramolecular polymerization in controlling molecular packing (polymorphism) and the properties of self-assembled structures.[2] In our recent studies, we have uncovered squaramides as intriguing hydrogen bonding units with a strong tendency to generate pathway complexity due to their ability to interact through different interaction patterns.[3,4] Through these studies, we have discovered new squaramide polymers featuring temperature-driven polymorph transitions that are completely reversible and occur under thermodynamic conditions.[5] Additionally, we have recently observed analogous thermoreversible polymorph transitions in cyanine-based supramolecular polymers featuring H and J-aggregates. Understanding the mechanistic, kinetic, and thermodynamic aspects of these polymer transformations is crucial for the further development of stimuli-responsive systems.

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Oral communication

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# UNRAVELLING THE REAL-TIME DYNAMICS OF HYDROGEN-BONDING MOLECULAR SHUTTLES

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Non-covalent interactions control the real-time kinetics and reversible operation of molecular motors. Quantitative information on these non-covalent interactions can be unraveled in the single-molecule regime by measuring nanometer displacements resulting from the application of picoNewton forces in optical trapping (OT) experiments. For example, the mechanical strength of non-covalent interactions can be quantified when studying the reversible breaking/formation of hydrogen bonds in individual host-guest systems[1] or the switching of a macrocycle between binding stations in a molecular shuttle.[2]

We present further insight into the operation under mechanical forces of rotaxane-based molecular shuttles featuring switchable hydrogen-bonding binding stations of variable distance between them (Figure 1). We have investigated the effects of hydrogen-bonding energies as well as Brownian ratcheting mechanisms on the shuttling dynamics of these molecular motors.

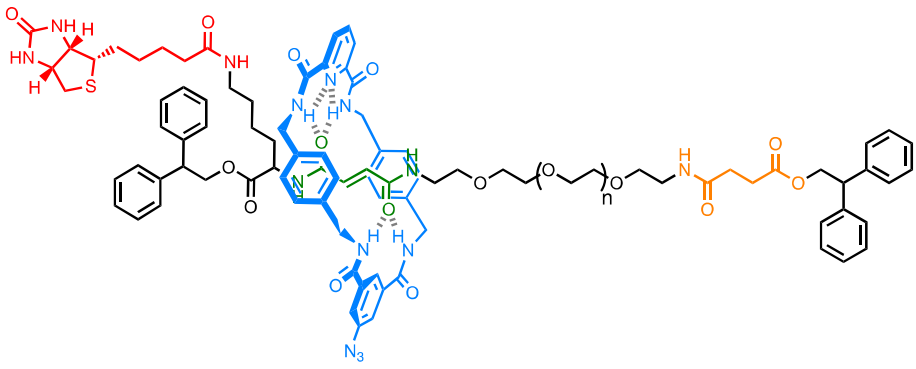

Figure 1. Chemical structure of rotaxane-based molecular shuttles with fumaramide (green) and succinimide-ester (orange) binding stations.

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# ORIGIN OF RATE ENHANCEMENT BY METALLOCAGES: A MOLECULAR DESCRIPTION

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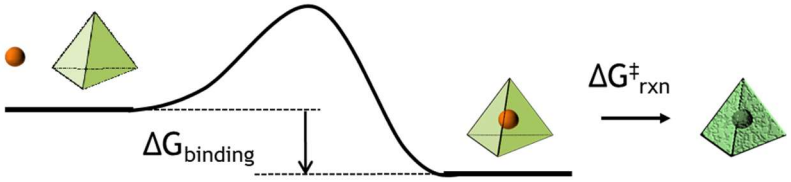
Reactivity within confined spaces, such as molecular cavities, encompasses the chemical and physical processes that take place in these restricted environments.[1] When these cavities are formed by metal organic cages (MOCs), it represents a fusion of host-guest chemistry and catalysis. This process initiates with the encapsulation of reactants (molecular guests) into the cavity (host), leading to the subsequent chemical reaction. Although conducting computational studies on these processes poses significant challenges,[2] achieving a molecular and computational understanding is crucial for gaining insights into the physicochemical properties driving these reactions.[3]




Chemical reactions can proceed more rapidly inside cavities than in a solvent environment. The question then arises: what factors contribute to this acceleration of reaction rates? To address this, we will delve into a multiscale computational analysis. We will explore some reactions facilitated by selected MOCs, examining how various physicochemical properties—such as the nature of the guest molecule, solvent influence, etc.—impact both encapsulation and the subsequent reactivity.[4] This investigation aims to shed light on the intricate dynamics at play within these unique chemical environments, offering a deeper understanding of how confinement within metallocages can enhance or alter the course of chemical reactions.

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# NEUTRAL METALLOCONTAINERS FOR ANION RECOGNITION

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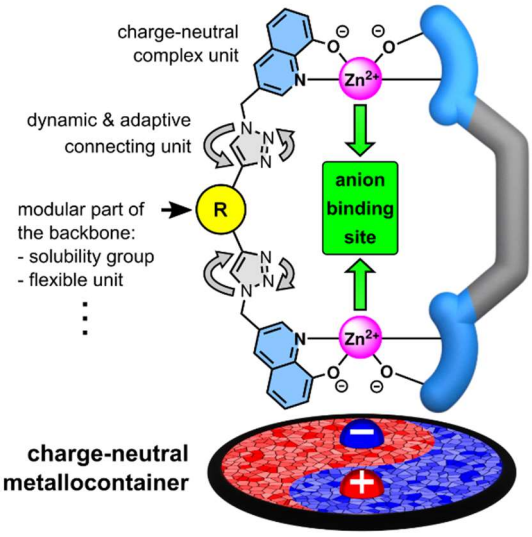
Anions are ubiquitous in our everyday lives and deeply interwoven with essential body processes which has drawn the interest of chemists towards the field of anion recognition. Numerous examples of uncharged organic receptors with a vast variety of suitable anion recognition units are reported. However, very high binding constants rely on well-preorganized hosts thus on the formation of macrocycles and organic cages which can be very challenging with classic synthetic methods. Metal-driven self-assembly offers an option to circumvent this synthetic bottleneck and researcher use this approach to design, e.g., well-preorganized metallocages with the capability to encapsulate anions in the past two decades.[1] The affinity is often boosted by the high positive charge of these structures which can help binding an anion but also increases the level of complexity since the positive cages are accompanied by counter anions.




Our research tackles this specific gap by combining the best of both worlds in a charge-neutral self-assembled metallocontainer which is free from “disturbing” counter anions. In the past, we were able to show extraordinary affinities (max. $K_{1:1}$ = 145,000,000 $M^{-1}$) of a $\mathbf{L}_2Zn_2$ receptor towards dicarboxylates and the analytes were detected at nanomolar concentrations using fluorescence spectroscopy.[2] Recently, we have investigated the chiroptical recognition capabilities of the host which arise from the dynamic interconversion of the three receptor isomers.[3] Current investigations focus on tuning the ligand backbone to achieve new properties like binding highly competitive guests which are very challenging for a lot of metal-based cages.

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# REMOTE AMINO ACID RECOGNITION ENABLES EFFECTIVE HYDROGEN PEROXIDE AT A MANGANESE OXIDATION CATALYST

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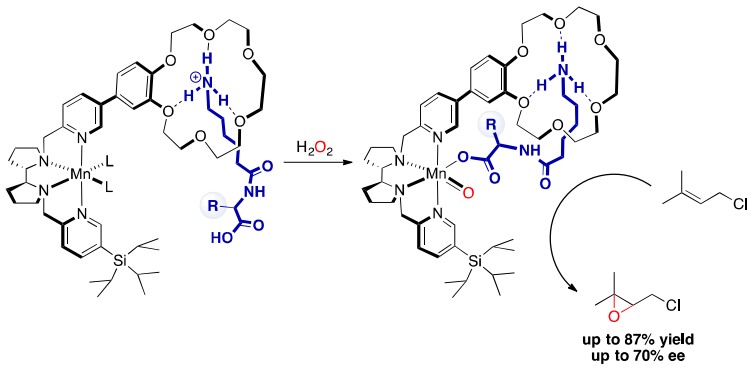
Oxygenation of organic substrates by iron metalloenzymes occurs with high levels of selectivity. [1] Due to its efficiency, chemists have tried to mimic these systems with artificial catalysts, with a very defined first coordination sphere.[2] One of the most studied families are Mn complexes with tetradentate *bis*-amine-*bis*-pyridine ligands, which can efficiently activate the $H_2O_2$ to form a high valent metal-oxo species able to oxidize a large range of substrates. However, a proton source is required for peroxide activation; and while a single acidic function is needed in enzymes, a high excess of carboxylic acid is required by artificial catalysts (up to 17500 equivalents with respect to the catalyst), resulting in the production of high amounts of carboxylic acid waste.[2]

Herein, we present an effective, enzyme-like hydrogen peroxide activation at a Mn catalyst with amounts of acid that are almost stoichiometric to the metal.[3] Our approach relies on supramolecular recognition of an α,ω-amino acid to a crown ether receptor present in the ligand. Such interaction occurs in the second coordination sphere of the manganese, and locates the carboxylic acid in an optimal position to access the first coordination sphere and get involved in the catalytic cycle, enabling effective $H_2O_2$ activation for asymmetric epoxidation reactions.

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Oral communication

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# (YRS) TRANSFORMATIONS AND SELF-SORTING IN AZULENE-BASED COORDINATION CAGES

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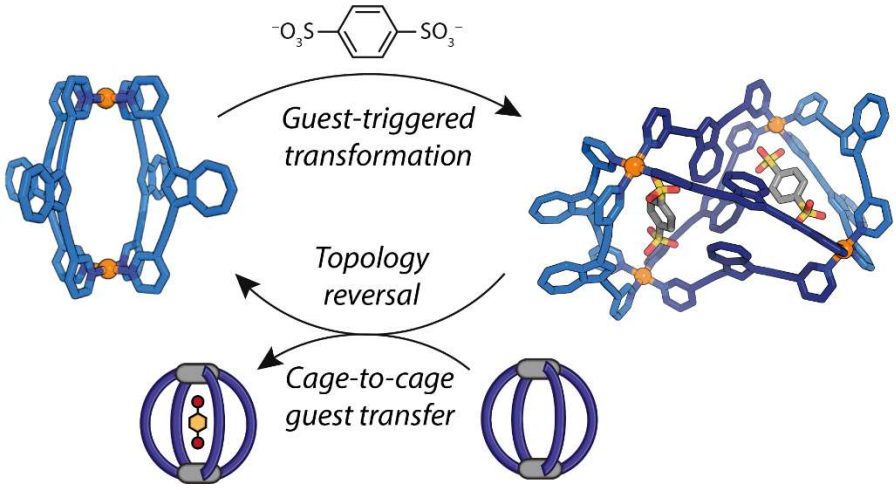
Coordination cages are often seen as purely synthetic mimics of biological receptors enzymes, possessing nanoscopic cavities capable of binding guest molecules, and extensive work has been published on the catalytic properties of coordination cages.[1] However, peptidic receptors can often undergo strong refolding and multimerisation upon guest binding, contrary to coordination cages, which are generally considered as more static species.

Here, we present a self-assembled coordination cage based on an azulene ligand, which can undergo an efficient and rapid dimerization from a $Pd_2\mathbf{L}_4$ cage to a $Pd_4\mathbf{L}_8$ tetrahedron upon guest binding. Moreover, the transformation is fully reversible by the addition of a second, competitive coordination cage, which can steal the guest away from the newly formed tetrahedron, and reform the initial cage.[2]

In addition, we present a new system based on a chiral bis-azulene backbone, which can undergo chiral self-sorting, depending on the solvent. Moreover, the mechanism of the self-sorting has been fully elucidated.

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Oral communication

Poster

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# P1 - UNVEILING ENHANCED MOLECULAR REACTIVITY OF IRON-OXO COMPLEXES BASED ON THE TOPOLOGY OF TETRAMETHYL CYCLAM

Faiza Ahsan[1], Bittu Chandra[2], Yuan Sheng[2], Marcel Swart[1,3]* and Lawrence Que, Jr.[2]*

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Oxo-iron (IV) species play a fundamental role as intermediates in both biological and abiological oxidation processes. Over the past few decades, extensive efforts have been made for the characterization of synthetic nonheme oxo-iron (IV) complexes, serving as analogs of nonheme iron oxygenases. In this regard, the revelation of the crystal structure of anti-$[Fe^{IV}(O)(TMC)(CH_3CN)]^{2+}$ (TMC = Me4cyclam) was embarked two decades ago named as TMC-*anti*[1]. Later in 2015, the other isomer *i.e* TMC-*syn* was synthesized[2]. Substantial focus has been directed towards hydrogen-atom transfer (HAT) reactions that result in in C–H bond hydroxylation[3]. Nevertheless, scarce attention has been devoted to oxygen-atom transfer (OAT) reactions, despite the observation of olefin epoxidation in selected nonheme iron enzymes. In this work, we have investigated the Hat and OAT reactivity exhibited by the anti and syn-isomers of $[Fe^{IV}(O)(TMC)(CH_3CN)]^{2+}$

Our investigation shows that TMC-*syn* is 1.3-3 times more reactive than TMC-*anti*. More interestingly, the reactivity of TMC-*syn* is increased upto 1000 times for oxygen atom transfer to sulfide substrates. To our surprise, only TMC-*syn* is capable of epoxidation of the olefins. With the help of DFT calculations, we have explained the factors driving reactivity for topologically different isomers of TMC. We find that reactivity of the complex lies beyond the structural steric effect. There are geometric as well as electronic parameters that are related to the reactivity of studied complexes.

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Poster

# P2 - CATALYTIC SYNTHESIS OF CONTORTED CHIRAL PICENE TRIMERS

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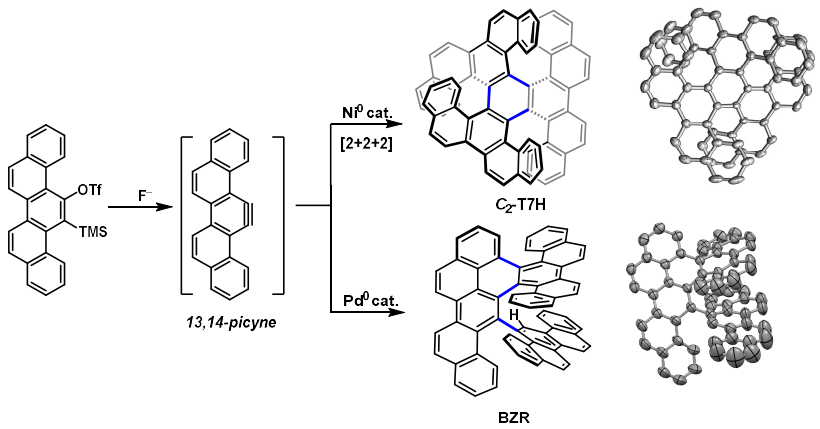
A highly contorted polycyclic aromatic hydrocarbon (PAH) displaying three carbo[7]helicene moieties fused in a central six-membered ring ($C_2$-**T7H**) was synthesized through the Ni0-catalyzed cyclotrimerization reaction of an aryne intermediate.[1] The reaction mechanism was studied in silico to explain the crucial role of the Ni catalyst to the reaction outcome and its diastereoselectivity. Additionally, the evaluation of the aromaticity in this triple carbo[7]helicene was analyzed utilizing magnetic and electronic criteria leading to important insights challenging the limitations of Clar's model of aromaticity. The conformational, structural and chiroptical properties of $C_2$-**T7H** were also studied. We observed that under certain Pd0 catalysts, the same aryne intermediate trimerizes in a completely different manner to provide a trimeric molecule displaying a double carbo[5]helicene moiety and a stereogenic axis (**BZR**). This reaction product was further modified by the Scholl reaction. The conformational and chiroptical properties were again explored and the mechanism was studied both experimentally and by DFT calculations to understand this unexpected reactivity.

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Poster

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# P3 - INTEGRATIVE COMPUTATIONAL MODELING OF DYNAMIC EFFECTS ON CATALYSIS IN CONFINED SPACE

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Catalytic activities within confined space occurring in supramolecular and biomolecular systems are regulated by complex mechanisms that usually include a sequence of steps that collectively determine the functional outcome of the process. These steps encompass substrate recognition, conformational changes to preorganize the catalytic site, and ultimately, the catalysis of the chemical step itself and are influenced by the intrinsic dynamics of the interacting molecules. From the conformational perspective, supramolecular and biomolecular systems must be described as an ensemble of differently populated conformations which interconvert over a wide range of time scales (from femtoseconds to seconds). Regarding the reaction mechanism, the intermediates involved in these catalytic processes are often highly reactive and have a short lifetime, which usually hampers their experimental characterization. Consequently, these dynamic features make the study of confined space catalytic mechanisms complex and challenging. Computational modeling offers a means to complement and address some of the current limitations of experimental methods, providing structural and mechanistic insights of (bio)chemical and supramolecular processes at both atomic and temporal resolutions. [1]

Here, we aim to develop and validate an integrative computational protocol that combines quantum mechanics (QM), hybrid quantum mechanics / molecular mechanics (QM/MM) approaches, molecular dynamics (MD) simulations, and enhanced sampling simulations, along with advanced techniques such as constant pH MD simulations to model dynamic effects on catalysis in confined spaces. This will ultimately allow us to accurately describe various mechanistic aspects, covering a broad range of time scales involved in catalytic reactions within the confined space in model supramolecular systems. This molecular information can then be used to guide the rational design of new supramolecular systems with enhanced and new functionalities.

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# P4 - EXOHEDRAL REACTIVITY OF ENDOHEDRAL METALLOFULLERENE $C_{36}$

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Fullerenes are a class of cage like allotropes of carbon with an even number of carbon atoms ($C_{24}$, $C_{28}$, $C_{36}$, $C_{40}$, $C_{50}$, $C_{60}$, … $C_{2n}$). Since the discovery of the first fullerene $C_{60}$ in 1985[1] it has been subjected to various theoretical and experimental studies which include encapsulating other molecules or metals inside the cage like architecture (endohedral fullerenes (EF) or endohedral metallofullerenes (EMF)) and doping the fullerenes with foreign atoms.[2][3][4]

Exohedral reactivity of metallofullerenes is crucial for its application in various fields. Systematically controlling the trapped species inside the fullerene, its reactivity can be tamed. In this work we report the preferential position of the 3d metal atom inside the $C_{36}$ cage and its exohedral reactivity in comparison with the pristine and dianionic cage. The Diels-Alder (DA) reaction between butadiene and the non-equivalent [5-5], [6-5] and [6-6] C-C bonds on the fullerene cage were considered for the analysis, density functional theory was used for our calculation to elucidate the complete mechanistic pathway. The results[5] are obtained using S12g functional and tz2p basis set and the solvent was incorporated in the study using COSMO: implicit solvation model. Our results indicate that the preferential position of the metal ion is the position towards the face of top hexagon and the general trend in the reactivity of bonds follows the order [5-5] > [6-5] > [6-6]. Moreover, the encapsulation of metal atoms further enhance the reactivity of these bonds.

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# P5 - EXPLORING THE CONFORMATIONAL DYNAMICS OF TRYPTOPHAN SYNTHASE

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Enzymes are versatile biomolecules that catalyze a wide variety of chemical transformations. Moreover, they perform efficiently under mild conditions, making them specially interesting from the point of view of sustainable catalysis.[1] Their powerful catalytic activities derive from sophisticated structural conformational dynamics, that allow them to have highly preorganized active-site pockets to efficiently stabilize the transition state of the process.[2]

Many enzymes are regulated by allosteric control, which occurs when two different sites inside the protein are functionally connected. This often promotes both the binding of the substrate, as well as the product release. In this line, tryptophan synthase (TrpS), is an allosterically regulated enzyme that catalyzes the biosynthesis of L-tryptophan.[3] TrpS is composed by two *α*-subunits (TrpA) and two β-subunits (TrpB), forming an αββα heterodimeric structure. TrpA and TrpB allosterically activate each other.[4] The TrpA subunit catalyze the retro-aldol cleavage of indole-3-glycerol phosphate (IGP) to produce glyceraldehyde-3-phosphate (G3P) and indole. Subsequently, indole diffuses through a tunnel that connects the subunits to enter TrpB, where a reaction involving multiple intermediates takes place in presence of pyridoxal phosphate (PLP) cofactor.[4]

In our work, the dynamic behaviour of TrpS is studied using Molecular Dynamics (MD) and Free Energy Landscape (FEL) reconstructions to enlighten the allosteric mechanisms involved within the enzyme, and elucidate other key steps of the process.

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# P6 - ENANTIOSELECTIVE LACTONIZATION AT NONACTIVATED PRIMARY AND SECONDARY C-H BONDS

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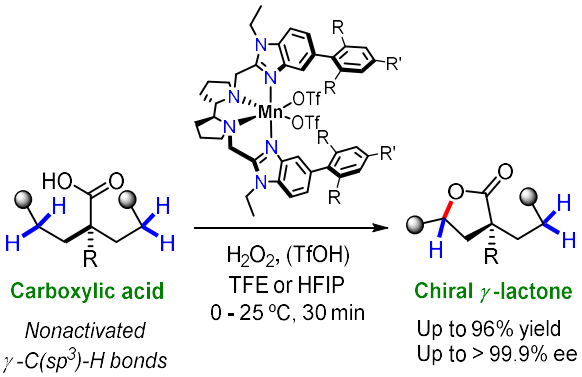
Chiral oxygenated aliphatic moieties are recurrent in bioactive molecules and constitute one of the most versatile functionalities for further elaboration.[1] A major challenge for developing synthetically useful C-H oxidation reactions is the control over the stereoselectivity.[2] Herein we report a protocol for straightforward and general access to chiral $\gamma$-lactones via enantioselective oxidation of strong nonactivated primary and secondary C($sp^3$)−H bonds in readily available carboxylic acids.[3] The key enabling aspect is the use of robust sterically encumbered manganese catalysts that provide outstanding site-selectivity with unprecedented levels of enantioselectivity (up to >99.9% ee) and yields (up to 96%) employing hydrogen peroxide as the oxidant. This is a broad, readily accessible class of substrates that can be converted, through site and enantioselective lactonization, into precious oxygenated cyclic skeletons with innumerable synthetic applications ranging from natural products to multifunctional materials. The potential of this methodology in enabling powerful retrosynthetic strategies is showcased in the streamlining of synthetic routes of important natural products.

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# P7 - SYNTHESIS OF CURVED PERYLENE-BASED NANOGRAPHENES

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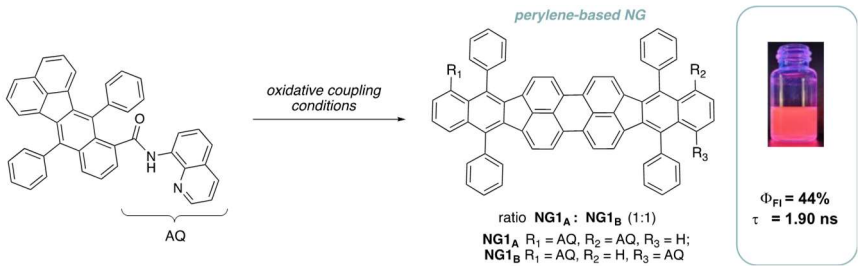
Nanographenes (NG) and graphene nanoribbons (GNRs) have been considered as promising candidates with application in material science, organic solar cells, among others.[1] The ''bottom-up'' protocols for the synthesis of NG use organic synthesis tools to control their sizes, topologies and edge structures precisely, giving rise to well-defined molecular structures.[2] 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($sp^2$)–F and C($sp^2$)–OMe functionalization under nickel catalysis using 8-aminoquinoline (8-AQ) directing group.[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 causes a flexible non-planar distortion depending on the 8-AQ orientation. Remarkably, the perylene-based nanographenes are pH-dependent fluorescent materials with high quantum yield at alkaline media.

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# P8 - SUPRAMOLECULARLY DIRECTED ENANTIOSELECTIVE γ-LACTONIZATION OF CARBOXYLIC ACIDS USING BIOINSPIRED MANGANESE CATALYSTS

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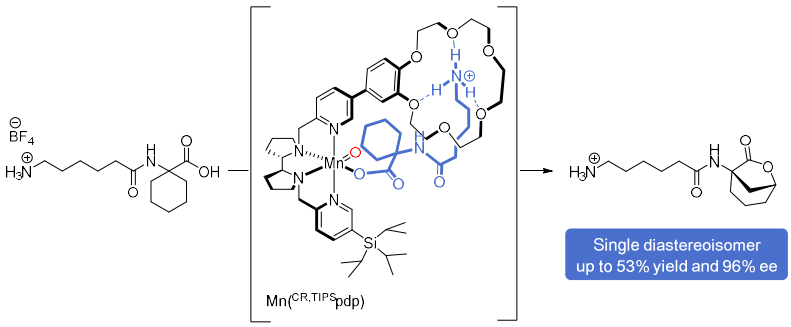
Lactones are known for their diverse and often potent biological activities, making them a fascinating group of molecules for biomedical and chemical research. One of the most desirable processes for obtaining novel lactone compounds is the direct lactonization of carboxylic acids. During the latest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

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

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# P9 - CONFINING GOLD COMPLEXES IN LARGE ANIONIC CAGES

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Gold complexes have been the subject of an intense research over the past decade.[1] The main driving force to this interest is to impart new reactivity to these complexes, that can be leveraged in catalysis. In addition to the widely used ligand engineering strategy,[2] the concept of confining gold complexes within supramolecular cages has also shown a great potential.[3] Toste et coll. have demonstrated, that small cationic gold complexes, generated within anionic cages show a markedly different reactivity compared to their non-confined analogues. However, the small cavity size of the cage (251 Å$^3$) has not allowed to extend this concept to larger complexes and substrates. Indeed, one obstacle to overcome is the synthesis of large anionic cages, that is far from being straightforward.

In order to design and synthesize large anionic cages, we have implemented a rational approach combining modelizations and cavity size calculations.[4] As a result, we have recently prepared an anionic, cyclotricatechylene based supramolecular cage 1 with a large cavity (558 Å$^3$). The host-guest chemistry of this cage has been studied, using different cationic guest (e.g. gold complexes, Au$^+$@1). Our efforts to demonstrate the confinement-driven reactivity in our larger system are currently underway (Figure 1).

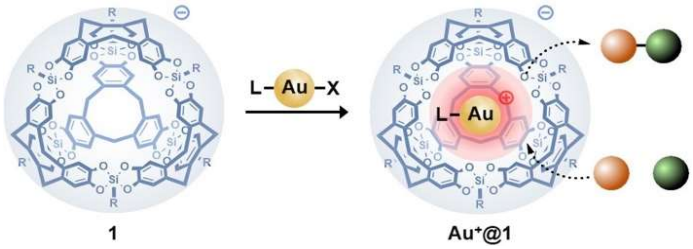


**Figure 1.** Concept: Using the confinement effect to alter the reactivity of gold complexes.

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# P10 - IMINE-BASED DYNAMIC COVALENT CHEMISTRY UNDER PHYSIOLOGICAL CONDITIONS

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Imine-based dynamic covalent chemistry has offered remarkable advantages in fields like Biochemistry, Systems Chemistry and Materials.[1] However, the high propensity of imines to be hydrolysed in aqueous media, together with the challenging competition with the $H_2O$ addition to the carbonyl group of the aldehydes, preclude their application under physiological conditions.[2] Consequently, many research efforts have been devoted to increase the stability of imines in water in the last decade. In Nature, imination reactions are efficiently achieved in the sophisticatedly-arranged active sites of enzymes, using pyridoxal phosphate (PLP) as the aldehyde.[3] We showed how attractive supramolecular interactions between the two components of imines enhance the stability of the reversible aldimine bond, showcasing the mode-of-action found in PLP-dependent enzymes.[4] In addition, we also studied the key structural features that an aldehyde should present to favour imination reactions while disfavouring the competing hydrate formation in water, which represents a major challenge when using diluted physiological conditions.[5] Such increased imine yields allowed for the dynamic bioconjugation to model enzymes and the reversible inhibition of their activity.

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# P11 - HYBRID MATERIALS OF LOW MOLECULAR WEIGHT GELS AND MOLYBDENUM CLUSTERS FOR APPLICATION IN CATALYSIS

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Molybdenum sulfide clusters, such as $Mo_3S_4$, occur as stable species that can tune their properties through the ligand coordination environment. Furthermore, these species can exhibit metal-metal, metal-sulfur and metal-ligand interactions that expand their possibilities in multifunctional catalysis, representing an intermediate class between mononuclear complexes and periodic solids [1]. The development of sustainable and environmentally friendly catalytic processes is a current challenge. Although heterogeneous processes are preferred in industry, homogeneous catalysis is dominant in organic synthesis and fine chemicals due to its higher selectivity. Therefore, the immobilization of metal molecular systems on diverse supports offers catalysts that combine the advantages of both processes.

Low molecular weight gels (LMWG) can be used as supports for catalyst immobilization and, in contrast to polymer gels, are formed by the self-assembly of small organic molecules. They offer a precision in molecular organization that polymers do not have, leading to a highly organized supramolecular structure and novel catalytic behaviors, like those found in natural enzymes [2]. Here we propose the preparation of supramolecular catalytic gels formed by amino acid and peptide-based low molecular weight gels and molybdenum catalytic clusters.

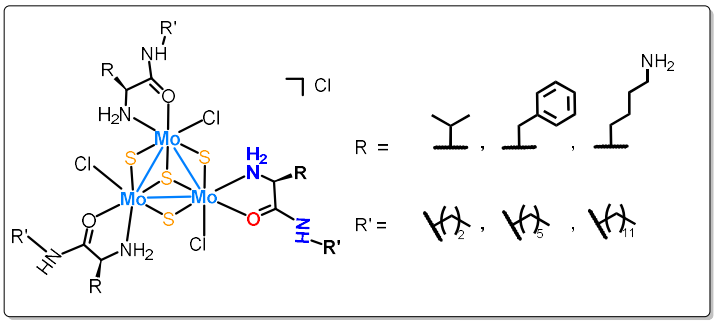


Figure 1: Structure of molybdenum clusters with ligands derived from amino acids.

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# P12 - SECONDARY BRACING LIGANDS DRIVE HETEROLEPTIC CAGES FORMATION

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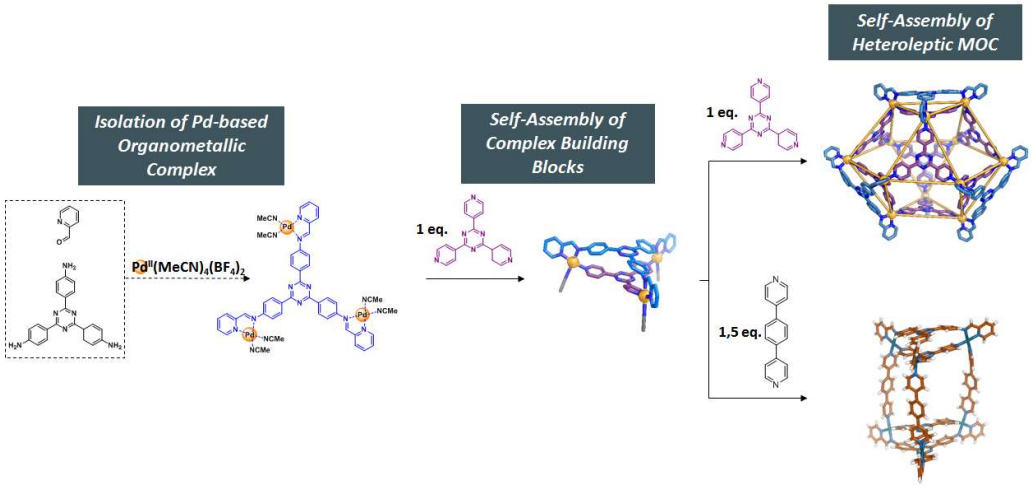
The structural complexity of self-assembled metal-organic capsules can be increased by incorporating two or more different ligands into a single discrete product.[1] Such complexity can be useful in enabling the binding of larger, less symmetrical, or more guests.[2] We designed a strategy for the use of subcomponent self-assembly to selectively prepare heteroleptic cages from simple, commercially available starting materials. Our strategy involves the initial isolation of a tris(iminopyridyl) $Pd^{II}_3$ complex, which reacts with a tris(pyridyl)triazine ligand to form a heteroleptic sandwich-like architecture (1).[3] The tris(iminopyridyl) ligand within 1 serves as a "brace" to control the orientations of the labile coordination sites on the $Pd^{II}$ centers. Self-assembly of 1 with additional pyridine-based tritopic or ditopic ligands, were thus directed to generate a series of heteroleptic cuboctahedrons[3] and trigonal prisms (TP), respectively. Upon encapsulation of a Δ-TRISPHAT guest within the cavities of the TP constructed with flexible ditopic ligands, the stereochemical information of the guest is transferred to the host, yielding a diastereomerically pure host-guest adduct. Furthermore, this host-guest adduct can be used for the enantioselective discrimination of large chiral molecules, such as (PP)-cryptophane-111 and (MM)-cryptophane-111, proving the synergistic effect between the host and the guest.

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# P13 - PHOTOREDOX-ACTIVE COORDINATION CAGES

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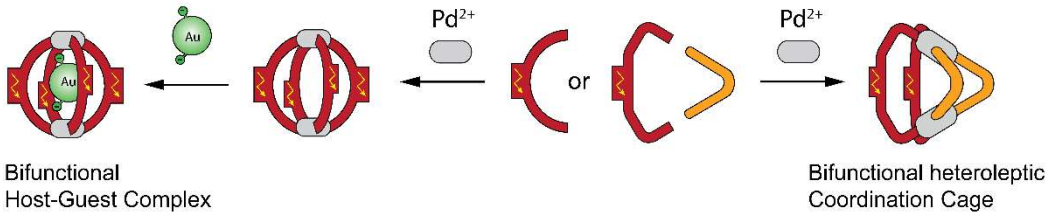
In nature, enzymes use their three-dimensional structure to create a distinct microenvironment equipped with substrate binding sites and reactive functional groups to perform highly selective and efficient catalysis. The self-assembly of organic ligands and metal-ions into supramolecular cages and capsules is an approach to mimic these properties by creating an inner environment that is different from bulk solution.[1] Through the use of shape-complementary ligands we can achieve a non-statistical self-assembly of multiple different ligands into a single coordination cage, which can be used to increase the number of functional moieties.[2] Additionally, further complexity can be achieved by encapsulation of a functionalized guest molecule into the cavity of the cage. In our research we investigate Pd(II)- and Zn(II)-based assemblies of photoredox-active ligands that can be combined with e.g. H-bond donors, chiral moieties or transition-metal catalysts to create multifunctional systems. These systems are studied towards their photophysical and electrochemical properties as well as their performance as catalysts in organic transformations. We could show guest encapsulation of a sulfonated Au(I) catalyst in a $Pd_2L_4$ coordination cage based on photoredox-active phenoxazine ligands as well as the non-statistical formation of $Pd_2A_2B_2$ cages bearing two ligands with different functional backbones.

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# P14 - CHIROPTICAL RECOGNITION OF ANIONS WITH NEUTRAL $L_2Zn_2$ HELICATES

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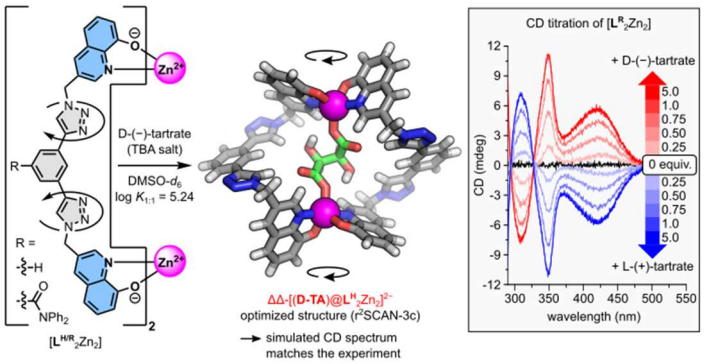
Chirality analysis of small molecules is crucial for determination of their enantiopurity. Current methods utilize streamlined chromatographic techniques with chiral stationary phases. However, chiroptical probes based on host-guest interactions offer an alternative approach, using common spectroscopic techniques like CD spectroscopy to distinguish enantiomers and quantify their ratio.[1]

Aiming at this, we explored the potential of charge-neutral double-stranded zinc(II) helicate-based anion receptors, incorporating triazole units that can rotate and give rise to a meso structure or a racemic mixture of the right- and left-handed complex. This receptor was proved to have high binding affinities towards dicarboxylates with association constants ranging up to 108 M-1 in DMSO as shown in previous study.[2] By utilizing chiroptical responses upon recognition of chiral mono- or dicarboxylates, we conduct chirality analysis of tartrate using CD spectroscopy. Enrichment of one of the enantiomers of the racemic helicate occurs upon chiral guest binding which results in cotton effects.[3] This receptor-based approach offers high-throughput screening capabilities with minimal waste production and provides an alternative to current methods in chiral analysis.

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# P15 - HYBDRID HYDROGEL BASED ON LMWG AND POLYAMINO ACIDS AS BIOCOMPATIBLE MATERIAL FOR NEURONS GROWTH

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In the last thirty years, low molecular weight gelators (LMWG) have received more and more attention from the scientific community due to its vast applicability, such as sensing and catalysis,[1] optoelectronics,[2] drug delivery,[3] tissue engineering[4] and cell culture[5]. The compounds that fall in this class of molecules are not defined by their structure, but rather by their ability of self-assemble under certain conditions thus creating a network of aggregates that trap the solvent inside resulting in a gel formation.

In this work, tetrapeptides-based LMWG combined with polyamino acids were employed as biocompatible material to grow foetal neurons as part of the study of spinal cord injury reparation. Preliminary results, including viability tests, immunogenic tests and confocal microscopy imaging will be presented.

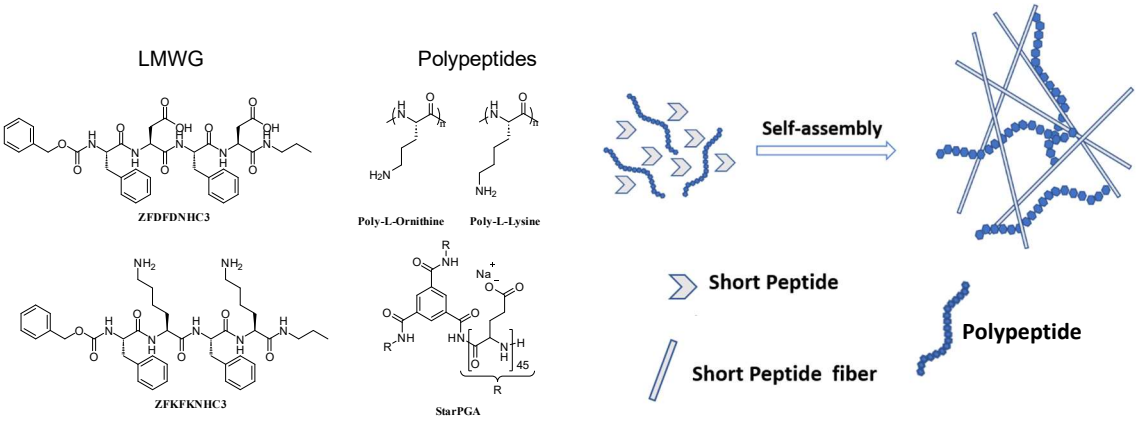


***Figure 2** a) Chemical structures of low molecular weight gelators and polypeptides b) Cartoon representation of the construction of two-component hydrogels.*

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# P16 - SUPRAMOLECULAR POLYMERIZATION MOTORS: "VIEWED AND FELT" BY ATOMIC FORCE MICROSCOPY

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The study of the processes occurring in living organisms is of fundamental importance and is also a key source of inspiration for the development of new intelligent mater [1,2]. All movement in living organisms is the result of the combined action of dynamic molecules working together to convert chemical energy into orderly activity. Given that the magnitude of the Brownian motion is several orders larger than any mechanical action produced by small molecules, biological molecular machinery operates within large supramolecular assemblies [3].

Molecular mechanisms operating at the level of self-assembly processes are known as polymerization and depolymerization motors [4]. They are capable of exerting pushing and pulling forces and perform useful mechanical tasks at the level of cross-linked polymer networks and at the level of individual fibers [5,6]. Examples of biological polymerization machines that operate on these principles are cellular microtubules and actin filaments [7,8].

Since methods for characterization of life-like systems are necessary for the re-engineering of biological principles of force generations, current project aims to develop a method for qualitative and quantitative assessment of the performance of artificial supramolecular motors using atomic force microscopy (AFM).

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# P17 - COMPUTATIONAL EXPLORATION OF THE PROMISCUOUS ACTIVITY OF ASPARAGINASE

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L-Asparaginase, which catalyzes the hydrolysis of L-Asparaginase to L-aspartic acid, has been used as an anticancer agent, as a part of a treatment protocol for childhood acute lymphoblastic leukemia (ALL) since its approval in 1978[1]. Unlike normal tissue, this type of blood cancer is incapable of synthetizing L-asparaginase, which makes them completely dependent on extracellular supplies[2]. Targeting this issue, the supply of L-Asparaginase drug acts to quickly deplete Asparagine in the blood, which specifically affects the ALL cells by starving them to death and leading to their apoptosis[1], while leaving normal cells largely intact. The major throwback of the application of L-Asparaginase drug is its glutaminase side reaction, while this enzyme promiscuity is required for a high efficacy[3], the resulting reduction of glutamine levels causes detrimental side effects on the patients, including: nausea, pancreatitis, etc[1].

Up to recent years, structural and biochemical properties of L-asparaginases have been extensively investigated, providing an accurate structural description of the enzyme isolated from a variety of sources, as well as clarifying the mechanism of its activity[1]. In efforts to improve the clinical properties of this important anticancer drug and taking advantage of the structural availability of the enzyme, in this study we use Quantum Mechanics (QM) and Molecular Dynamics (MD)[4] to elucidate the differences in substrate specificity and activity.

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# P18 - TOWARDS EFFICIENT OLEDS: TWISTED TRIAZINE MATRICES AND EMITTERS

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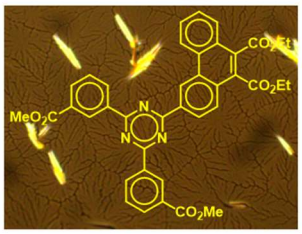
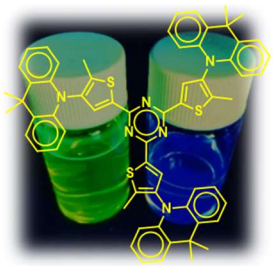
Donor-acceptor scaffolds with an inner electron-accepting aromatic unit and three twisted outer electron-donating units exhibit enhanced oscillator strength compared to simple donor-acceptor systems. They are efficient electroluminescent dyes, as strong spin-orbit coupling (SOC) allows for fast singlet-triplet intersystem crossing leading to emission from both singlet and triplet states.[1] OLED efficiency is hindered by poor light-out coupling. When emitter layers, containing a high-quantum-yield luminogen within a large-band-gap matrix, are in a randomly oriented glassy state, emission becomes largely isotropic. This results in a portion of emitted light being trapped within the device cavity. However, aligning emitting dipoles parallel to device interfaces promotes mainly perpendicular emission, reducing light trapping. This alignment can lead to up to a 50% increase in light output.[2] To maintain a homogeneously aligned configuration in a robust solid, liquid crystalline order should be present in a glassy state around and above room temperature. To effectively support third-generation delayed fluorescence (DF) emitter materials, which rely on reverse intersystem crossing between excited triplet and singlet states, the matrix material should possess a higher triplet excited state energy than the emitting guest molecules. Ideally, the $T_1$ state energy should be approximately or above 3 eV to enable emission across all visible wavelengths, including blue. We identified triphenyl-triazine[3] as a suitable large-$T_1$-energy core with threefold symmetry for developing liquid crystalline derivatives. To prevent crystallization and promote high viscosity, which favors a glassy columnar LC state, we utilize short alkyl chains and a non-planar core with rotational freedom and low symmetry.[4] Additionally, the incorporation of heavy atoms, such as thiophene bridges in new $C_3$-symmetric emitters based on a triazine core, has improved DF and room temperature phosphorescence (RTP) by enhancing singlet-triplet interconversion, facilitated by spin-orbit coupling.[5] These materials offer promising pathways for the development of highly efficient OLED devices.

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# P19 - TRANSMISSION OF CHIRALITY WHITHIN [2]ROTAXANES: FROM MECHANICALLY PLANAR-TO-POINT CHIRALITY

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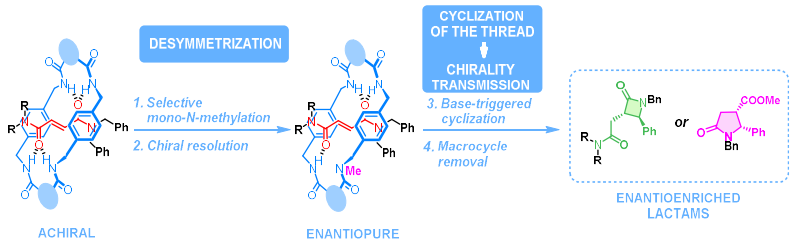
In recent years, there has been a growing interest in enantioenriched mechanically interlocked molecules (MIMs),[1] with potential application in various fields, such as asymmetric catalysis.[2] The architecture of MIMs, comprising at least two interlocked components, offers diverse avenues for introducing chiral information. In rotaxanes, strategies commonly employed involve incorporating point or axial stereogenic elements at the thread or the macrocycle. However, MIMs can exhibit stereochemistry solely reliant on the mechanical bond, known as mechanically planar chirality (MPC), having all components achiral. In this study, we present an approach to transmit chirality from MPC to point chirality in [2]rotaxanes.[3] A highly selective mono-*N*-methylation of one amide N atoms within the macrocyclic component of achiral rotaxanes generates mechanically planar chirality, and both enantiomers were separated by chiral resolution. Subsequent base-promoted intramolecular cyclization of each enantiomer leads to the formation of new lactam moieties. Remarkably, the mechanically planar chiral information is effectively transferred to the resulting stereocenters (covalent chirality) of the newly formed heterocycles.

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# P20 - INTRAMOLECULAR INTERCEPTION OF THE REMOTE POSITION OF VINYLCARBENE SILVER COMPLEX INTERMEDIATES BY C(SP3)−H BOND INSERTION: A DFT PERSPECTIVE

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Transition metal-catalyzed functionalization of C-H bonds provides an alternative to classical methods for constructing C-C and C-heteroatom bonds. Metal carbenes are especially powerful reagents for C-H insertion, although controlling the selectivity poses a major challenge.[1] Vinylcarbene metal complexes are a powerful subclass of metal carbenes that exhibit electrophilic reactivity at the vinylogous position in addition to the carbenic site. This opens new possibilities but further complicates the reaction control.[2]

Herein we report a mechanistic study of the first example in which the vinylogous position of a metal vinyl carbene has been selectively functionalized by a C($sp^3$)-H bond insertion, a reaction that was possible under $Tp^x$-silver complex catalysis. The silver vinyl carbene was in situ generated through a carbene/alkyne metathesis (CAM). The donor-donor vinyl silver carbene species exhibits selective vinylogous C($sp^3$)−H bond insertion, resulting in the synthesis of a new group of benzoazepines. The reaction mechanism was investigated using comprehensive Density Functional Theory (DFT) calculations, revealing a stepwise C−H bond insertion with the hydrogen shift identified as the rate-determining step. The factors influencing the selectivity of the vinylogous versus carbenic reaction have also been studied by computing the reaction with different catalytic systems. This study presents a significant advancement in synthetic methodology and contributes to a detailed mechanistic understanding, paving the way for further developments in carbene chemistry.[3]

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# P21 - FLEXIBILITY DRIVES OXALATE RECOGNITION WITH NEUTRAL $L_2Zn_2$ CONTAINERS.

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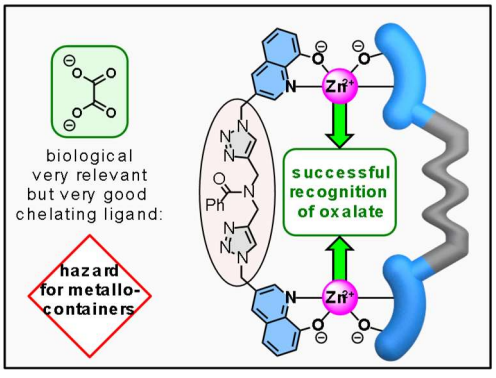
Dicarboxylic acids and their corresponding anions are involved in several industry processes and are omnipresent in nature. Many dicarboxylic acids are, for example, intermediates in the biosynthesis of proteins and environmental metabolites.[1,2] Oxalic acid, the simplest dicarboxylic acid, may cause a multitude of health problems including kidney stones and liver damage.[3-4] Thus, research tackling new receptors for especially oxalate is of great importance. Recently, our group published the first version of a charge-neutral metal-based self-assembled $L_2Zn_2$ helicate with the capability of binding dicarboxylates with astonishing binding affinities in competitive media.[5] Inspired by its size selectivity regarding the dicarboxylate length with naphthalene-2,6-dicarboxylate as aromatic and pimelate as aliphatic analyte being ideal matches for the receptor, the goal of this project is to bind now even shorter dicarboxylates. By modulation of the planar backbone with rather rigid bond angles to a more flexible backbone based on dipropargyl amine, the host-system increases its degree of freedom. Hence the system is capable of binding oxalate.[6]

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Poster

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# P22 - METAL OXIDES TOWARDS THE FIXATION OF $CO_2$ WITH EPOXIDES: FROM HOMOGENEOUS TO HETEROGENEOUS CATALYSIS

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Cycloaddition of $CO_2$ with epoxides is currently one of the most attractive, straightforward and green protocols to fixate $CO_2$,[1] with the potential to do so under mild conditions if the proper catalytic system is applied and having the extra advantage of yielding products of industrial interest: five-membered cyclic carbonates. This type of compounds can be used as an intermediate for polycarbonate, dimethyl carbonate and polyurethanes, as a solvent in paint, personal care and cosmetics products, and as an electrolyte in lithium-ion batteries.[2]

The reaction mechanism was studied through Density Functional Theory (DFT) calculations with metal oxides as catalysts, with symbiotic approaches of heterogeneous periodic calculations to describe their solid nature and the adsorption and desorption processes on the surface, and of small clusters, like nanoparticles, to have a better understanding of transition states and the role of H in the reaction.

The investigation focused on zinc (II) oxide (ZnO) and tin (IV) oxide ($SnO_2$) nanomaterials as potential environmentally friendly, easily recoverable and cost-effective catalysts to achieve this, based on the experimental results of D'Elia and collaborators,[3] who recently studied nanoparticles (NP), nanorods (NR), nanosheets (NS) and microplates (μPLs), in combination with small amounts of tetrabutylammonium iodide (TBAI) as a nucleophile. Unlike the general case of metal oxides, which often require harsh reaction conditions, they were able to catalyze the cycloaddition of $CO_2$ to various terminal epoxides at atmospheric pressure at moderate temperatures (60-80 °C), and found to have better yielding in the presence of H.

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Poster

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# P23 - SELECTION OF ORDER DRIVES ADAPTATION AND COMPLEX PROCESSES IN CONSTITUTIONAL DYNAMIC NETWORKS WITHIN MICRO-COMPARTMENTS

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The understanding of processes governing the transition from chaotic mixtures of molecules to systems of high compositional and functional complexity remains a challenge. The development of artificial models suggests that the formation of self-assemblies leading to increasing order may be the driving force for selection mechanisms that could rationalize the emergence of complexity.[1] However, the examples supporting such ''cosmetic imperative'' only passively relies on environmental factors and chemical reaction networks. Therefore, this work aims to shine light on the mechanisms of selection by self-assembly in adaptive networks with lipidic micro-environments—the only chemical entity that possesses the three hallmarks of complexity,[2] namely: catalysis, reproduction and containment. Gradual increase in complexity requires processes involving diversity and selection. Dynamic Covalent Libraries generate the compositional complexity for diversity affording a large variety of interconnected species defining Constitutional Dynamic Networks where competition for building blocks underlies the rules of selection.[3][4] To study such insights, dynamic covalent chemistry focused on imine bond is in presence of micellar micro-compartments demonstrates their selective propensity to prevent hydrolysis and that constitutional dynamic networks can be affected by micro-environments.[5] Such proof of concepts is extended to the formation of dynamic covalent micelles and vesicles in a mixture of constituents to unravel the selection mechanisms in the accretion of order, leading to dynamic mixed catalytic micelles capable to sustain complex functions.

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Poster

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# P24 - SIMULATIONS ON THE REGIO-FUNCIONALIZATION OF SPHERICAL MOLECULES WITH SUPRAMOLECULAR MASKS

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Spherical molecules, like fullerenes and diamondoids, are a key interest for many applications. But, due to their symmetry and spherical shape, their functionalization is a challenging task.
Molecular dynamic simulations is a powerful predictable tool to explain, at molecular level, how the molecules interact between them. Here, the host-guest chemistry of diamondoids with nanorings, such as cycloparaphenylenes (CPP) and cucurbiturils (CB), is studied. Furthermore, the construction of ternary assemblies with supramolecular cages is investigated.[1] The $C_{70}$ encapsulated inside a nanocapsule has been functionalized through the Bingel reaction[2] and also the Diels-Alder reaction,[3] obtaining full control in its regio-selectivity due to the mask strategy, analogous to the reported works for the $C_{60}$.[4,5] The goal is to explain how this reactivity takes place through simulations, that provide information on how the molecules moves and orients inside the cavity of the cages.

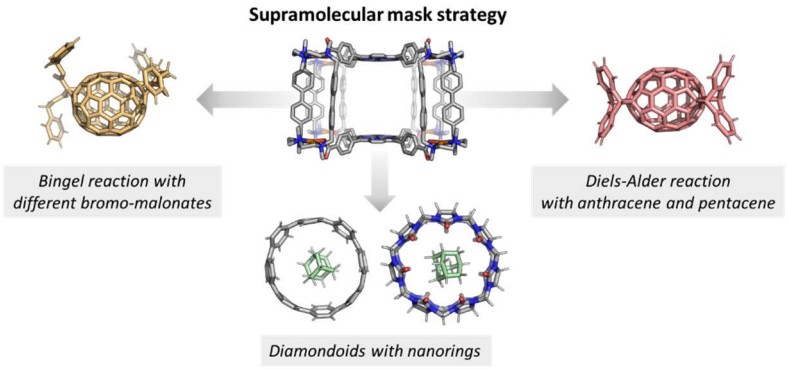


**Figure 1.** Schematic representation of the applications of the supramolecular cages.

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Poster

# P25 - LUMINESCENT CHIRAL FURANOL-PAHs VIA STRAIGHFORWARD Ni-CATALYZED Csp2-F FUNCTIONALIZATION: MECHANISTIC INSIGHTS INTO THE SCHOLL REACTION

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In the recent years, polycyclic aromatic hydrocarbons (PAHs) compounds such as nanographenes and graphene nanoribbonds (GNRs) have received more attention due to their wide applications in material science, optoelectronic devices and supramolecular chemistry. Hence, the development of efficient and novel strategies for the synthesis of these compounds stands as a research topic of interest. [1,2] 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 and $C_{sp2}$-F functionalization strategy (Figure 1).[5] Interestingly, most of these compounds exhibited fluorescence in solution, for this reason we have also explored their fluorescent properties including absorption and emission spectra, quantum yields and lifetimes.

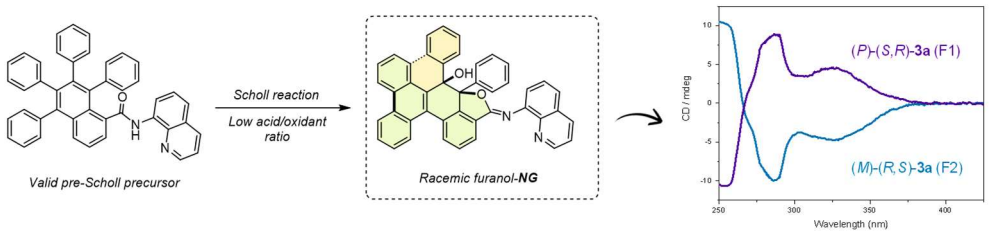


**Figure 1**. Synthesis of chiral furanol-NG compounds.

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Poster

# P26 - ENANTIOSELECTIVE ALDOL REACTION CATALYZED BY A ORGANOCATALYST ENCAPSULATED IN A SUPRAMOLECULAR METALLOCAGE

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Inspired by Nature, the construction of various supramolecular hosts, either synthetic or natural, to mimic the catalysis of enzymes has been the subject of intensive research for decades in supramolecular chemistry.[1][2][3] While remarkable acceleration in reactivity and improvement of regioselectivity have been achieved in many reactions via supramolecular strategy. However, there are a less number of reports on enantioselective surpamolecular catalysis, particularly those related to biomimetic asymmetric catalysts that could work favorably under normal enzymatic conditions. To elucidate the possible connections between recognition and chiral catalysis with a simple supramolecule-linked asymmetric catalyst will certainly shed new light on supramolecular catalyst design and strengthen our understanding of enzymatic catalysis as well. Enantioselective aldol reactions are important methods to synthesize *β*-hydroxy carbonyl compounds in optical pure form, and as such, numerous successful chiral catalysts were designed and applied for asymmetric aldol reactions.[4] Herein, we present a new approach of asymmetric organocatalysis has been developed by combining the supramolecular metallocage and the organocatalyst (Figure 1). The resulted encapsulated organocatalyst will be studied in enantioselective direct aldol reactions under mild conditions.

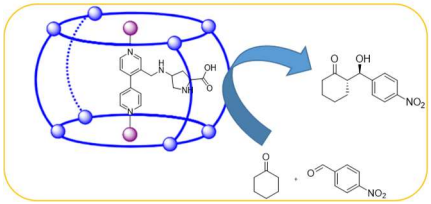

Figure 1. Enantioselective direct aldol reaction at the confined space.

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# P27 - Design Parameters and Thermodynamic Insights in Multicomponent Supramolecular Hydrogel Assemblies

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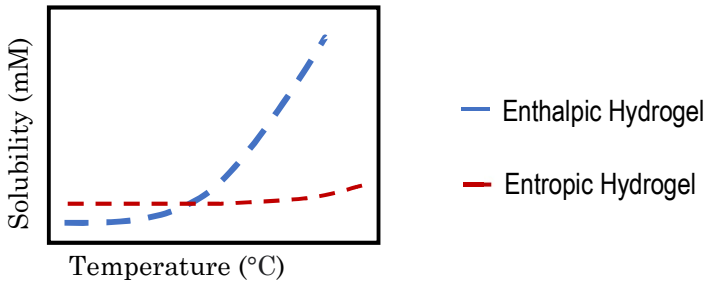
Multicomponent gel materials can be obtained by the combination of different supramolecular gelators allowing the manipulation of extra variables and improving characteristics that would not be possible with only one component.[1] However, when such gelators are combined to form a multi-component system, they can behave in different manners: they can self-sort into separate networks, co-assemble into intimately interacting fibers, or mutually disrupt, among other scenarios. Therefore, it is very interesting to devise design rules to control multicomponent self-assembly.[2] Here we utilize low molecular weight supramolecular gelators for hydrogel preparation, with a focus on creating assemblies driven by either enthalpy or entropy, emphasizing their crucial role as design parameters to prepare multicomponent materials.[3] Notably, it is relatively easy to identify entropic or enthalpic gels experimentally. To achieve this, one could use $^1$H NMR studies of solubility versus temperature or the concentration dependence of Tgel.[4] Further on, the combination of enthalpic gelators (T sensitive) with entropic gelators (T insensitive) is used as a strategy to prepare two-component networks with temperature-controlled mechanical properties.[5] Systems of this nature can be employed to enhance the observation and understanding of additional polymorphic transitions.[6]

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# P28 - Unveiling Local Atomic Structure in functionalized Zr-MOFs through X-ray Absorption Spectroscopy

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In this study, we employed a comprehensive approach combining simultaneous measurements of X-ray diffraction and X-ray absorption spectroscopy (XANES and EXAFS) at Pd and Zr *K*-edge to investigate the structural evolution of Pd-functionalized Zr-based metal-organic framework (MOF) UiO-67 during operando carbon dioxide hydrogenation.[1]

Initially, the MOF was prepared with Pd atoms incorporated as modified bipyridine linkers, followed by activation through temperature treatment in a hydrogen-containing atmosphere to generate Pd nanoparticles.[2] Subsequently, $CO_2$ hydrogenation experiments were conducted at varying temperatures (240, 200, and 170 °C) and pressures (1 and 8 bar), with online mass spectrometry employed to monitor catalytic activity.

Analysis of XANES spectra was conducted using the MCR-ALS procedure,[3] allowing determination of the number of distinct species, their respective spectra, and concentration profiles, observing three main components: a metallic palladium, and two mixed palladium hydride and carbide phases. To elucidate these observed changes, theoretical spectra were computed for the Pd surface with adsorbed atomic species. Simulation of XANES spectra utilized the FDMNES code,[4] with the highest resemblance to experimental data observed for bridge CO, suggesting its role as stabilizing agents for smaller Pd.

During CO2 hydrogenation, a reduction in Zr–O coordination within the inorganic building units of UiO-67 occurs at higher temperatures, although the overall UiO-67 lattice remains structurally stable under all conditions. Notably, an interface between Zr and Pd is identified in EXAFS analysis, indicating its involvement in methanol formation within UiO-67-Pd samples.

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Poster

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# P29 - *NIDO* CAGE···Π AND CAGE⁻···CAGE⁻ INTERACTIONS: TWO NEW NON-COVALENT INTERACTIONS

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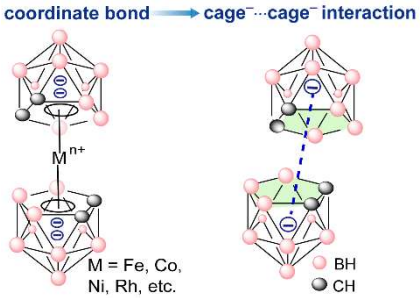
We discuss first the three-dimensional aromaticity of *closo* and *nido* boranes.[1] Then, we report two new type of non-covalent interactions. First, the *nido*-cage···π bond, between the boron cluster $C_2B_9H_{12}^-$ and an aromatic π system.[2] The X-ray diffraction studies indicate that the *nido*-cage···π bonding presents the same parallel-displaced or T-shaped geometries as π···π interactions does.[3] The contacting distance between the cage and the π ring varies with the type and the substituent of the aromatic ring. Quantum chemical calculations reveal that this *nido*-cage···π non-covalent interaction shares a similar nature to the conventional anion···π or π···π[3] bond found in classical aromatic ring systems. Our theoretical calculations reveal a major electrostatic character or orbital- and dispersion-dominated interaction, similar to those found in cyclopentadienyl anion···π or π···π interactions. And second, the non-covalent interaction (denoted as cage⁻···cage⁻ interaction) between two *nido*-carborane clusters was successfully realized by using a pyridinium-based molecular barrier.[4] The X-ray diffraction studies uncover that the cage⁻···cage⁻ interaction has a contacting distance of 5.4–7.0 Å from centroid to centroid in the systems reported here. Theoretical calculations validate the formation of the non-covalent interaction and disclose its repulsive bonding nature that is overcome thanks to the positively charged pyridinium-based framework.

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Poster

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# P30 - INNOVATIVE SYNTHESIS OF CCC–NHC AU(III) PINCER COMPLEXES: A ROBUST PLATFORM FOR ISOLATING ELUSIVE SPECIES

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Pincer ligands incorporating N-heterocyclic carbene (NHC) fragments have shown intriguing characteristics, leveraging their strong donor ligand properties to enhance metal center nucleophilicity.[1-3] However, exploration of NHC-pincer ligands in Au(I) and Au(III) chemistry remains limited, with few examples described.[4] Our study delves into the reactivity of novel CCC–NHC Au(III) pincer complexes synthesized through innovative methods. These complexes, featuring a central aryl moiety and NHC ligands, demonstrate notable stability, enabling isolation of elusive Au(III) species such as Au(III)–formate, Au(III)–F, Au(III)–Me, and Au(III)–alkyne (Figure 1). Additionally, we uncover Au(III)–H species and investigate their formation, stability, and reactivity. Despite room temperature stability, decomposition of the CCC–NHC Au(III)–H complex is observed at higher temperatures, especially under acidic conditions. Our experiments reveal the potential of Au(III)–formate for β–hydride elimination, pivotal in formic acid dehydrogenation. Ultimately, the CCC–NHC Au(III) pincer complex serves as a versatile platform for isolating reactive species and elucidating fundamental catalytic mechanisms.

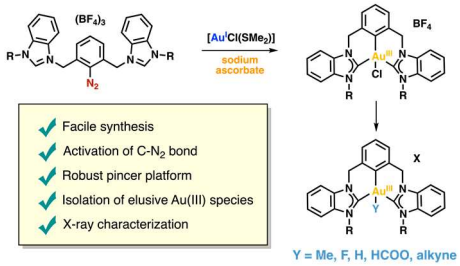


Figure 1. Synthesis of CCC–NHC Au (III) pincer complexes

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# P31 - SPURIOUS OSCILLATIONS IN THE ELECTRONIC CONTRIBUTIONS OF NONLINEAR OPTICAL PROPERTIES

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Nowadays, great attention has been paid to materials characterized by a large nonlinear optical (NLO) response due to their applications in electrooptics, among others. An example of an NLO process is the second harmonic generation, in which two photons with the same frequency interact with a noncentrosymmetric material, and are combined resulting in the refraction of a photon with double frequency. Despite the interest shown for NLO properties, only a few quantum chemistry methods provide accurate values for them.

Density Functional Theory (DFT) methods can be an attractive alternative for computing these properties, as they yield accurate results for other properties, such as reaction energies, at a low computational cost. However, a grid of points for numerical integration is required to calculate the approximate exchange and correlation functional in the framework of DFT.

In this project, the results obtained with the M06-2X and wB97X methods employing different grids have been compared, using HF as a reference. It has been observed that for certain systems, the calculation of NLOPs exhibits huge spurious oscillations in the first hyperpolarizabilities, which describe the second-order NLO process at the molecular level. In previous works, spurious oscillations of the first hyperpolarizabilities associated with nuclear displacement have been detected[1], but it is the first time that they are observed in the field-dependent variation of the first hyperpolarizabilities. This implies the possibility that these functionals have intrinsic limitations that go beyond NLOP calculations. It is expected that these results will contribute to the development of more robust DFT functional approximations.

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