3RD FRENCH SUPRAMOLECULAR CHEMISTRY CONGRESS

May 15-17, 2024

Book of ABSTRACTS

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WELCOME TO THE 3RD FRENCH SUPRAMOLECULAR CHEMISTRY CONGRESS – SUPR@PARIS 2024!

On behalf of the organizing committee of Supr@Paris, I am delighted to warmly welcome you all in Paris for this major event for the French Supramolecular chemistry community held under the auspices of the Supramolecular chem group of the French Chemical Society.

Supr@Paris is the third in this series, which began in Lyon in 2018, then in Strasbourg in 2021. More than 250 participants from France, Europe, and around the world are now gathered at Sorbonne University, in the heart of Paris, from 15 to 17 May 2024. We will have 4 plenary lectures, 10 keynote lectures, 22 oral communications and 21 short communications and many posters giving the opportunity to a maximum of people at different stages of their career to show their science.

We have built a program encompassing various fields of supramolecular chemistry: catalysis, machines, assemblies, surfaces, nanotechnology, intertwined molecules, polymers… Everyone should find something to their taste!

We hope that you will enjoy this exciting and unique moment of supramolecular science in Paris!

Matthieu Sollogoub

Chairman of the Organizing committee of Supr@Paris 2024

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The Supr@Paris conference will take place at the Farabeuf amphitheatre and in the cloister galleries of the Cordeliers campus, 15 rue de l'Ecole de Médecine, Paris, 6th arrondissement.

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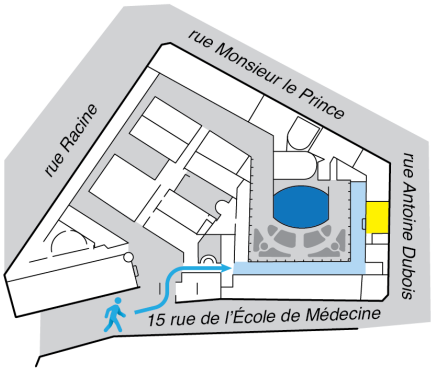

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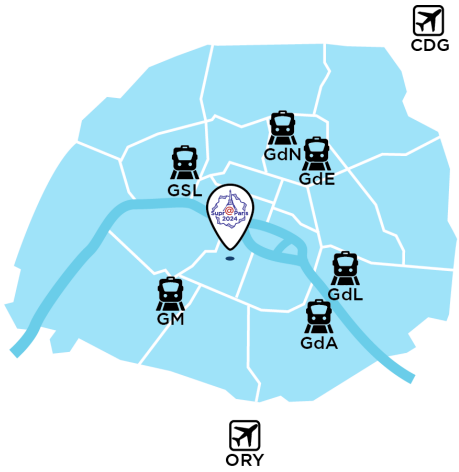

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PROGRAM

Wednesday 15th

8:00	Registration	
9:00	Opening remarks	
Session 1	*Chair: M. Sollogoub*	
9:15	**Hanadi Sleiman** *DNA Nanostructures: From Design to Function*	**PL-1**
10:00	Jonathon Beves *Switchable catalysis within molecular cages*	SC-1
10:05	Lisa Gourdon-Grünewald *DNA mimic foldamers: Tools for Targeting Protein-DNA Interactions*	SC-2
10:10	Yannick Geiger *Competitive exclusion in self-replicating fibres*	SC-3
10:15	Interchim	exhibitor
10:20	Magritek	exhibitor
10:25	Alexandre Martinez *Recent developments in the chemistry of hemicryptophane cages: from recognition to confined catalysis.*	KN-1
10:50	coffee break	
Session 2	*Chair: C. Fave*	
11:20	Fabien Cougnon *Foldaknots*	OC-1
11:35	Emmanuelle Dubost *Design and synthesis of molecular hosts cryptophanes- application in imaging*	SC-4
11:40	Igor Koshevoy *Aggregation of platinum luminophores: from stimuli-responsive emission to through space sensitization*	SC-5
11:45	Karen De La Vega Hernández *Investing in Entropy: The Strategy of Cucurbit[n]urils to Accelerate the Intramolecular Diels-Alder Cycloaddition Reaction of Tertiary Furfuryl Amines*	SC-6
11:50	Pablo Msellem *Molecular tweezers for multifunctional switchable organogels*	SC-7
11:55	Noël Pairault *Design of Rotaxane-based Molecular Machines for Regulation of Dynamic Photon Up-conversion*	SC-8
12:00	Amparo Ruiz Carretero *Small, chiral and self-assembled molecules: the new recipe for supramolecular electronics*	KN-2
12:25	lunch break & posters session (odd numbers)	

Wednesday 15th

Session 3 *Chair: G. Izzet*

14:15	**Steve Goldup** *Mechanically Chiral Molecules: Synthesis and Applications*	KN-3
14:40	**Charlie Mcternan** *Metal-Peptidic Cages - Helical Oligoprolines Generate Highly Anisotropic Nanospaces with Emergent Isomer Control*	OC-2
14:55	**Stéphane Le Gac** *Parallel Chirality Inductions in Möbius Zn(II) Hexaphyrin Transformation Networks*	OC-3
15:10	**Hennie Valkenier-Van Dijk** *Synthetic transmembrane transporters for phosphates*	OC-4
15:25	**Henri-Pierre Jacquot De Rouville** *Multi-Responsive Acridinium Supramolecular Systems: An Increasing Complexity*	OC-5
15:40	**Helena Roithmeyer** *Multifunctional macrocyclic host-modified electrodes for electrocatalysis over a wide pH range*	OC-6
15:55	coffee break	

Session 4 *Chair: B. Colasson*

16:20	**Claire Kammerer** *Design and synthesis of molecular cogwheels for on-surface intermolecular gearing*	KN-4
16:45	**Titouan Chetot** *Switching dynamic covalent reactions of CO2 capture using host-guest chemistry*	SC-9
16:50	**Greta Fogar** *Bis-porphyrin metallacycles: the role of the metal fragment*	SC-10
16:55	**Maxime Roger** *Self-Assembly and Mixed-Valence Species of Pentannulated BisAzaCoronene Diimide*	SC-11
17:00	**Laura Bickerton** *Mechanistic Insights into High Activity Cage Catalysis*	SC-12
17:05	**Geoffrey Groslambert** *In search of elusive species: the paramagnetic pimers of viologens*	SC-13
17:10	**Sébastien Berruée** *Tuning self-assembly of hydrophilic polymers in water through an aromatic supramolecular structure directing unit (SSDU)*	SC-14
17:15	**Leonard Prins** *Towards active matter: chemical energy to assemble high-energy molecular structures*	KN-5
17:40	end of the session	

Thursday 16th

Session 5 — *Chair: L. Sosa Vargas*

9:00	**Paolo Samori** *Chemical and physical sensing with low-dimensional nanostructures: the disruptive power of supramolecular chemistry*	**PL-2**
9:45	Charalampos Pappas *Phosphate-Driven Systems Chemistry*	OC-7
10:00	Shaymaa Al Shehimy *Endergonic adaptive behavior upon fueling of dynamic covalent networks*	SC-15
10:05	Ben Pilgrim *Structural transformations of metal-organic cages through tetrazine-alkene reactivity*	SC-16
10:10	Véolia	exhibitor
10:15	Serlabo	exhibitor
10:20	Elicityl	exhibitor
10:25	Sophie Beeren *Enzyme-Mediated Dynamic Combinatorial Chemistry*	KN-6
10:50	coffee break	

Session 6 — *Chair: M. Ménand*

11:20	Patrice Woisel *Thermoresponsive polymers and host-guest chemistry: a win-win combination*	OC-8
11:35	Sercan Akbaba *Controlled Activation of Supramolecular Catalysts via Chemical and Electrochemical Redox-Switching*	SC-17
11:40	Hasnaa El Said El Sayed *Light-responsive self-assembly of semi-conducting nanoplatelets*	SC-18
11:45	Emilien Husson *Tuning the spectroscopic properties of merocyanines through hybridization of foldamers*	SC-19
11:50	Rajaa Benchouaia *Toward new cryptophane analogs: synthesis and encapsulation properties of an unprecedented water-soluble azacryptophane*	SC-20
11:55	Kevin Mall Haidaraly *Self-organized mesomorph Donor-Acceptor Hybrid material: from molecular design to device performances*	SC-21
12:00	Emmanuel Cadot *Chaotropic effect as an assembly motif in polyoxometalate supramolecular chemistry*	KN-7
12:25	lunch break & posters (even numbers)	

Thursday 16th

Session 7 *Chair: S. Vidal*

14:15	**Ghislaine Vantomme** *Synthesis and assembly of light-responsive supramolecular nanostructures: A step toward adaptive materials*	KN-8
14:40	**Rebecca Churamani** *Architecture modulation by structural modification of cyclodextrins co-assembling with DNA*	OC-9
14:55	**David Leboeuf** *Macrolactonization Enabled by Supramolecular Interactions*	OC-10
15:10	**Jessica Groppi** *Orthogonal Stimuli Responsive Tri-stable Rotaxanes*	OC-11
15:25	**Sander Wezenberg** *Control of Transmembrane Transport by Photoswitchable Molecular Tweezers*	OC-12
15:40	**Payel Khanra** *Pathway complexity in supramolecular polymerization: significance in block co-polymerization and enzyme inhibition*	OC-13
15:55	coffee break	

Session 8 *Chair: B. Hasenknopf*

16:20	**Yann Trolez** *Threading a linear molecule through a macrocycle thanks to boron: an access to highly emissive compounds*	OC-14
16:35	**Fahmi Himo** *Modeling Amine Methylation in Methyl Ester Cavitand*	OC-15
16:50	**Jennifer Bou Zeid** *Cage to cage conversion controlled by redox stimulation*	OC-16
17:05	**Luisa De Cola** *TBA*	**PL-3**
17:50	end of the session	

Friday 17th

Session 9 *Chair: M. Raynal*

9:00	**Dean Toste** *Supramolecular Hosts as Enzyme Mimics*	**PL-4**
9:45	Anthony Kermagoret *Internal dynamics in responsive 3:2 cb[n] complexes*	OC-17
10:00	Lydia Sosa Vargas *Functional patterning of graphene via an all-supramolecular strategy*	OC-18
10:15	Vicente Martí-Centelles *A molecular trojan horse: encapsulating drugs within cages for targeted delivery in cancer*	OC-19
10:30	Reiko Oda *Nanometric inorganic helices for chiral induction, crystallization, amplification and recognition*	KN-9
10:55	coffee break	

Session 10 *Chair: G. Vives*

11:20	David Gonzalez Rodriguez *Molecular encapsulation within tubular supramolecular polymers*	OC-20
11:35	Ran Chen *Switchable supramolecular helices for asymmetric stereodivergent catalysis*	OC-21
11:50	Iwona Nierengarten *Solution and solvent-free stopper exchange reactions for the preparation of pillar[5]arene-containing [2] and [3]rotaxanes*	OC-22
12:05	Guido Clever *From Heteroleptic Coordination Cages to Complex Molecular Systems*	KN-10
12:30	Prizes and closing remarks *Short comm. awards sponsored by Activation* *Posters awards sponsored by Chemical Reviews*	
12:50	end of the congress	

PLENARY LECTURES

DNA SELF-ASSEMBLY: FROM PATHWAY COMPLEXITY TO DRUG DELIVERY

Hanadi Sleiman

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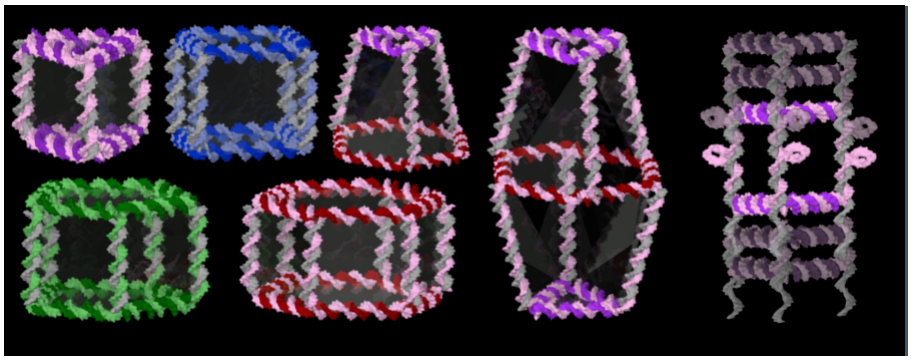
DNA nanotechnology can assemble materials on the nanoscale with exceptional predictability and programmability. In a sense, this field has reduced the self-assembly space into a simple 'alphabet' composed of four letters (A, T, G, C). Nature, on the other hand, relies on many more interactions to build its functional structures, and supramolecular chemistry has taken advantage of these interactions to assemble materials with diverse structures and functions.

This talk will describe our efforts to merge the field of supramolecular chemistry with DNA nanotechnology. This approach results in new motifs and functionalities that are unavailable with base pairing alone. Starting from a minimum number of DNA components and combining them with organic molecules and polymers, we create 3D-DNA host structures, such as cages, nanotubes, and spherical, cylindrical, or lamellar nucleic acids. These nanostructures are fascinating in their self-assembly behaviour and promising for targeted drug delivery. They can encapsulate and selectively release drugs and nucleic acid therapeutics. We find that they resist nuclease degradation, and silence gene expression in vitro and in vivo, in tissues and cell types that are difficult to access with other constructs. We will also discuss the ability of small molecules to reprogram the assembly of DNA, away from Watson-Crick base-pairing into new motifs. This is a fundamental shift in the field, as it expands the DNA 'alphabet' without complex synthesis. The resulting DNA structures can be applied to gene delivery, tissue regeneration and materials science.



References

1. N. Seeman, H. Sleiman, DNA Nanotechnology, ***Nat. Rev. Mat.***, 2017, 17068.
2. F. Rizzuto, C. Platnich, X. Luo, M. Dore, C. Lachance-Brais, G. Cosa, H. Sleiman, A dissipative pathway for the structural evolution of DNA fibers, ***Nat. Chem.***, 2021, 13, 843–849.
3. M. Dore, T. Trinh, D. de Rochambeau, P. Xu, J. Li, H. F. Sleiman, Thermosetting supramolecular polymerization of compartmentalized DNA fibers with stereo sequence and length control, ***Chem***, 2021, 7, 2395-2414.
4. K. E. Bujold, J. C. C. Hsu and H. F. Sleiman; Optimized DNA "Nanosuitcases" for Encapsulation and Conditional Release of siRNA***, J. Am. Chem. Soc.*** 2016, 138, 14030–14038.

Chemical and physical sensing with low-dimensional nanostructures: the disruptive power of supramolecular chemistry

Paolo Samorì

ISIS, University of Strasbourg & CNRS, 67000 Strasbourg, France.

Email: samori@unistra.fr

Low-dimensional nanostructures exhibit a high surface-to-volume ratio which makes their physical and chemical properties highly sensitive to environmental changes. While such a unique sensitivity can be used for the realization of chemical sensors, the unspecific nature of the interactions with the environment drastically limits the selectivity in the sensing events. On the other hand, supramolecular (multi)functional materials are held together by reversible and highly specific interactions between suitably designed building blocks. The use of non-covalent interactions to build sophisticated supramolecular architectures makes it possible to transduce the modifications of their environment into precise modulation of their self-assembly behaviour. The changes of properties upon small environmental variations can be enhanced or amplified by integrating the assemblies into working devices.

Low-dimensional nanostructures chemically functionalized with supramolecular receptors of the analyte of interest can therefore be the key active components for the development of the next generation of sensors exhibiting detection limits down to sub-ppb level combined with fast response speed and unprecedented selectivity. Such a strategy can enable the future fabrication of ultrasensitive and ultraselective sensors for food safety, environmental and biohealth monitoring, as well as for chemical- and biodefense, thus providing a decisive contribution to the improvement of people's quality of life.

In my lecture, I will review our recent endeavour on the tailoring of low-dimensional nanostructures chemically functionalized with the receptors of the target analytes and on the use of these hybrid assemblies to fabricate chemical sensors with an electrical or optical read our, which combine high sensitivity, selectivity, response time and reversibility. In particular, we will focus on chemically functionalized 0D (network of metallic nanoparticles), 1D (supramolecular fibers) and 2D (graphene and other layered materials) for humidity, heavy metal and polyaromatic sensing as well as for the generation of pressure sensors for the diagnosis of cardiovascular diseases.

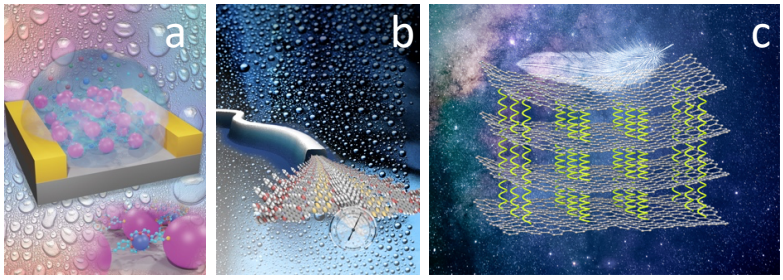


Figure (a) ion-sensing with networks of 0D nanostructures; (b) humidity sensing with 1D supramolecular fibers; (c) pressure sensing with 2D based hybrids.

References

1. Review on supramolecular interactions in chemical sensing: Mater. Horiz., 2021, 8, 2685–2708.
2. Review on 0D nanostructures for chemical sensing: Chem. Soc. Rev. 2021, 50, 1269–1304
3. For review on 2D nanostructures for chemical sensing: Chem. Soc. Rev. 2018, 47, 4860-4908.

Supramolecular Hosts as Enzyme Mimics

F. Dean Toste,[1]

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Email: fdtoste@berkeley.edu

Modern organic synthesis relies heavily on selective reactions to enable sustainable access to fine chemicals and pharmaceuticals. In enzymatic catalysis, nature employs various mechanisms to achieve the desired selectivity and activity. Similarly, we have explored organic and organometallic reactions catalyzed by self-assembled water-soluble supramolecular clusters. These supramolecular hosts offer a confined environment that can enhance selectivity and accelerate reaction rates, as well as enable new product formation not achievable by uncatalyzed processes. The lecture will focus on the research in the field of supramolecular catalysis, discussing the reactions promoted by encapsulation, the underlying interactions enabling catalysis, and the mechanisms involved

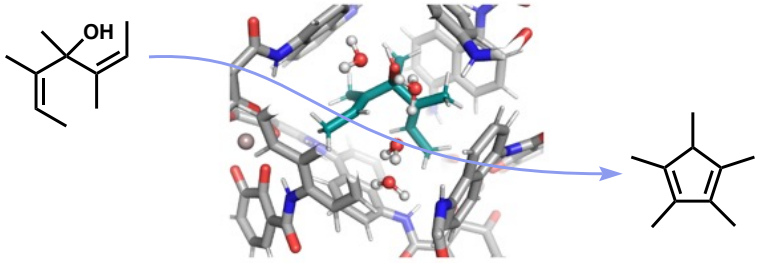

Figure. Calculated Transition state structure of supramolecular-catalyzed Nazarov cyclization.

Acknowledgements

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References

[1] M. Morimoto, S. M. Bierschenk, K. Y. Xia, R. G. Bergman, K. N. Raymond, F. D. Toste, *Nature Catal.* **2020,** *3*, 969-984.

KEYNOTES

Recent developments in the chemistry of hemicryptophane cages: from recognition to confined catalysis.

Alexandre Martinez,[1]

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Hemicryptophanes are host molecules, combining a cyclotribenzylene (or cyclotriveratrylene CTV) unit with another different C_3-symmetrical moiety.[1] Although the synthesis of the first hemicryptophane was described in 1982 by J.-M. Lehn and A. Collet, this class of host received very little attention during the 20 years following this first promising result.[2] Nevertheless, since 2005, hemicryptophanes have aroused growing interest, and new aspects have been developed (Figure 1).[1] Hemicryptophanes revealed able to complex various guests, including charged and neutral species like neurotransmitters or carbohydrates. They can also act as molecular switches leading to stimuli-responsive supramolecular systems. Furthermore, they can lead to supramolecular catalysts: the endohedral functionalization of their cavity providing nanoreactors with improved stability, selectivity or reaction rates compared to their model parents, lacking cavity. Here, recent developments will be described and we will focus in particular on their properties as confined catalysts.

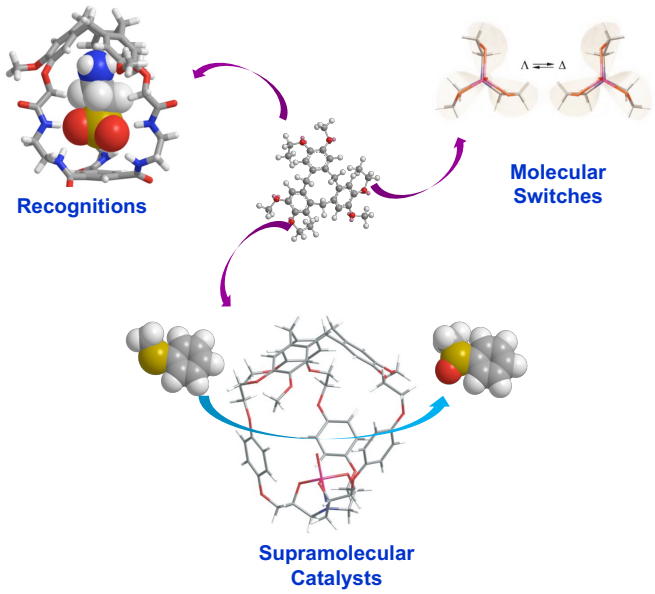

Figure 1. three different applications of hemicryptophane cages.

References

[1] D. Zhang, A. Martinez, J.-P. Dutasta, *Chem. Rev*. **2017**, *117*, 4900–4942. A

[2] Canceill J, Collet A, Gabard J, Kotzyba-Hibert F, Lehn J. *Helvetica Chimica Acta*. **1982**, *65*, 1894-1897.

Small, chiral and self-assembled molecules: the new recipe for supramolecular electronics

Amparo Ruiz-Carretero,[1] Gabriel Martinez,[1] Kyeong-Im Hong,[1] Shu Seki,[2] Subrata Majumder,[3] Rocio Ponce[4]

[1]University of Strasbourg, Institute Charles Sadron (CNRS), Strasbourg, France; [2]University of Kyoto, Department of Molecular Engineering, Graduate School of Engineering laboratory, Kyoto, Japan. [3]National Institute of Technology, Department of Physics, Patna, India. [4]University of Málaga, Department of Physical Chemistry, Málaga, Spain.

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Providing global energy supply in a sustainable manner is one of the main challenges of our generation. We are therefore, in the urge to find alternative resources and materials. In this sense, organic materials are the best candidates to fabricate electronic devices since we can tailor their properties by molecular design. They have other advantages such as flexibility, light weight, portability and scalability. Still, the efficiency of organic devices is far from the one of inorganic materials or perovskites. Despite the progress made in the field, the race for achieving efficiency records, has hampered research focused on solving other fundamental issues, such as device morphology and charge recombination. In this seminar, I will show different strategies to demonstrate how noncovalent interactions can enhance charge transport and device efficiency in organic photovoltaic devices (Figure 1a).[1] In our group we incorporate hydrogen bonds to extraordinarily small semiconductors to enhance charge carrier mobility and lifetime, [2,3] and introduce chiral centers to explore the Chiral Induced Spin Selectivity (CISS) effect to decrease charge recombination.[4] The synthesis, self-assembly and optical properties will be shown and correlated to the charge transport results obtained by using electrodeless techniques and full devices. The spin selectivity results explored by scanning tunnel microscopy (STM) on spectroscopy mode (STS), show how it is possible to guide charge carriers through opposite chirality supramolecular structures (Figure 1b).[4]

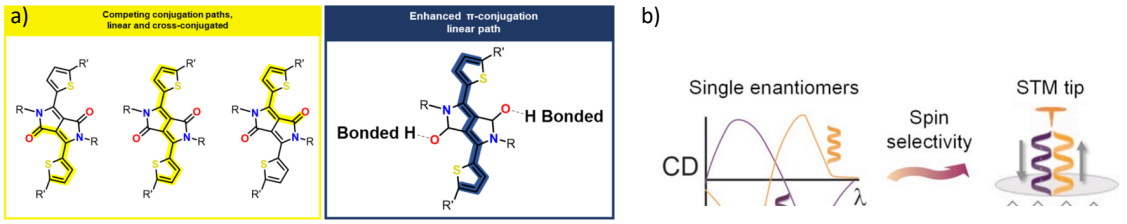

Figure 1. Strategy to enhance charge transport in small molecules. b) Study of the CISS effect using STM on STS mode

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References

[1] T. Aytun, L. Barreda, A. Ruiz-Carretero, J. A. Lehrman, S. I. Stupp. *Chem. Mater.* **2015**, *27*, 1201

[2] N. R. Avila-Rovelo, G. Martinez, W. Matsuda, S. Sinn, P. Leveque, D. Schwaller, P. Mesini, S. Seki, A. Ruiz-Carretero. *J. Phys. Chem. C*, 2022, *126*, 10932

[3] S. Militzer, N. Nishimura, N. A. Avila-Rovelo, W. Matsuda, D. Schwaller, P. J. Mesini, S. Seki. A. Ruiz-Carretero. *Chem. Eur. J.* **2020**, *26*, 9998. A. M. Garcia, A. Ruiz-Carretero. *Chem. Commun*. **2022**, *4*, 529

[4] K. Hong, A. Kumar, A. M. Garcia, S. Majumder, A. Ruiz-Carretero. *J. Chem. Phys.* **2023**, *159*, 114903

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.[1] We have pioneered the use of a "small" macrocycle[2,3] mediated active template[4] reaction in in combination with covalent chiral auxiliaries in order to allow the synthesis of mechanically planar chiral rotaxanes[5,6,7,8] and catenanes (Figure 1),[9,10,11] as well as discovering new forms of mechanical stereochemistry.[12,13,14] and their applications in enantioselective sensing and catalysis.[15]

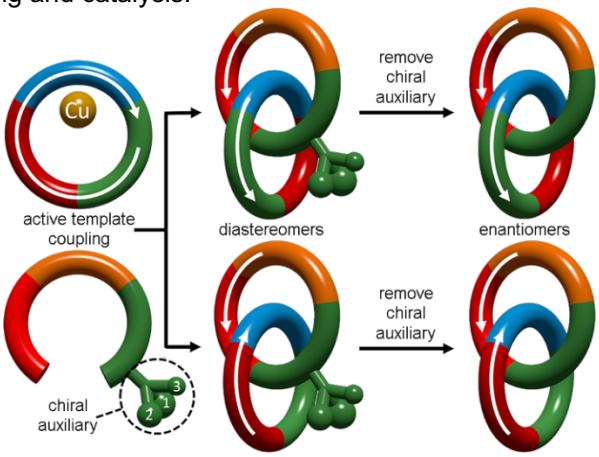

Figure 1. Schematic of our auxiliary approach to a mechanically planar chiral catenane

References

[1] E. M. G. Jamieson, F. Modicom, S. M. Goldup, *Chem. Soc. Rev.* **2018**, *47*, 5266.
[2] H. Lahlali, K. Jobe, M. Watkinson, S. M. Goldup, *Angew. Chem. Int. Ed.* **2011**, *50*, 4151.
[3] J. E. M. Lewis, R. J. Bordoli, M. Denis, C. J. Fletcher, M. Galli, E. A. Neal, E. M. Rochette, S. M. Goldup, *Chem. Sci.* **2016**, *7*, 3154.
[4] M. Denis, S. M. Goldup, *Nat. Rev. Chem.* **2017**, *1*, 0061.
[5] R. J. Bordoli, S. M. Goldup, *J. Am. Chem. Soc.* **2014**, *136*, 4817.
[6] M. A. Jinks, A. de Juan, M. Denis, C. J. Fletcher, M. Galli, E. M. G. Jamieson, F. Modicom, Z. Zhang, S. M. Goldup, *Angew. Chem. Int. Ed.* **2018**, *57*, 14806.
[7] A. de Juan, D. Lozano, A. W. Heard, M. A. Jinks, J. M. Suarez, G. J. Tizzard, S. M. Goldup, *Nat. Chem.* **2022**, *14*, 179.
[8] S. Zhang, A. Rodríguez-Rubio, A. Saady, G. J. Tizzard, S. M. Goldup, *Chem* **2023**, *9*, 1195.
[9] M. Denis, J. E. M. Lewis, F. Modicom, S. M. Goldup, *Chem* **2019**, *5*, 1512.
[10] A. Rodriguez-Rubio, A. Savoini, F. Modicom, P. Butler, S. M. Goldup, *J. Am. Chem. Soc.* **2022**, *144*, 11927.
[11] N. Pairault, F. Rizzi, D. Lozano, E. M. G. Jamieson, G. J. Tizzard, S. M. Goldup, *Nat. Chem.* **2023**, *15*, 781.
[12] J. R. J. Maynard, P. Gallagher, D. Lozano, P. Butler, S. M. Goldup, *Nat. Chem.* **2022**, *14*, 1038.
[13] P. R. Gallagher, A. Savoini, A. Saady, J. R. J. Maynard, P. W. V. Butler, G. J. Tizzard, S. M. Goldup, *J. Am. Chem. Soc.* **2024**, *146*, 9134.
[14] A. Savoini, P. R. Gallagher, A. Saady, S. M. Goldup, *J. Am. Chem. Soc.* **2024**, *146*, 8472.
[15] A. W. Heard, S. M. Goldup, *Chem* **2020**, *6*, 994.

DESIGN AND SYNTHESIS OF MOLECULAR COGWHEELS FOR ON-SURFACE INTERMOLECULAR GEARING

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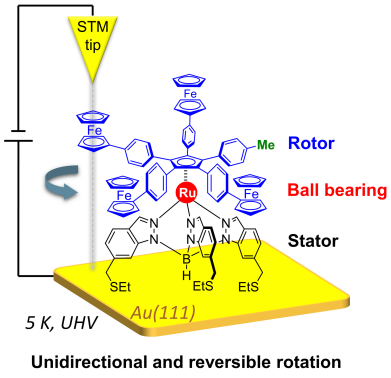
In a context of ultimate miniaturization, obtaining nanometer-sized devices and mastering their controlled motion triggered by an external stimulus is highly desirable.
Following a bottom-up approach, our group has designed and synthesized various molecular machines to be studied on surface at the single-molecule scale by Scanning Tunneling Microscopy (STM). Among these, an electron-fueled ruthenium-based organometallic motor, featuring a dissymmetric rotating subunit, has been shown to undergo unidirectional rotary motion upon excitation, with a direction of rotation governed by the location of the STM tip.[1]



The next milestone is now to master the assembly of several individual molecular machines into complex functional nanoscale machineries. In this regard, gear systems appear as essential elementary units to propagate the motive power delivered by a motor,[2] and our current aim is thus to investigate the mechanical transfer of rotary motion between neighboring molecules.

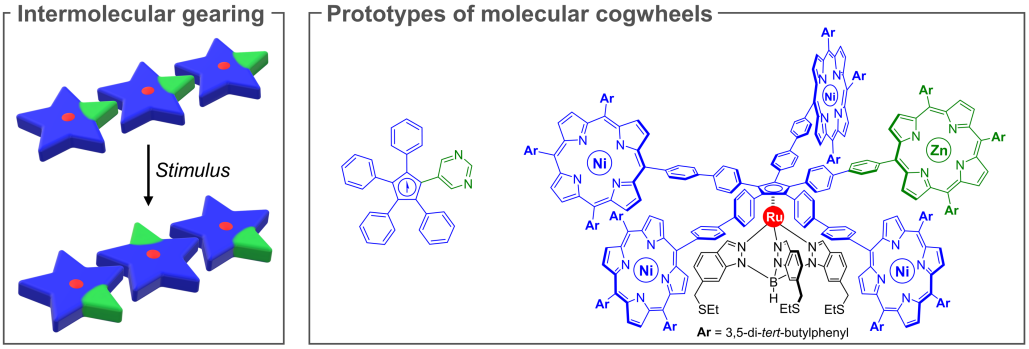


Figure 1. Principle of on-surface molecular gearing (left) and structures of molecular cogwheels (right).

Our efforts towards on-surface molecular gearing will be presented, with a special emphasis on the design and synthesis of star-shaped molecules, geometrically analogous to cogwheels, displaying diameters up to 5 nm.[3]

References

[1] U. G. E. Perera, F. Ample, H. Kersell, Y. Zhang, G. Vives, J. Echeverria, M. Grisolia, G. Rapenne, C. Joachim, S.-W. Hla, *Nat. Nanotechnol*. **2013**, *8*, 46-51.
[2] Y. Gisbert, S. Abid, C. Kammerer, G. Rapenne, *Chem. Eur. J.* **2021**, *27*, 12019-12031.
[3] G. Erbland, S. Abid, Y. Gisbert, N. Saffon-Merceron, Y. Hashimoto, L. Andreoni, T. Guérin, C. Kammerer, G. Rapenne, *Chem. Eur. J.* **2019**, *25*, 16328-16339; S. Abid, Y. Gisbert, M. Kojima, N. Saffon-Merceron, J. Cuny, C. Kammerer, G. Rapenne, *Chem. Sci.* **2021**, *12*, 4709-4721.

Towards active matter:

Non-equilibrium chemistry exploiting chemical energy

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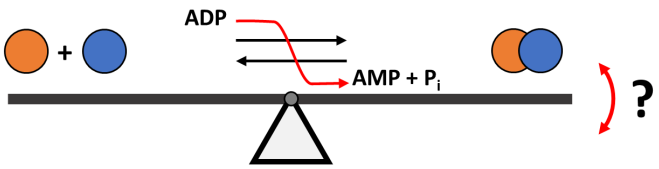
The development of synthetic active matter requires the ability to rationally design materials capable of harnessing energy from a source to carry out work.[1,2] Nature achieves this using metabolic cycles in which energy released from an exergonic chemical reaction, e.g. ATP hydrolysis, is used to drive endergonic biochemical processes. Extensive theoretical and experimental studies on synthetic molecular machinery have demonstrated that energy and information ratchet mechanisms play an essential role in transferring energy from the energy source to the system.[3, 4] Recently, it has been understood that these mechanisms can also be exploited for the development of active matter [5, 6]. Here, we report our progress made on the use of energy and information ratchet mechanisms for the synthesis of high-energy molecular structures [8, 9].



References

[1] Cheng, C.; McGonigal, P. R.; Stoddart, J. F.; Astumian, R. D. Design and Synthesis of Nonequilibrium Systems. *ACS Nano* **2015**, *9*, 8672–8688

[2] Walther, A. Viewpoint: From Responsive to Adaptive and Interactive Materials and Materials Systems: A Roadmap. *Adv. Mater.* **2020**, *32*, 1–10.

[3] Kay, E. R.; Leigh, D. A.; Zerbetto, F. Synthetic Molecular Motors and Mechanical Machines; Angew. Chem. Int. Ed. 2007, 46, 72-191.

[4] Feng, Y.; Ovalle, M.; Seale, J. S. W.; Lee, C. K.; Kim, D. J.; Astumian, R. D.; Stoddart, J. F. Molecular Pumps and Motors. *J. Am. Chem. Soc.* **2021**, *143*, 5569–5591.

[5] Ragazzon, G.; Prins, L. J. Energy Consumption in Chemical Fuel-Driven Self-Assembly. N*at. Nanotechnol.* **2018**, *13*, 882–889.

[6] Das, K.; Gabrielli, L.; Prins, L. J. Chemically Fueled Self-Assembly in Biology and Chemistry. *Angew. Chem. Int. Ed.* **2021**, *60*, 20120-20143.

[7] Marchetti, T.; Frezzato, D.; Gabrielli, L.; Prins, L.J. ATP Drives the Formation of a Catalytic Hydrazone through an Energy Ratchet Mechanism *Angew.Chem.Int.Ed.* **2023**, *62*, e202307530.

[8] Marchetti, T. (+); Roberts, B.M.W.(+); Frezzato, D.; Prins, L.J. A minimalistic synthetic metabolic cycle that consumes ADP, **2024**, e202402965.

Enzyme-mediated dynamic combinatorial chemistry

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Biomolecular templates define the outcomes of enzymatic reactions in some of the most fundamental of biological processes, such as DNA replication, transcription and translation. In synthetic chemistry, molecular templates have enabled the synthesis of highly complex molecular architectures and interlocked structures. With *Enzyme-Mediated Dynamic Combinatorial Chemistry* we explore the possibility of using synthetic templates to direct enzymatic reactions and obtain alternative products to those generated in Nature.

α-, β- and γ-cyclodextrin are industrially important macrocyclic hosts formed from 6, 7, and 8 α-1,4-linked glucopyranose units. While cyclodextrins are usually considered as stable, static molecules, we generate dynamic mixtures of interconverting cyclodextrins by the action of *cyclodextrin glucanotransferase* (CGTase). As the system is dynamic, the product distribution can be manipulated via supramolecular interactions with template molecules. We use templates to direct the selective synthesis of 'natural' cyclodextrins as well as modified cyclodextrins, and employ stimuli-responsive templates to control the system using light and redox chemistry.[1]

Large-ring cyclodextrins, formed from more than 8 glucose units have received very little attention due to synthetic inaccessibility. Using the approach of template-directed enzymatic synthesis, we can now obtain δ-CD (formed from 9 glucose units) in unprecedented yields[2] and on a multi-gram scale.[3] Investigations are ongoing to explore the molecular recognition capabilities of this newly accessible macrocyclic host.

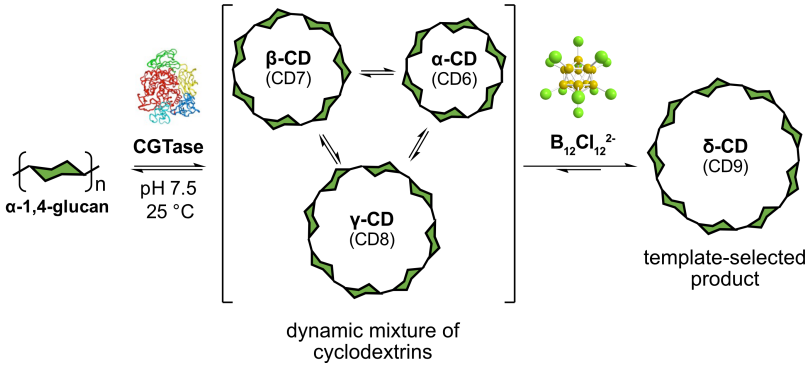

Figure 1. Template-directed enzymatic synthesis of δ-cyclodextrin.

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References

[1] D. Larsen, S. R. Beeren, *Chem. Sci.*, **2019**, *10*, 9981–9987.
[2] A. Erichsen, G. H. J. Peters, S. R. Beeren, *J. Am. Chem. Soc.*, **2023**, *145*, 4882–4891.
[3] K. Hansen, A. Erichsen, D. Larsen, S. R. Beeren, 'Method for the production of large-ring cyclodextrins' **2024**, WO/2024/042228.

Chaotropic effect as an assembly motif in polyoxometalate supramolecular chemistry

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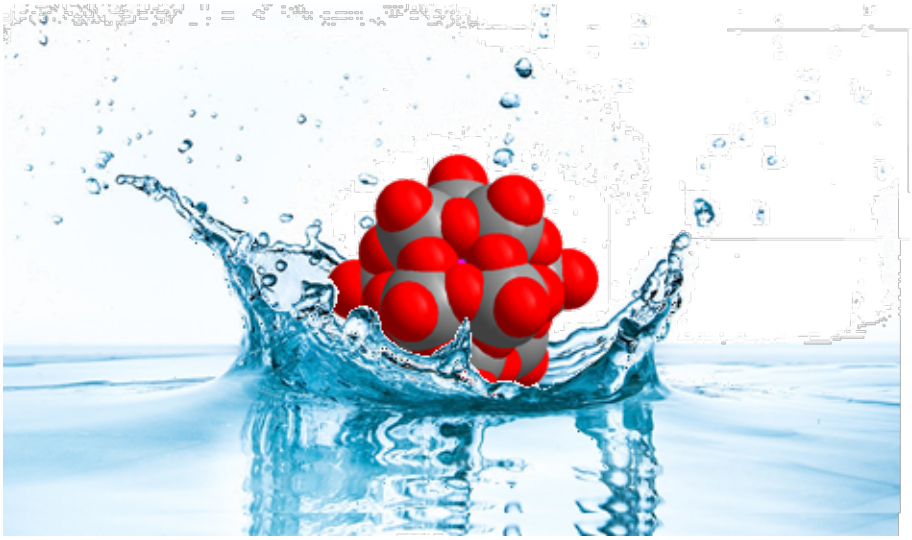

Abstract. The ability of biochemical substances such as phospholipids, glycans, or proteins to interact with discrete inorganic species is essential for some biological functions.[1] Then, designing supramolecular hybrid architectures including dynamics and responsive behavior requires a fine balance between the conglomerate of weak forces such as electrostatic, ion-dipole, dipole-dipole, hydrogen-bonding, dispersion, etc., that drives the aggregation processes. Recent reports highlight the intriguing properties of certain inorganic polynuclear anions, such as polyoxometalates (POMs) or polynuclear clusters for their extremely high propensity to interact strongly in aqueous solution with non-ionic organic components such as macrocycles or surfactants.[2,3,4] This striking driving force has been identified as a strong solvent effect arising from the chaotropic nature of polyoxometalates in aqueous solution. In this communication, we will highlight the origin of this effect by proposing a classification of the chaotropic character of a large series of polyoxometalates, ranging from the Keggin type ions to the large nanoscopic ring-shaped molybdenum blue. Furthermore, we will give some relevant examples showing how the chaotropic effect can be used to monitor supramolecular hybrid assemblies such as core-shell type assemblies, CD-MOFs, redox responsive supramolecular polymers or POM-containing bilayer type membrane.[5]

References

[1] Zhong *et al*. *Angew. Chem. Int. Ed.* **2004**, *43* (44), 5914–5918.
[2] Assaf, K. I *et al*. *Angew. Chem. Int. Ed.* **2015**, *54* (23), 6852–6856.
[3] Moussawi, M. A. et al. *J. Am. Chem. Soc.* **2017**, *139* (41), 14376–14379.
[4] Falaise, C. *et al*. *Angew. Chem. Int. Ed.* **2021**, *60* (25), 14146–14153.
[5] Falaise *et al. J. Am. Chem. Soc*. **2024**, 146 (2), 1501-1511.

SYNTHESIS AND ASSEMBLY OF LIGHT-RESPONSIVE SUPRAMOLECULAR NANOSTRUCTURES:

A STEP TOWARD ADAPTIVE MATERIALS

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The need for functional supramolecular systems is growing, driven by interest in device miniaturization, the emergence of smart materials, and efforts to mimic biological processes. Mastering the non-covalent synthesis of these supramolecular architectures requires control over their structure, dynamics, and function at all length scales. In particular, the precise positional arrangement of molecules facilitates the control of supramolecular interactions and the design of materials with unconventional responses. However, the construction of these systems is challenging due to their inherent complexity resulting from their sensitivity to small perturbations, the large number of interacting components, and the multiple aggregation pathways by which the systems can evolve.[1] In the lecture, we will illustrate our approach to functional supramolecular materials.[2] The focus is on the synthesis of highly ordered morphologies that will change their properties upon exposure to light, coupling cooperative molecular events to macroscopic function.

References

[1] G. Vantomme, E.W. Meijer, *Science*, **2019**, *363*, 1396-1397.

[2] B.W.L. van den Bersselaar, A.P.A. van de Ven, B.F.M. de Waal, S.C.J. Meskers, F. Eisenreich, G. Vantomme, *Advanced Materials*, **2024**, 2312791.

Nanometric inorganic helices for chiral induction, crystallization, amplification and recognition

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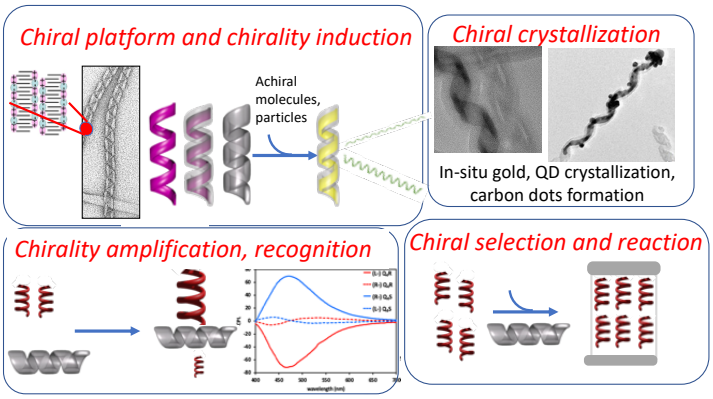
Chiral nanoparticles (NP) show very promising properties in many fields such as enantioselective recognition, catalysis and spin selectivity [1]. Among the various routes to induce chiroptical properties to these NPs which are in majority dominated by molecular chirality in interaction with gold surface, and/or chiral arrangement of achiral gold NPs [2], morphology-based "helical" NPs are of particular interest however quite difficult to obtain. We successfully created helical perovskite Nanocrystals [3] and plasmonic helical gold nanohelices within a confined chiral nano space in a colloidal suspension. Such helices exhibited remarkable chiroptical activity across a broad spectrum ranging from visible to infrared regime with high dissymmetry factors (~0.2). They are also capable of enantioselective recognition with small molecules in spite of the absence of any chiral molecules on their surface. Our approach, which relies on soft chemistry and molecular self-assembly offers a simple and scalable method for producing gold nanosystems which also holds the potential for extending this strategy to other metals or composite materials.



Nanometrical crystalline helical nanoparticles as platforms for chiral induction, crystallization, amplification and recognition

Acknowledgements: This work was supported by European Union's H2020- FET-OPEN grant 828779 (INITIO), France-Japan International Research Project, (LIA_CNPA_RO_R175_UBx-DRI DAJDIRVED) as well as the Centre National de la Recherche Scientifique and Université de Bordeaux, JSPS Overseas Research Fellowship, Chinese Scholarship, Council (CSC).

Reference:

[1] Mark A. G., Gibbs J. G., Lee T.-C., Fischer P. Nature Materials.12, 802–807 (2013): Lee H.-E., Kim R. M., Ahn H. Y., Lee Y. Y. , Byun G. H., Im S. W., Mun J., Rho J., Nam K. T. Nature Comm 11-263 (2020)

[2] Lan X., Liu T., Wang Z., Govorov A. O. Yan H., Liu Y. *J. Am. Chem. Soc. 2018, 140, 11763, Cheng J., Le Saux G., Gao J., Buffeteau T., Battie Y., Barois P., Ponsinet V., Delville M.-H., Ersen* O. Pouget E., Oda R., ACS Nano 2017, 11, 4, 3806

[3] P. Liu, Y. Battie, T. Kimura, Y. Okazaki, P. Pranee, H. Wang, E. Pouget, S. Nlate, T. Sagawa, R. Oda, Nano Letters 23 (8), 3174-3180

From Heteroleptic Coordination Cages to Complex Molecular Systems

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Advanced self-assembly strategies enable the targeted synthesis of supramolecular systems and materials with increasing structural and functional complexity. We react bis-monodentate ligands with transition metal cations to coordination compounds showing a broad range of topologies. To combine different functionalities in the same metallosupramolecular structure, we develop non-statistical assembly strategies such as “shape complementary assembly” (SCA) and “coordination sphere engineering” (CSE).[1]

We then implement various functionalities, with a focus on multi-chromophore systems.[2] These are studied then, e.g., for light-induced charge separation, vectorial excitation transport and as potential photo-redox catalysts. By combining chiral with emissive ligands, heteroleptic cages showing guest-modulated circularly polarized luminescence (CPL) were obtained.[3] We further introduce stimuli-responsive behavior in photochromic cages[4] allowing to control guest affinity[5] and established a light-fueled dissipative system.[6] Cages capable of fullerene encapsulation[7] give rise to confinement-controlled reactivity, such as long-term C_{60} radical anion stabilization.[8]

Recently, we mastered the non-statistical and robust assembly of dinuclear Pd(II) cages containing four chemically different ligands [Pd_2ABCD].[9] The collected results now set the stage for looking into ‘complex systems’ behaviour by following the stimuli-responsive population and evolution of co-existing species in mixtures.[10] In this direction, we study multi-step cage interconversions, guest-binding/release cascades and propagation of chiral information.

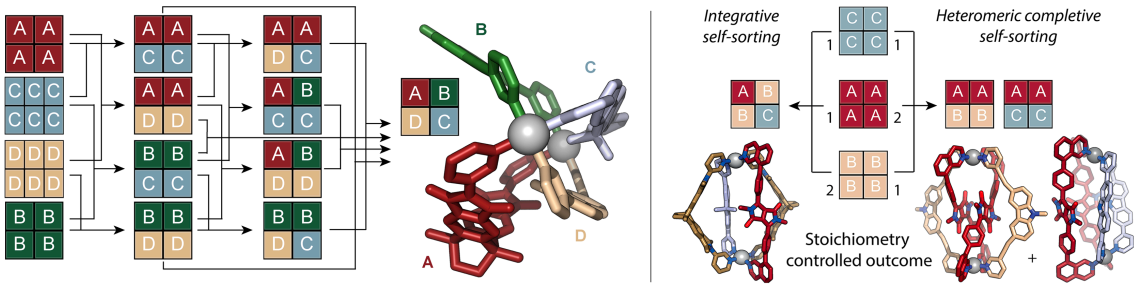

Figure 1. Non-statistical multicomponent self-assembly (left) and complex systems behavior (right)

References

[1] Pullen, S.; Tessarolo, J.; Clever, G. H. *Chem. Sci.* **2021**, *12*, 7269.

[2] Regeni, I.; Chowdhury, R.; Terlinden, K.; Horiuchi, S.; Holstein, J. J.; Feldmann, S.; Clever, G. H. *Angew. Chem. Int. Ed.* **2023**, *e202308288*.

[3] Wu, K.; Tessarolo, J.; Baksi, A.; Clever, G. H. *Angew. Chem. Int. Ed.* **2022**, *61*, e202205725.

[4] Benchimol, E.; Tessarolo, J.; Clever, G. H. *Nat. Chem.* **2024**. (Perspective Article)

[5] Li, R.-J.; Tessarolo, J.; Lee, H.; Clever, G. H. *J. Am. Chem. Soc.* **2021**, *143*, 3865.

[6] Lee, H.; Tessarolo, J.; Langbehn, D.; Baksi, A.; Herges, R.; Clever, G. H. *J. Am. Chem. Soc.* **2022**, *144*, 3099.

[7] Chen, B.; Holstein, J. J.; Platzek, A.; Schneider, L.; Wu, K.; Clever, G. H. *Chem. Sci.* **2022**, *13*, 1829.

[8] Hasegawa, S.; Meichsner, S. L.; Holstein, J. J.; Baksi, A.; Kasanmascheff, M.; Clever, G. H. *J. Am. Chem. Soc.* **2021**, *143*, 9718.

[9] Wu, K.; Benchimol, E.; Baksi, A.; Clever, G.H. *Nat. Chem.* **2024**, 10.1038/s41557-023-01415-7.

[10] Benchimol, E.; Regeni, I.; Zhang, B.; Kabiri, M.; Holstein, J. J.; Clever, G. H. *J. Am. Chem. Soc.* **2024**, *146*, 6905.

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Synthesizing fully organic, multiply entangled macromolecules without resorting to metal templation represents a formidable challenge. [1] In this presentation, I will discuss the efforts of our group to develop reliable metal-free methodologies to direct the folding of increasingly complex entangled macromolecules. [2] These methodologies allow access to exceptionally compact entangled macromolecules, a feature that affects their conformational states, chirality, [3] and ability to bind small molecules [4] and anions. [5]

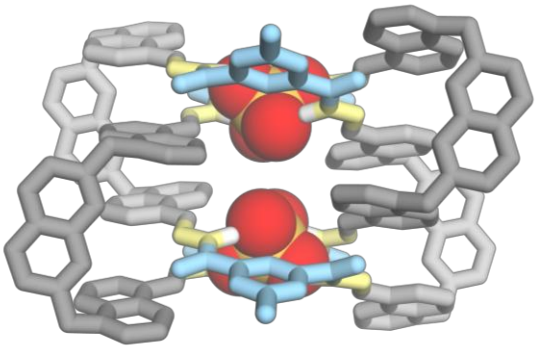

Figure 1. A Solomon link able to bind sulfate with remarkably high affinity (K_d = 39 nM) in pure water.

Acknowledgements

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References

[1] (a) J. F. Stoddart, *Nano Lett.* **2020**, *20*, 5597-5600; (b) S. D. P. Fielden, D. A. Leigh, S. L. Woltering, *Angew. Chem. Int. Ed. Engl.* **2017**, *56*, 11166-11194.

[2] F. B. L. Cougnon, K. Caprice, M. Pupier, A. Bauzá, A. Frontera, *J. Am. Chem. Soc.* **2018**, *140*, 12442-12450.

[3] K. Caprice, D. Pál, C. Besnard, B. Galmés, A. Frontera, F. B. L. Cougnon, *J. Am. Chem. Soc.* **2021**, *143*, 11957-11962.

[4] K. Caprice, M. Pupier, A. Bauzá, A. Frontera, F. B. L. Cougnon, *Angew. Chem. Int. Ed.* **2019**, *58*, 8053-8057.

[5] C.D. Do, D. Pál, A. Belyaev, A. Kiesilä, E. Kalenius, B. Galmés, A. Frontera, A. Poblador-Bahamonde, F. B. L. Cougnon, *Chem. Commun.* **2023**, *59*, 13010-13013.

Metal-Peptidic Cages – Helical Oligoprolines Generate Highly Anisotropic Nanospaces with Emergent Isomer Control

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Advances in metal-organic cage self-assembly have enabled the construction of of increasingly complex, discrete three-dimensional architectures reminiscent of proteins from simple building blocks.[1] The current state-of-the-art, however, is almost exclusively built from rigid and flat aromatic panels, limiting binding selectivity and, often, water solubility.

Herein, we disclose a new class of cages - metal-peptidic cages - which utilise water-soluble, chiral and helical oligoproline strands of varying length to generate highly anisotropic nanospaces.[2,3] We demonstrate the assembly of a range of Pd_2L_4 cages, with lengths from c. 1 - 4 nm, and find formation of the *cis* isomer of the cage is strongly favoured - an emergent property of using complex and chiral building blocks in the formation of defined nanospaces. Further, the use of biologically relevant components enables targeted binding of therapeutic molecules, highlighting the potential of these systems for selective drug delivery. Finally, we report recent breakthroughs in self-sorting, hierarchical assembly, and biological applications.

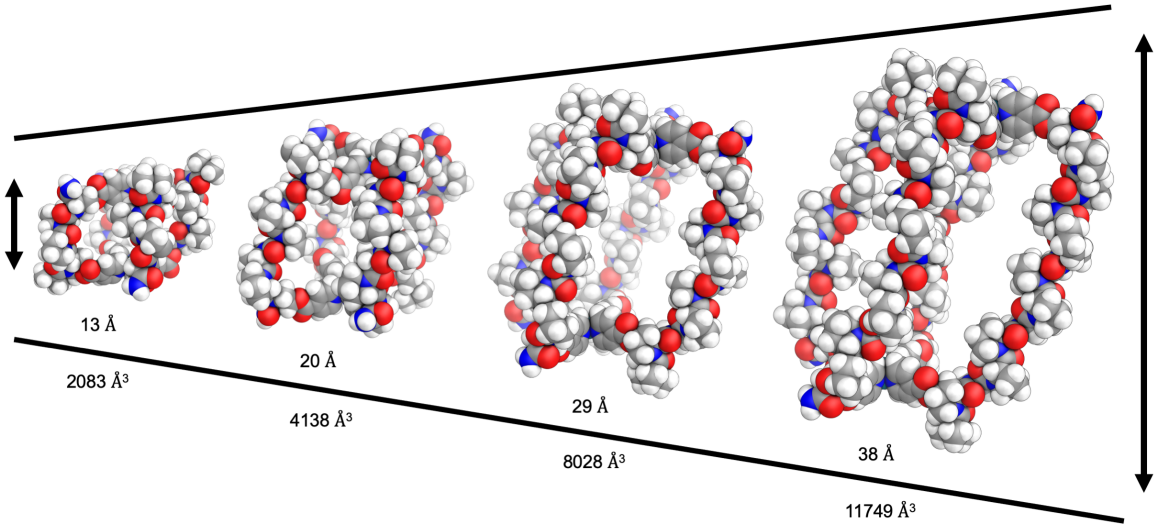

Figure 1. Metal-Peptidic Cages

References

1. C. T. McTernan, J. A. Davies and J. R. Nitschke, *Chem. Rev.*, 2022, **122**, 10393–10437.

2. P. Wilhelm, B. Lewandowski, N. Trapp and H. Wennemers, *J. Am. Chem. Soc.*, 2014, **136**, 15829–15832.

3. B. E. Barber, E. M. G. Jamieson and L. E. M. White and C. T. McTernan, doi.org/10.26434/chemrxiv-2023-89mz0.

Parallel Chirality Inductions in Möbius Zn(II) Hexaphyrin Transformation Networks

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Networked chemical transformations[1] are key features of biological systems, in which complex multi-component interactions enable the emergence of sophisticated functions. Being interested in chirality induction phenomena with dynamic Möbius π-systems,[2],[3] we have designed a pair of Möbius [28]hexaphyrin ligands in order to investigate mixtures rather than isolated molecules.[4] Thus, an hexaphyrin bearing a chiral amino arm was first optimized and found to bind a ZnOAc moiety, triggering an impressive quasi-quantitative chirality induction over the Möbius π-system. Secondly, this amino-type hexaphyrin was mixed with a second hexaphyrin bearing a chiral carboxylate arm, affording at first ill-defined coordination assemblies in the presence of zinc. In contrast, a social self-sorting behavior occurred upon addition of two exogenous achiral effectors (AcO^- and $BuNH_2$), leading to a well-defined 1:1 mixture of two Möbius complexes featuring a sole Möbius twist configuration (parallel chirality inductions). We next successfully achieved a compartmentalized switching, *i.e.* a single-component transformation from such a complex mixture. The $BuNH_2$ effector was selectively protected with Boc_2O, owing to a lower reactivity of the arm's NH_2 function intramolecularly bound to zinc, and subsequent addition of $BuNH_2$ restored the initial mixture retaining parallel chirality inductions (five cycles). By changing the nature and twist configuration of only one of the two complexes, at initial state or by switching, this approach enables a 'two-channel' tuning of the chiroptical properties of the ensemble. Such multiple dynamic chirality inductions, controlled by selective metal-ligand recognition and chemical reactivity, set down the basis for Möbius-type stereoselective transformation networks with new functions.

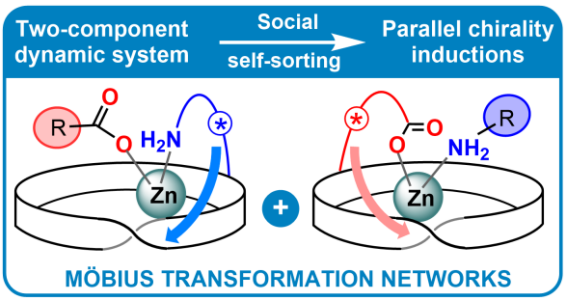

Figure 1. Multiple chirality inductions in mixtures of Möbius rings.

References

[1] A. Goswami, S. Saha, P. K. Biswas, M. Schmittel, *Chem. Rev.*, **2020**, *120*, 125-199.

[2] Review on Möbius rings: R. Herges, *Chem. Rev.*, **2006**, *106*, 4820-4842.

[3] a) H. Ruffin, G. Nyame M. B., T. Roisnel, V. Dorcet, B. Boitrel, S. Le Gac, *J. Am. Chem. Soc.*, **2017**, *139*, 13847-13857; b) R. Benchouaia, N. Cissé, B. Boitrel, M. Sollogoub, S. Le Gac, M. Ménand, *J. Am. Chem. Soc.*, **2019**, *141*, 11583-11593; c) B. Boitrel, S. Le Gac, *Chem. Commun.*, **2020**, *56*, 9166-9169; d) B. Boitrel, S. Le Gac, *Chem. Commun.*, **2021**, *57*, 3559-3562.

[4] a) H. Ruffin, A. Fihey, B. Boitrel, S. Le Gac, *Angew. Chem. Int. Ed.*, **2022**, *61*, e202113844; b) T. Nédellec, B. Boitrel, S. Le Gac, *J. Am. Chem. Soc.*, **2023**, *145*, 27067-27079.

Synthetic transmembrane transporters for phosphates

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Anion receptors can be used to transport of anions across lipid membranes. This research is warranted by the potential biological applications of anion transporters, which range from the replacement of defective transport proteins to the disruption of homeostasis. The vast majority of the research on anion transport focusses on the transmembrane transport of chloride and nitrate,[1] or bicarbonate.[2]

While chloride is the most abundant anion in organisms, phosphates play crucial roles in biology as well, but their transport is hardly explored. The transmembrane transport process requires: *i)* the extraction of the anion from the aqueous phase into the lipophilic membrane interior, *ii)* followed by the diffusion of the complex, and *iii)* anion release on the other side of the membrane. Because inorganic phosphate and phosphate groups are strongly hydrated, this first step is much more challenging as compared to chloride.

Here, I will present our recent breakthroughs in this field. This includes the first example of a synthetic transporter for $H_2PO_4^-$,[3] as well as trends observed in the transport of phosphate esters by different anion transporters.[4]

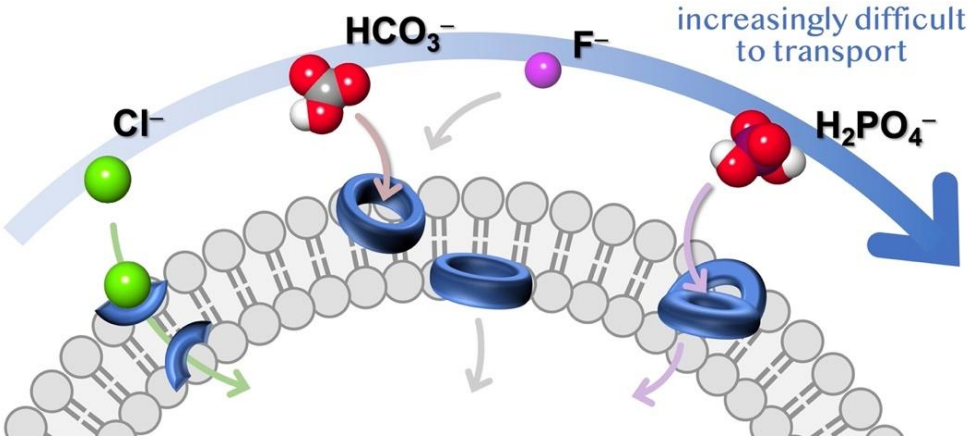

Figure 1. Schematic representation of the transmembrane transport of anions by synthetic transporters.

Acknowledgements

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References

[1] J. T. Davis, P. A. Gale, R. Quesada, *Chem. Soc. Rev.* **2020**, *49*, 6056–6086.
[2] L. Martínez-Crespo, H. Valkenier, *ChemPlusChem* **2022**, *87*, e202200266.
[3] A. Cataldo, K. Norvaisa, L. Halgreen, S. E. Bodman, K. Bartik, S. J. Butler, H. Valkenier, *J. Am. Chem. Soc.* **2023**, *145*, 16310–16314.
[5] A. Torres-Huerta, K. Norvaisa, A. Cataldo, P. O. Tits, S. E. Bodman, S. J. Butler. *manuscript prepration.*

Multi-Responsive Acridinium Supramolecular Systems: An Increasing Complexity

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Equilibria involving multiple interacting life components gave rise to complex assemblies (double helix of DNA, G-quadruplex secondary structures). In addition, living organisms are endowed with numerous remarkable and complex functions (transmission of information, chemical transformations, transport, regulation) mediated by physical and chemical stimuli. In consequence, understanding and mimicking these functions using switchable artificial supramolecular systems is of paramount importance and still remains a current challenge.
We recently reported bis-acridinium supramolecular receptors able to bind guest molecules (Figure 1).[1] Surprisingly, acridinium-based receptors are scarcely exploited in supramolecular chemistry despite their multi-responsive properties. Indeed, they respond to chemical and redox signals by reversibly modifying their shape, their chemical and optical properties.[2] This class of receptors exhibits i) self-complementary behaviors leading to the formation of entwined dimers,[1a] ii) narcissistic self-sorting,[1b] iii) π-donor/π-acceptor host-guest behaviors and were also studied as selective phase transfer agents in perfluorocarbons.[3] In addition, the multi-switching properties of these receptors were investigated to alter their recognition events with guests. An increasing complexity has been achieved by the introduction of acridinium units in mechanically interlocked molecules.[4] The dual-readout of the mechanical response of a [2]rotaxane structure was thus probed.

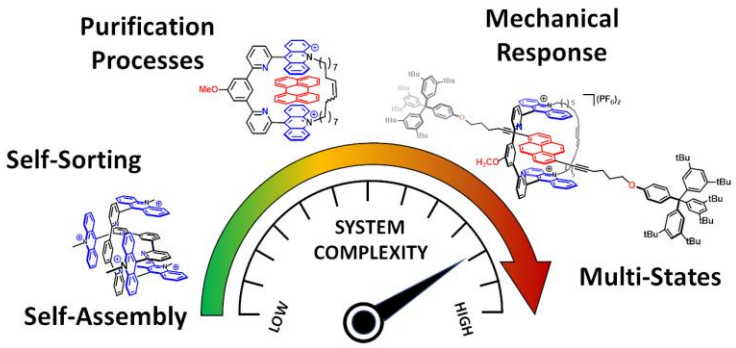

Figure 1. Increasing Complexity in Multi-Responsive Acridinium Supramolecular Systems.

Acknowledgements

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References

[1] a) H.-P. Jacquot de Rouville, N. Zorn, E. Leize-Wagner, V. Heitz, *Chem. Commun.*, **2018**, *54*, 10966–10969; b) H.-P. Jacquot de Rouville, C. Gourlaouen, V. Heitz, *Dalton Trans.*, **2019**, *48*, 8725–8730.
[2] H.-P. Jacquot de Rouville, J. Hu, V. Heitz, *ChemPlusChem*, **2021**, *86*, 110–129.
[3] J. Hu, J. S. Ward, A. Chaumont, K. Rissanen, J.-M. Vincent, V. Heitz, H.-P. Jacquot de Rouville, *Angew. Chem. Int. Ed.*, **2020**, *59*, 23206–23212.
[4] J. Hu, S. Adrouche, E. S. Gauthier, N. Le Breton, M. Cecchini, C. Gourlaouen, S. Choua, V. Heitz, H.-P. Jacquot de Rouville, *Chem. Eur. J.*, **2022**, *28*, e202202840.

Multifunctional macrocyclic host-modified electrodes for electrocatalysis over a wide pH range

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Surface-anchored macrocycles enable the immobilisation of catalytically active guest molecules on electrodes via host-guest complexation. This heterogenised electrocatalytic approach allows for recycling the host functionalised electrode multiple times and the reabsorption of the catalytic active guest molecule after electrocatalysis, as reported in our previous work.[1] Previously we anchored a bisphosphonated *ß*-cyclodextrin to an electrode and could achieve high faradaic efficiencies for ammonia oxidation in aqueous medium at pH 10.86 with a [Ru(tpada)(bpy-NMe_2)(Cl)](PF_6) guest catalyst.[2] Additionally, we found that with the host-modified *meso*-porous indium tin oxide (mITO) electrode, the exchange of the catalytically active guest molecule is possible, which enables the utilisation of the molecular immobilised electrode for a range of catalytic reactions in different media, such as ammonia oxidation or alcohol oxidation. The host-modified electrode is stable over a wide pH range (2.4 to 10.8) and can be reused multiple times after electrocatalysis by reabsorbing guest molecules for different reactions.

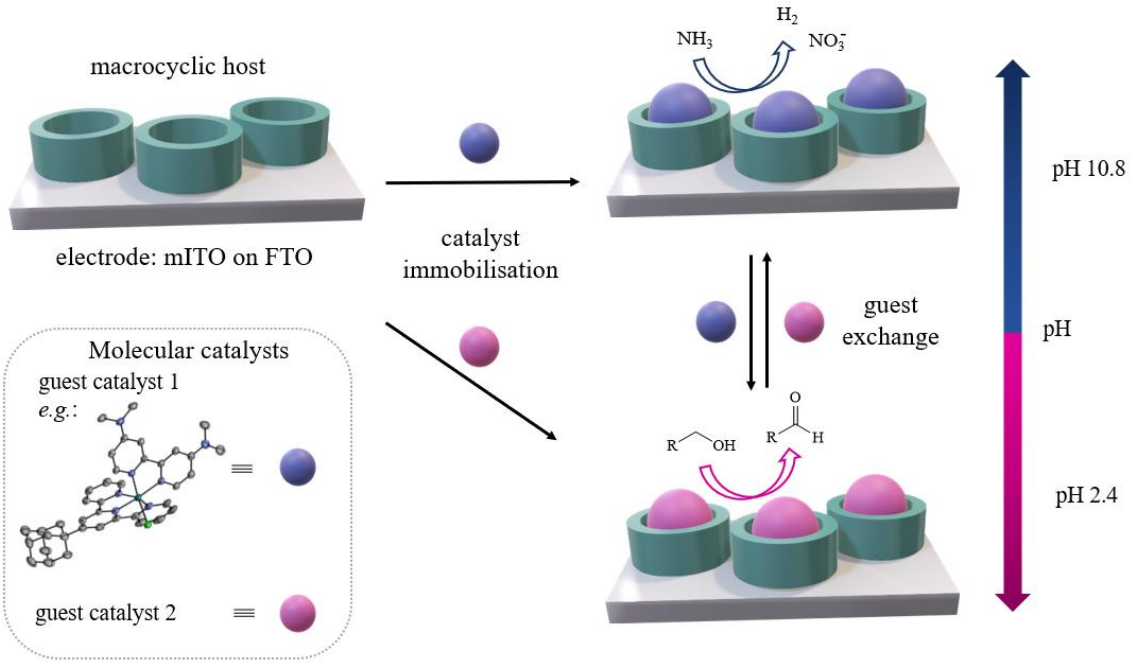

Figure 1. Host-modified electrode with different guest molecules catalysing different reactions in aqueous medium (pH 2.4 to 11)

Acknowledgements

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References

[1] L. Sévery, J. Szczerbiński, M. Taskin, I. Tuncay, F. B. Nunes, C. Cignarella, G. Tocci, O. Blacque, J. Osterwalder, R. Zenobi, M. Iannuzzi and S. David Tilley, Nat. Chem. **2021**,13(6), 523–529. DOI: 10.1038/s41557-021-00652-y.

[2] H. Roithmeyer, L. Sévery, T. Moehl, B. Spingler, O. Blacque, T. Fox, M. Iannuzzi and S. D. Tilley, *J Am Chem Soc*, **2024**, 146, 430–436. DOI: 10.1021/jacs.3c09725

Phosphate-Driven Systems Chemistry

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Phosphates and phosphate esters underpin biological information transfer, signal transduction and contribute to the energetics of life. Biochemical energy carriers, such as triphosphates, (ATP, GTP) drive selective processes, by incorporating chemical information (Adenine vs. Guanine) in their structure. These recognition elements match with complex machineries through a variety of non-covalent interactions, enabling specific functions. We aim to develop roles for phosphates outside of biology and capitalize on the idea of providing chemical information within abiotic phosphates to control selectivity and reactivity in chemical reaction networks.[1] The information is provided by chemical functionalization of energy-rich aminoacyl phosphate esters (Figure 1), whereby the information encodes structural assembly of phosphates prior to their consumption, or transfer large chemical groups onto self-assembling species, enabling activation of various pathways. In particular, we explore the ways in which phosphate esters give rise to spontaneous and selective peptide oligomerization in water, as a result of the construction of autonomous phase changes. Moreover, depending on the chemical nature of peptide nucleophiles used in the network, we demonstrated the construction of non-equilibrium assemblies. Within these systems, the transfer of energy and reactivity from phosphates activates cascade reactions, involving multiple high-energy molecules. Incorporating structural elements around non-biological phosphates and coupling them to dynamic chemistry represents an unexplored opportunity to impact reaction networks, by developing phosphate-driven supramolecular systems chemistry.

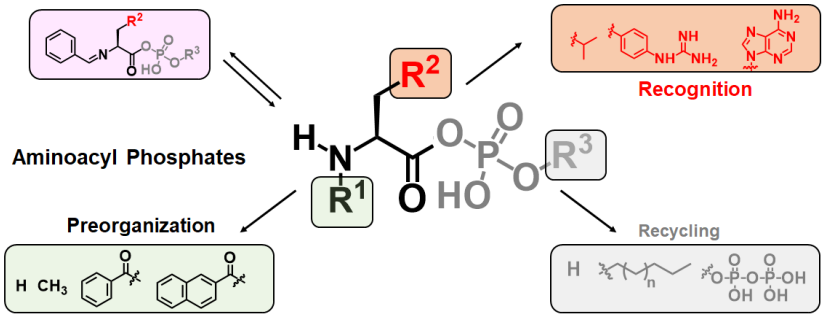

Figure 1. Incorporating structural and recognition elements around non-biological phosphates to construct phosphate-driven systems chemistry.

Acknowledgements

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References

[1] K. Dai, M. D. Pol, L. Saile, A. Sharma, B. Liu, R. Thomann, J. L. Trefs, D. Qiu, S. Moser, S. Wiesler, B. N. Balzer, T. Hugel, H. J. Jessen, C. G. Pappas, *J. Am. Chem. Soc.* **2023**, *145*, 26086-26094.

OC-8

Thermoresponsive polymers and host-guest chemistry: a win-win combination

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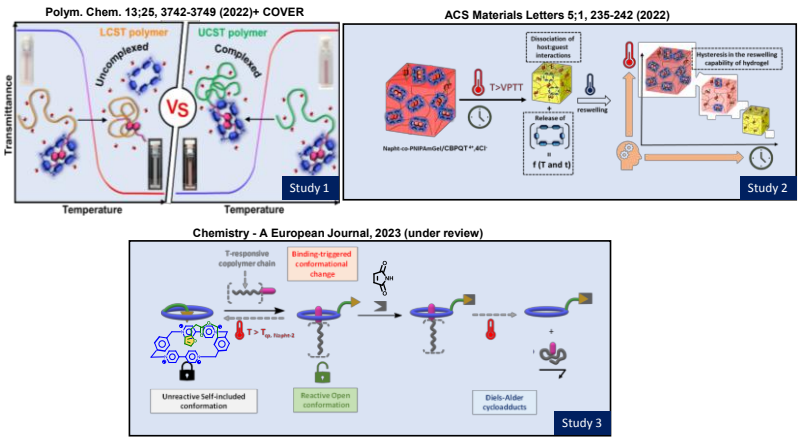
Keywords: Thermoresponsive polymers, Host-guest complexation, memory function, synergistic control of host reactivity

Abstract:

The combination of heat-sensitive polymers and supramolecular chemistry has recently led to the development of fascinating adaptive materials. In this context, most studies have focused on exploiting host-guest interactions to control the physicochemical properties of polymeric materials.[1] This approach has notably enabled the creation of materials with programmable thermosensitivity and sensor properties.[2] In contrast, the exploitation of polymer thermoresponsiveness to control the recognition properties of host-guest systems at the molecular level is much less developed, and a perfect understanding of the mechanisms triggering thermo-induced decomplexation or complexation is still elusive.

In this communication, we will illustrate through three studies how the host-guest chemistry and the thermo-induced phase separation mechanisms can "talk together" to synergistically tune the coil↔globule transition and the complexation state of polymeric systems. The first example[3] will concern a comparative analysis of the behaviour of complexes formed from different naphthalene end-functionalized LCST or UCST polymers and the electron-deficient cyclobis(paraquat-p-phenylene) tetrachloride (**$CBPQT^{4+}$, 4Cl**)[3] host when subjected to heat treatment. This study provided an understanding of the mechanisms triggering the thermo-induced (de)complexation of such complexes. The second study will report a supramolecular approach for developing an intelligent thermoresponsive polymeric hydrogel featuring a dual temperature and time memory function based on a kinetic control of the material's (de)complexation and (re) swelling behaviours. The last study will illustrate how a thermo-induced phase separation mechanism can regulate on demand the Diels-alder reactivity of a synthetic self-complexing host-guest molecular switch **$CBPQT^{4+}$-Fu**, consisting of an electron-rich furan unit covalently attached to the electron-deficient $CBPQT^{4+}$host, with maleimide in water. Thanks to a supramolecular control over the topology of **$CBPQT^{4+}$-Fu** combined with a thermoresponsive supramolecular regulator, we reported a rare example of decreased reactivity upon increasing temperature.



References :

1) V. R. de la Rosa and coll., *Mater. Today*, **2016**, 19, 44-55; 2) N. Herzer and coll. J. *Am. Chem. Soc*. **2012**, 134, 7608–7611; 3) H. Guo and coll. *Polym. Chem.* **2022**,13;25, 3742-3749, 4) P. R. Ashton and coll. *Angew. Chem.*, **1988**, 27, 1550-1553; 5) L. De Smet and coll. *ACS Materials Letters*, **2022**,5;1, 235-242; 6) C. Ribeiro and coll. *Chem.Eur. J.*, **2024**,30, e2023023

ARCHITECTURE MODULATION BY STRUCTURAL MODIFICATION OF CYCLODEXTRINS CO-ASSEMBLING WITH DNA

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Gene therapy is a crucial scientific field we must further develop, and the Covid-19 crisis only confirmed it. Viruses are known to be highly effective genetic material vectors. Among them, the tobacco mosaic virus (TMV) whose coat proteins can self-assemble in a cooperative hierarchical co-assembly with RNA, inspired our group to design a synthetic artificial virus based on cyclodextrins (CDs).

We synthesized adamantyl-functionalized CD **1** and demonstrated its ability to self-assemble into a supramolecular polymer. We then showed that CD **1** could induce transfection with nucleic acids (NA).[1] To understand its mode of assembly we studied the CD **1**/DNA mixture by Cryo-EM. We found that very long thin fibers were formed. We further proved that they contain many copies of dsDNA 18-mer, which are surrounded by self-assembled CD **1**, a structure highly reminiscent of TMV. We also proved that identical architectures are observed with different sizes of single and double stranded DNA.

Amazingly, a slight change of structure of CD **1** into CD **2**, where the adamantyl group is positioned in the center of the cavity, induces a drastic modification of the assembly architecture: nanotubes were obtained instead of fibers. (Figure 1) We elucidated the multi-step mechanism of the nanotubes formation by Cryo-EM. We are currently studying these systems and other CDs variations with NA in terms of shape, size and structure to optimize transfection of mRNA and we obtained recently very promising preliminary results.

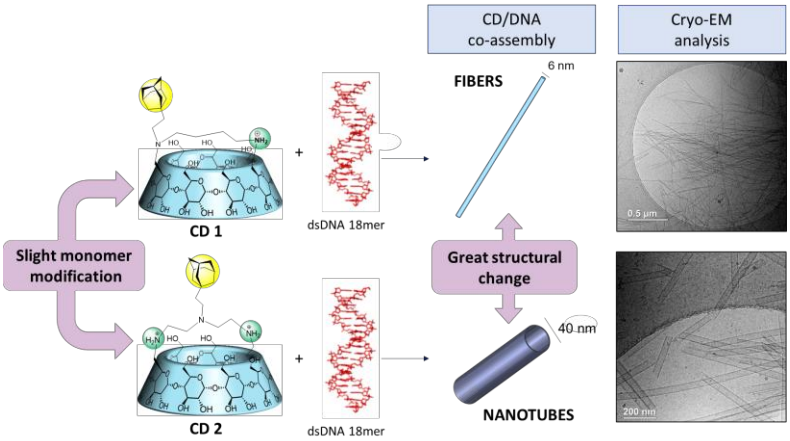

Figure 1. Control of the hierarchical co-assembly architecture built from CDs **1** or **2** and dsDNA-18mer

Acknowledgements

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References

[1] Evenou P., Rossignol J., Pembouong G., Gothland A., Colesnic D., Barbeyron R., Rudiuk S., Marcelin A-G., Ménand M., Baigl D., Calvez V., Bouteiller L., Sollogoub M., *Angew. Chem. Int. Ed.*, **2018**, *57*, 7753-7758. PCT/EP2016/070892, 5th september **2016**, WO/2018/041377, 8th mars **2018**

Macrolactonizations Enabled by Supramolecular Interactions

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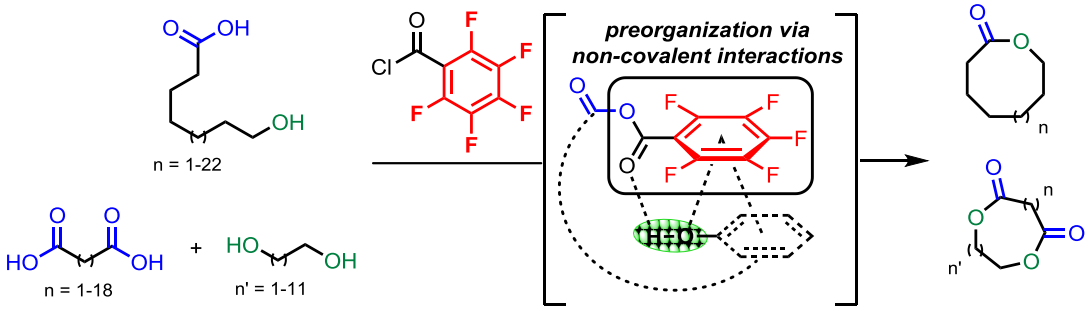
Macrolactones are present in a large range of fine chemicals and natural products, including marine macrolides, pharmaceuticals, cosmetics, and agrochemicals.[1] As an example, 1000 tons of Exaltolide, a 16-membered ring lactone, are produced in the perfume industry every year. Considering the industrial importance of these molecules, numerous efforts have been dedicated to the development of new methodologies, which are efficient, user-friendly, and simple to operate. One of the most prominent methods is the macrocyclization of *seco*-acids, which typically involves the activation of the carboxylic acid to promote the transformation.[2] However, most of them are fraught with different drawbacks that can limit their utility. Highly diluted reactions or a slow addition protocol can be required to prevent oligomerizations. Several potentially toxic by-products can be generated, making the purification of the target product challenging, without mentioning their cost-effectiveness as they must be used in stoichiometric amounts.

In this context, we investigated a new simple and efficient method allowing a straightforward access to macrolactones from *seco*-acids in the presence of pentafluorobenzoyl chloride.[3] The reaction can be performed in a one pot fashion and does not require any complex work-up/treatment. In our case, the formation of lactones is favored by supramolecular interactions (lone pair-π),[4] providing the lactone in excellent yields. These conditions were also extended to intermolecular reactions to provide macrodiolides.



Scheme 1. Use of a Supramolecular Template to Favor Macrolactonizations

Acknowledgements

We thank the ANR (ANR-16-CE07-0022) and the ERC for funding (grant agreement No 648558, STRIGES CoG grant).

References

[1] S. K. Sartori, M. A. Nogueira Diaz, G. Diaz-Munoz, *Tetrahedron* **2021**, *84*, 132001.
[2] (a) A. Parenty, X. Moreau, G. Niel, J.-M. Campagne, *Chem. Rev.* **2013**, *113*, PR1. (b) M. Van Hoof, G. Force, D. Lebœuf, *Synthesis* **2024**, doi: 10.1055/a-2181-9800.
[3] G. Force, A. Perfetto, R. J. Mayer, I. Ciofini, D. Lebœuf, *Angew. Chem. Int. Ed.* **2021**, *60*, 19843-19851.
[4] M. Egli, S. Sarkhel, *Acc. Chem. Res.* **2007**, *40*, 197-205.

Orthogonal Stimuli Responsive Tri-stable Rotaxanes

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Early prototypes of molecular machines, molecular shuttles, were based on bi-stable rotaxanes: structures where the presence of two recognition sites, one responsive to an external stimulus, allowed the reversible and controlled movement of a macrocycle along the thread.[1] An evolution of such systems are tri-stable rotaxanes potentially including multiple rings. We report the synthesis and characterization of rotaxanes comprising a DB24C8 macrocyclic component and a thread containing three recognition sites: ammonium (AmH^+), bipyridinium (BPY^{2+}) and triazolium (Trz^+) (Figure 1). AmH^+ and BPY^{2+} are responsive to fully orthogonal stimuli, pH and electrochemical, which allowed to precisely direct the macrocycle translation along the thread and eventually reset the system. Moreover, the determination of the thermodynamic parameters gave a complete description of the behaviour of the system. Orthogonal stimuli responsive tri-stable rotaxanes represent the starting point for the creation of molecular logic gates and they could be introduced in oligomeric structures, to develop linear motors, through a careful design of the system kinetics.

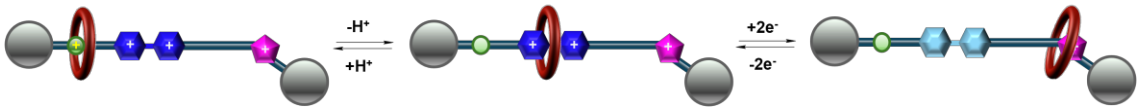

Figure 1. Schematic representation of the stimuli induced motion of the macrocycle along the axle.

References

[1] C. J. Bruns, J. F. Stoddart, "*The Nature of the Mechanical Bond: from Molecules to Machines*", **2017** by John Wiley & Sons, Inc. Hoboken, New Jersey

CONTROL OF TRANSMEMBRANE TRANSPORT BY PHOTOSWITCHABLE MOLECULAR TWEEZERS

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Many of Nature's protein receptors and machines operate within the lipid bilayer membrane and exploit environmental stimuli, as well as concentration and potential gradients, to operate and perform their task. Their malfunctioning has been associated to various diseases. Synthetic molecular chemists therefore actively pursue the creation of artificial membrane-embedded systems that imitate protein function. Although significant advances have been made in the application of synthetic molecular receptors as transmembrane transporters,[1] integration of stimuli-responsiveness and machine-like mechanical motions is still a major challenge.[2]
Our group has developed various tweezer-type anion receptors that can be switched between different affinity modes using light.[3] These receptors were used to reversibly control trans-membrane anion transport and to trigger membrane depolarization.[4] Here, we will share our most recent results, which includes insight into the (un)importance of changing binding affinity to modulate transport, and the visible-light activation of transport using photosensitizers.

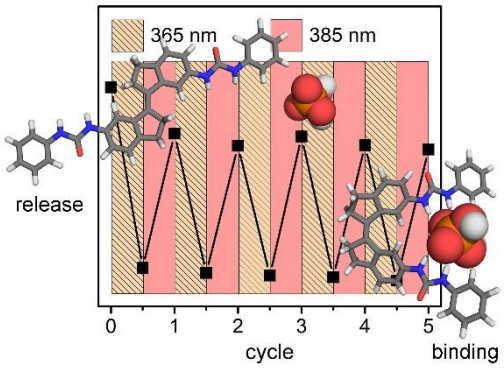

Figure 1. Photocontrol of anion binding to a stiff-stilbene based bis-urea receptor.

Acknowledgements

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References

[1] P. A. Gale, J. T. Davis, R. Quesada, *Chem. Soc. Rev.*, **2017**, *46*, 2497-2519.
[2] J. de Jong, J. E. Bos, S. J. Wezenberg, *Chem. Rev.*, **2023**, *123*, 8530-8574.
[3] S. J. Wezenberg, *Chem. Commun.*, **2022**, *58*, 11045-11058.
[4] S. J. Wezenberg, L.-J. Chen, J. E. Bos, B. L. Feringa, E. N. W. Howe, X. Wu, M. A. Siegler, P. A. Gale, *J. Am. Chem. Soc.*, **2022**, *144*, 331-338.

PATHWAY COMPLEXITY IN SUPRAMOLECULAR POLYMERIZATION: SIGNIFICANCE IN BLOCK CO-POLYMERIZATION AND ENZYME INHIBITION

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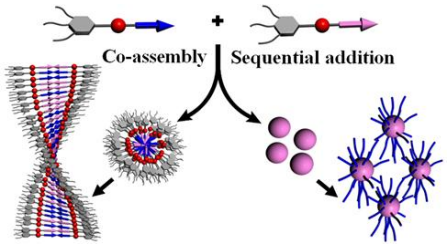
Achieving precise microstructural control in multicomponent supramolecular polymers is challenging due to the fast dynamics of monomer exchange, unlike their sequence-controlled covalent copolymer counterparts. As a result, the majority of reports in this area are based on examples of supramolecular copolymers, with only a handful of reports on supramolecular block copolymers. "Seed"-induced living supramolecular polymerization (LSP) offers a promising strategy for constructing kinetically controlled supramolecular block copolymers and complex heterostructural topologies with controlled shapes and dimensions. This study delves into the pathway complexities of two amide-functionalized chiral dipolar naphthalene monoimide (NMI) building blocks (**O-NMI** and **S-NMI**), differing merely by a single heteroatom (O-/S-). In **O-NMI**, pathway complexity leads to the initial formation of kinetically controlled metastable nanotapes that transform into thermodynamically controlled helical 1D fibers within 24 hours. In contrast, **S-NMI** reveals distinct supramolecular polymerization features, showing a stable spherical structure due to the predominance of stronger amide-amide H-bonding. This study further demonstrates the synthesis of unprecedented core-multiarmed supramolecular star block topologies by surface-catalyzed hetero-seeded supramolecular polymerization following the sequential addition of these two monomers through a kinetic route. Contrarily, the copolymerization of **O-NMI** and **S-NMI** under thermodynamic conditions reveals temporally controlled helical supramolecular copolymers. We further investigated the scope of this molecular design for temporally controlled supramolecular polymerization in water from amide-functionalized NMI building block (**O-NMI-2**) with hydrophilic oligo-oxyethylene (OE) wedges. The morphological transformation of **O-NMI-2** from collapsed spherical particles to organized 2D nanosheets influences the nonspecific adsorption of the enzyme α-Chymotrypsin (α-ChT) and temporally controls its activity. This work highlights the impact of seed-induced living supramolecular polymerization on enzyme activity control.



Scheme. Schematic presentation of supramolecular polymerization

Acknowledgements

P.K. thanks DST INSPIRE and IACS for the instrumental facilities.

References

[1] P. Khanra, A. K. Singh, L. Roy and A. Das, *J. Am. Chem. Soc.* **2023**, *145*, 5270–5284.
[2] P. Khanra, P. Rajdev, A. Das, *Angew. Chem. Int. Ed.* **2024**, e202400486 ***(Just Accepted).***
[3] A. Das, Maity, B. Maity, D. Koley, S. Ghosh, *Chem. Commun.* **2013**, *49*, 5757-5759.

THREADING A LINEAR MOLECULE THROUGH A MACROCYCLE THANKS TO BORON: AN ACCESS TO HIGHLY EMISSIVE COMPOUNDS

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While boron has extensively been used to build complex assemblies like macrocycles,cages and helicates,[1] it has never been used to thread a linear molecule through a macrocycle.

In this presentation, we will show it is in fact possible to use boron to thread BODIPYs and other species through macrocycles designed on purpose.[2] These new assemblies were unambiguously characterized by NMR spectroscopy as well as by X-ray diffraction for some of them (figure 1).

Interestingly, fluorescent threaded species may show higher quantum yields (up to 91%) than their non-threaded counterparts. We will discuss why these compounds possess these peculiar optical properties, with the help of theoretical calculations.

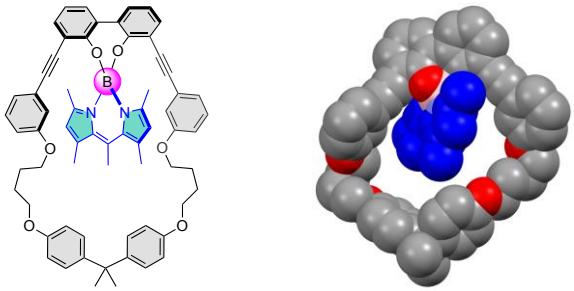

Figure 1. An example of threaded BODIPY through a macrocycle and its X-ray structure.

References

[1] M. Hähsler, M. Mastalerz, *Chem. Eur. J.,* **2021**, *27*, 233-237; H. Takata, K. Ono, N. Iwasawa, *Chem. Commun.,* **2020**, *56*, 5613; S. Yamamoto, H. Iida, E. Yashima, *Angew. Chem. Int. Ed*, **2013**, *52*, 6849-6853; N. Christinat, R. Scopelliti, K. Severin, *Chem. Commun.*, **2008**, *31*, 3660-3662; B. Nisanci, S. Sahinoglu, E. Tuner, M. Arik, I. Kani, A. Dastana, Ö. A. Bozdemir, *Chem. Commun.* **2017**, *53*, 12418-12421; T. Nakamura, G. Yamaguchi, T. Nabeshima, *Angew. Chem. Int. Ed.* **2016**, *55*, 9606-9609; D. Stoltenberg, S. Lüthje, O. Winkelmann, C. Näther, U. Lüning, *Eur. J. Org. Chem.,* **2011**, 5845-5859; J. Yu, M. Gaedke, S. Das, D. L. Stares, C. A. Schalley, F. Schaufelberger, **2023**, *ChemRxiv* https:///doi.org/10.26434/chemrxiv-2023-v95p8.

[2] M. Hicguet, L. Verrieux, O. Mongin, T. Roisnel, F. Berrée, A. Fihey, B. le Guennic, Y. Trolez, *Angew. Chem. Int. Ed.*, **2024**, e202318297, https://doi.org/10.1002/anie.202318297.

Modeling Amine Methylation in Methyl Ester Cavitand

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This talk will present our recent work using a combination of molecular dynamics simulations and density functional theory calculations to model the binding and methylation of amines inside a resorcinarene-based methyl ester cavitand.[1] Methylation of some the amines inside the cavitand has experimentally been shown to be accelerated by more than four orders of magnitude compared to the solution reactions. We characterize the binding and reactivity of eight amine substrates, and good agreement is found with the experiments. In particular, the rate enahancement is reproduced and its origins can be analyzed.

References

[1] G. Norjmaa, J. Rebek Jr., F. Himo, *Chem. Eur. J.*, **2024**, in press. e202303911.

CAGE TO CAGE CONVERSION CONTROLLED BY REDOX STIMULATION

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Coordination driven self-assembly has allowed the preparation of a wide variety of molecular rings and cages.[1] The corresponding host cavities offer promising molecular recognition properties, some of them being able to modulate their binding abilities through application of an external stimulus.[2] On this ground and in order to control the guest binding/release process through a redox stimulus, we were interested in our previous work in designing electron-rich self-assembled rings/cages incorporating π-donating and S-rich frameworks.[3] Some of them are based on the so-called *extended-TTF* skeleton (**exTTF**, Fig. 1a). A key feature of this unit lies in a drastic change of the molecular shape upon oxidation. The latter evolves from a highly bent butterfly-like structure in the neutral state (**exTTF**) to a fully aromatic dicationic species (**exTTF^{2+}**) in which both1,3-dithiolium rings are linked to a planar anthracene moiety. We already exploited these unique properties with molecular cages able to reversibly release a guest upon the cage disassembly[4] or through an exchange with counter anions.[5] We are currently focused on the preparation of Ruthenium-based molecular cages featuring **exTTF** units, designed to offer an alternative mechanism of the guest release. In this communication, we depict our latest findings regarding the metalla-assembly **L_2Ru_4**. The latter undergoes an important conformational transformation when subjected to a redox stimulus, leading to the formation of the **$L^{2+}{}_2Ru_4$** cage, with drastic modification of the shape, volume, and charge of the cavity (Fig. 1b).

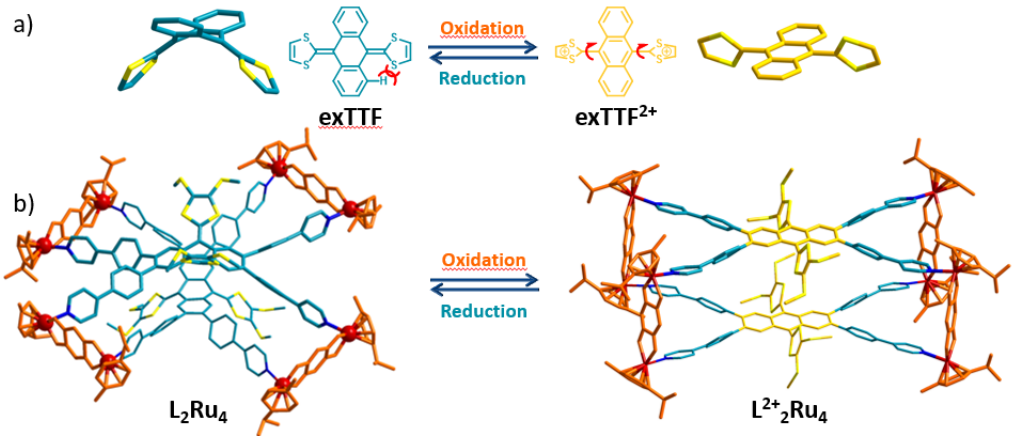

Figure 1. a) Geometric changes occurring during the oxidation/reduction of **exTTF**, b) X-Ray crystal structures showing the transformation of **L_2Ru_4** to **$L^{2+}{}_2Ru_4$** upon redox stimulation

References

[1] T. R. Cook, P. J. Stang, *Chem Rev.* **2015**, 115, 7001.
[2] T. Y. Kim, R. A. S. Vasdev, D. Preston, J. F. Crowley, *Chem. Eur. J.* **2018**, 24, 14878.
[3] S. Goeb, M. Sallé, *Acc. Chem. Res.* **2021**, 54, 1043.
[4]. V. Croué, S. Goeb, G. Szalóki, M. Allain, M. Sallé, *Angew. Chem. Int. Ed.* **2016**, 55, 1746.
[5] G. Szalóki, V. Croué, V. Carré, F. Aubriet, O. Alévêque, E. Levillain, M. Allain, J. Arago, E. Ortí, S. Goeb and M. Sallé, *Angew. Chem. Int. Ed.* **2017**, 56, 16272.

INTERNAL DYNAMICS IN RESPONSIVE 3:2 CB[n] COMPLEXES

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The control of the stoichiometry in oligomeric complexes remains a major issue[1] but primordial for construction of efficient molecular machinery.[2] Recently, we showed that cucurbit[8]uril (CB[8]) macrocycles combined with linear di-viologens initially form 1:2 complexes as precursors of unusual 3:2 host:guest complexes, exhibiting remarkable responsive dynamic properties, host self-sorting, and external ring-translocation.[3]

Peripheral host binding appeared to considerably rigidify the whole 3:2 complexes, drastically reducing host and guest translational movements, in turn impacting the rotation of the central stations. This type of translational-rotational coupling between the host and the guest dynamics is unprecedented in large host:guest complexes in water.[3]

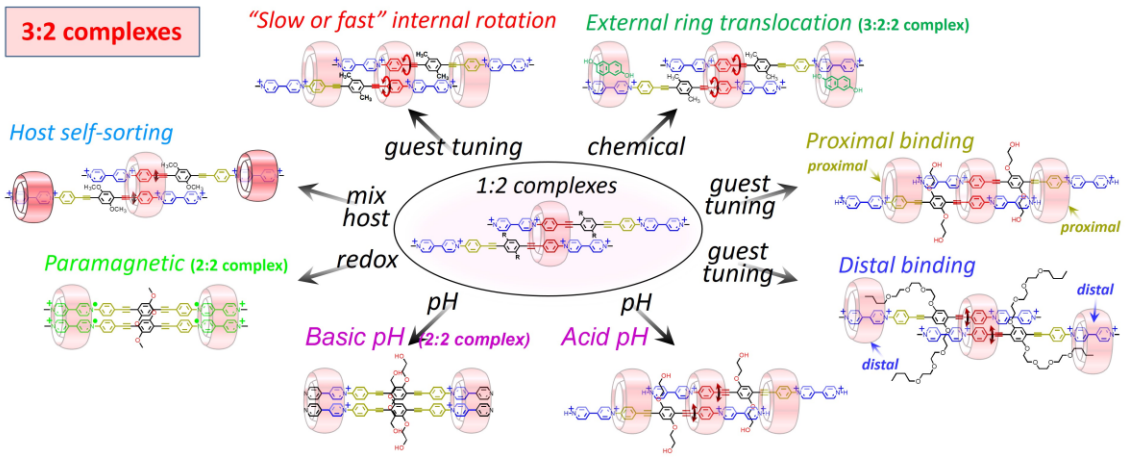

Figure 1. Illustration of the huge diversity of 3:2 CB[n]:di-viologens complexes, presenting various responsive properties and internal self-assemblies.

Acknowledgements

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References

[1] a) X. Yang, R. Wang, A. Kermagoret, D. Bardelang, Angew. Chem. Int. Ed. **2020**, *59*, 21280-21292; F. Liu, A. Kriat, R. Rosas, D. Bergé-Lefranc, D. Gigmes, S. Pascal, O. Siri, S. Liu, A. Kermagoret, D. Bardelang, Org. Biomol. Chem. **2023**, *21*, 9433-9442.

[2] A. Kermagoret, D. Bardelang, Chem. Eur. J. **2023**, e202302114; Q. Cheng, H. Yin, R. Rosas, D. Gigmes, O. Ouari, R. Wang, A. Kermagoret, D. Bardelang, Chem. Commun. **2018**, *54*, 13825-13828.

[3] H. Yin, R. Rosas, S. Viel, M. Giorgi, V. Monnier, L. Charles, D. Siri, D. Gigmes, Y. Nassar, F. Chevallier, C. Bucher, R. Wang, A. Kermagoret, D. Bardelang, Angew. Chem. Int. Ed. **2024**, 63, e202315985.

Functional patterning of graphene via an all-supramolecular strategy

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Surface-confined, supramolecular self-assembly has been the focus of extensive research in the past decade[1]. A number of strategies have been developed and reported for surface patterning leading to novel applications in molecular electronics, photonics and nano-mechanical devices.[2] Despite this, we are still at the early stages of exploiting them in viable, practical technologies since we are limited by their inability to form reproducible, ordered, integrated systems [3]. More specifically, in the case of graphene, we also have to overcome the strong charge-transfer that occurs when electronically-active molecules are adsorbed on its surface.

To address this problem, we have developed a series of molecular dyads that can form ordered assemblies on graphene-like substrates and also bear an emissive component located out-of-the plane of the substrate. These dyads are held together via non-covalent interactions, which enable us to easily mix & match the components, resulting in a highly tunable system.

This relatively simple design allows us to control the orientation and distance of an emissive component above a graphene-like substrate through different supramolecular interactions and opens up an accessible route to electronically de-couple an optically-active molecule from graphene.[4]

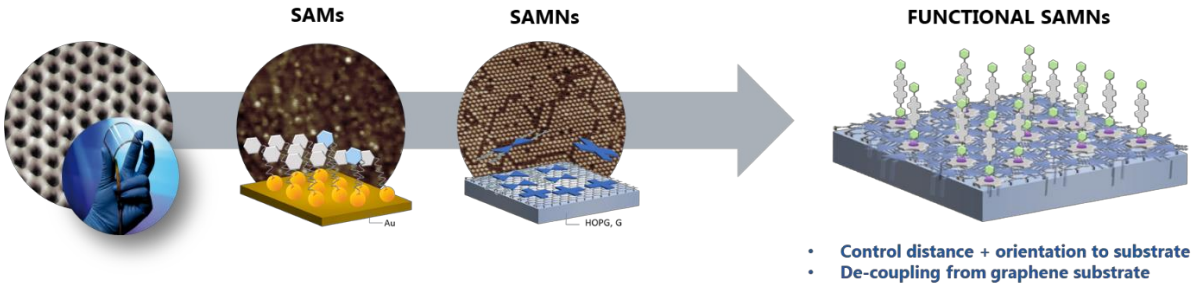

Figure 1. Different approaches for surface functionalisation; self-assembled monolayers (SAMs), self-assembled molecular networks (SAMNs), and our proposed strategy: functional SAMNs.

References

[[1] L. Sosa Vargas, E. Kim, A.-J. Attias, *Mater. Horiz*. **2017**,*4*, 570-583.

[2a] A. Ciesielski, C.-A. Palma, M. Bonini, P. Samori, *Adv. Mater*.,**2010**,22, 3506-3520; [2b] J. V. Barth, G. Constantini, K. Kern, *Nature*, **2005**, *437*, 671-679. [2c] S. Le Liepvre, P. Du, D. Kreher, F. Mathevet, A.-J. Attias, C. Fiorini-Debuisschert, L. Douillard, F. Charra , *ACS Photonics*, **2016**, *3* (12), 2291–2296.

[3] K. Ariga, Q. Ji, J. P. Hill, Y. Bando, M. Aono, *NPG Asia Mater*.,**2012**, *4*, e17.

[4] Q. Fernez, S. Moradmand, M. Mattera, W. Djampa-Tapi, C. Fiorini- Debuisschert, F. Charra, D. Kreher, F. Mathevet, I. Arfaoui, L. Sosa Vargas*, J. Mat. Chem. C.* **2022***,10, 13981-1398.*

A MOLECULAR TROJAN HORSE: ENCAPSULATING DRUGS WITHIN CAGES FOR TARGETED DELIVERY IN CANCER

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Molecular cages with custom-made cavities are an emerging type of hosts that have the potential to encapsulate guest molecules for a variety of applications including molecular recognition, catalysis, gas separation, materials science, and emerging biomedical drug delivery.[1] Cage synthesis typically involves the self-assembly of building blocks with accurate shapes and geometries.[1b] Molecular modeling can be used to design cage structures to obtain any desired cavity size and shape with specific functional groups directed into the cavity. [1b] In this communication, we will show the molecular modelling and synthetic strategies to obtain both fully organic cages and metal-organic cages with customized properties cavities for encapsulating and releasing anticancer drugs. Then, we will shot the biological properties of the cages, including anticancer drug delivery *in vitro* (Figure 1).

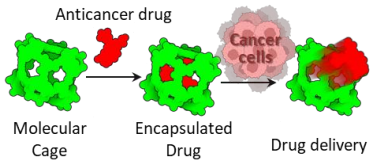

Figure 1. Scheme showing the encapsulation of a guest molecule by a molecular cage.

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References: [1] (a) G. Montà-González, F. Sancenón, R. Martínez-Máñez, V. Martí-Centelles, *Chem. Rev.* **2022**, *122*, 13636. (b) V. Martí-Centelles, *Tetrahedron Lett.* **2022**, *93*, 153676. (c) T. K. Piskorz, V. Martí-Centelles, T. A. Young, P. J. Lusby, F. Duarte, *ACS Catal.* **2022**, *12*, 5806.

MOLECULAR ENCAPSULATION WITHIN TUBULAR SUPRAMOLECULAR POLYMERS

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In this communication, we would like to show recent examples in our group in which we exploit the confined nanospaces purposedly created in different self-assembled structures to selectively host specific molecules. One of them comprises tubular nanostructures with custom-tailored pores, which are assembled by coupling two cooperative supramolecular processes of different hierarchy and acting in orthogonal directions. Chiral cyclic tetramers are first formed from 4 monomeric π-conjugated subunits by H-bonding interactions between nucleobase directors. A proper monomer preorganization affords high chelate cooperativities in solution.[1] .When these cyclic species are subjected to a supramolecular polymerization process, helical self-assembled nanotubes are formed *via* nucleation-growth cooperative mechanisms in organic solvents[2] and in water.[3] Interestingly, the inner pore of these nanotubes can be coated with functional groups of opposite solvophilicity to the external medium, so as to host molecules that show an affinity for this environment.

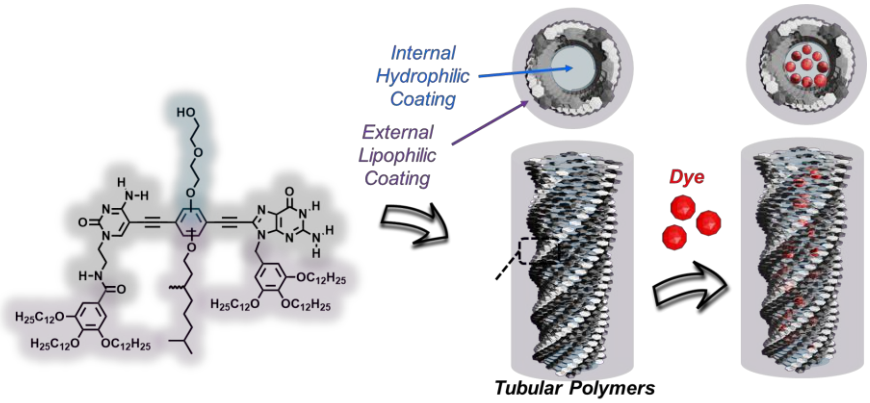

Figure 1. Molecular encapsulation within tubular supramolecular polymers.

Acknowledgements

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References

[1] D. Serrano-Molina, C. Montoro-García, M. J. Mayoral, A. de Juan, D. González-Rodríguez, *J. Am. Chem. Soc.* **2022**, 144, 5450–5460.

[2] a) V. Vázquez-González, M. J. Mayoral, R. Chamorro, M. M. R. M. Hendrix, I. K. Voets, D. González-Rodríguez, *J. Am. Chem. Soc.* **2019**, *41*, 16432-16438; b) M. González-Sánchez, M. J. Mayoral, V. Vázquez-González, M. Paloncýová, I. Sancho-Casado, F. Aparicio, A. de Juan, G. Longhi, P. Norman, M. Linares, D. González-Rodríguez, *J. Am. Chem. Soc.* **2023**, *145,* 17805−17818.

[3] a) F. Aparicio, P. Chamorro, R. Chamorro, S. Casado, D. Gonzalez-Rodriguez, *Angew. Chem. Int. Ed.* **2020**, *59*, 17091-17096.

Switchable supramolecular helices for asymmetric stereodivergent catalysis

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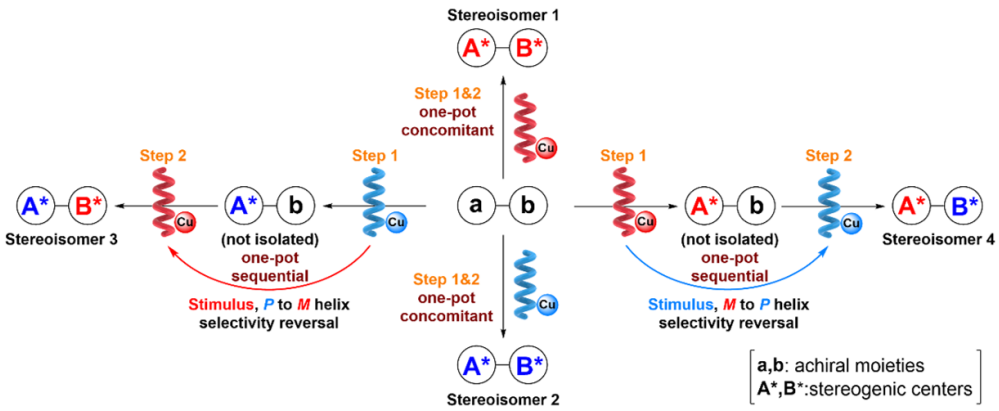
Despite recent developments on the design of dynamic catalysts, none of them have been exploited for the in-situ control of multiple stereogenic centers in a single molecular scaffold. To reach this challenge, hydrogen-bonded assemblies between a benzene-1,3,5-tricarboxamide (BTA) achiral phosphine ligand coordinated to copper and a chiral BTA comonomer are engaged in a copper-hydride catalyzed hydrosilylation[1] and hydroamination[2] cascade process. The nature of the product stereoisomer is related to the handedness of the helices and can thus be directed in a predictable way by changing the nature of the major enantiomer of the BTA comonomer present in the assemblies. The strategy allows all stereoisomers to be obtained one-pot with similar selectivities by conducting the cascade reaction in a concomitant manner, i.e. without inverting the handedness of the helices, or sequentially, i.e. by switching the handedness of the supramolecular helices between the hydrosilylation and hydroamination steps. Supramolecular helical catalysts appear as a unique and versatile platform to control the configuration of molecules or polymers embedding several stereogenic centers.[3]



Scheme 1. Copper-catalyzed asymmetric stereodivergent syntheses of all the possible stereoisomers by supramolecular switchable helices.

Acknowledgements

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References

[1] Y. Li, A. Hammoud, L. Bouteiller, M. Raynal, *J. Am. Chem. Soc*. **2020**, *142*, 5676–5688.

[2] P. Aoun, A. Hammoud, M. A. Martínez-Aguirre, L. Bouteiller, M. Raynal, *Catal. Sci. Technol*. **2022**, *12*, 834–842.

[3] R. Chen, A. Hammoud, P. Aoun, M. A. Martínez-Aguirre, N. Vanthuyne, R. Maruchenko, P. Brocorens, L. Bouteiller, M. Raynal, under revision in *Nature Communications* (minor). Preprint: https://chemrxiv.org/engage/chemrxiv/article-details/65313bb12431cc1dacf33ae5

Solution and solvent-free stopper exchange reactions for the preparation of pillar[5]arene-containing [2] and [3]rotaxanes

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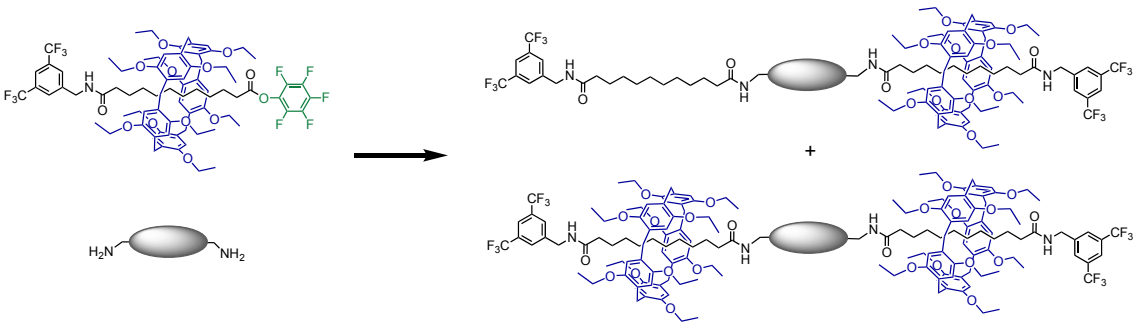
The most classical approach to prepare rotaxanes is based on the grafting of bulky stoppers onto a linear building block associated to a macrocyclic moiety in an inclusion complex. This strategy is efficient as long as the reaction conditions are compatible with the formation of the supramolecular complex. This requirement is however often problematic, in particular when weak intermolecular interactions are used to assemble the two components. This is for example the case when pillar[5]arene is used as the macrocyclic component for the preparation of rotaxanes.[1] The direct preparation of rotaxanes from pillar[5]arene-based inclusion complexes is highly dependent on the nature of the reagents even when similar reactions are used for their synthesis and yields are often quite moderate.[1] To solve this problem, we have developed the preparation of pillar[5]arene-containing [2]rotaxane building blocks allowing their efficient post-modification by a stopper exchange reaction.[2] In this poster, we will show how this strategy can be used for the direct synthesis of [2]rotaxanes with elongated axle moieties and [3]rotaxanes.



Acknowledgements

Financial support from the ANR (projects FastGiant ANR-17-CE07-0012-01 and Pillar ANR-19-CE06-0032) and the *Fondation Jean-Marie Lehn* is gratefully acknowledged.

References

[1] R. Milev, A. Lopez-Pacheco, I. Nierengarten, T. M. N. Trinh, M. Holler, R. Deschenaux, J.-F. Nierengarten, *Eur. J. Org. Chem*. **2015**, 479-485.

[2] a) I. Nierengarten, E. Meichsner, M. Holler, P. M. Pieper, R. Deschenaux, B. Delavaux-Nicot, J.-F. Nierengarten, *Chem. Eur. J.* **2018**, *24*, 169-177; b) I. Nierengarten, J.-F. Nierengarten, *ChemistryOpen* **2020**, *9*, 393-400. c) M. Rémy, I. Nierengarten, B. Park, M. Holler, U. Hahn, J.-F. Nierengarten, *Chem. Eur. J.* **2021**, *27*, 8492-8499. d) N. Becharguia, E. Wasielewski, R. Abidi, I. Nierengarten, J.-F. Nierengarten, *Chem. Eur. J*. **2024**, *30*, e202303501. e) N. Becharguia, I. Nierengarten, J.-M. Strub, S. Cianférani, M. Rémy, E. Wasielewski, R. Abidi, J.-F. Nierengarten, *Chem. Eur. J*. **2024**, *30*, e202304131.

SHORT COMM.

Switchable catalysis within molecular cages

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We have been preparing visible light switchable molecular cages for a few years,[1,2] and our latest results of switchable catalysis within molecular cages will be discussed.

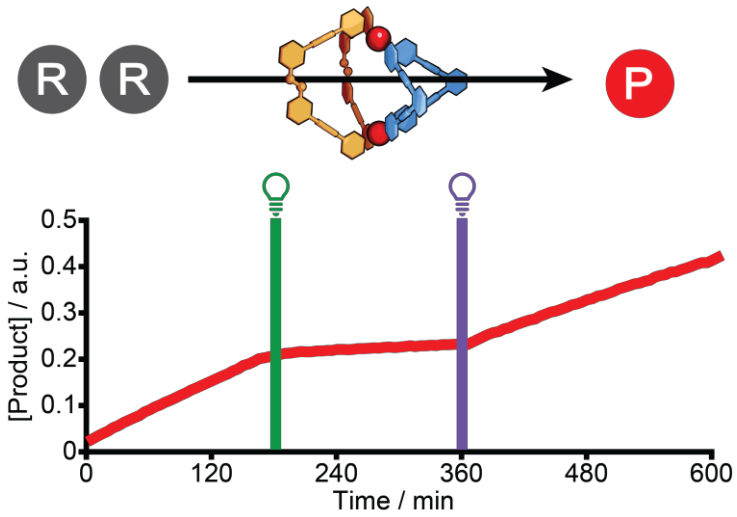

Figure 1. Self-assembled metallosupramolecular that respond to visible light to catalyse non-photo reactions.

Acknowledgements

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References

[1] R. DiNardi, A. O. Douglas, R. Tian, J. R. Price, M. Tajik, W. A. Donald, J. E. Beves, *Angew. Chem. Int. Ed.* **2022**, e202205701

[2] A. D. W. Kennedy, R. DiNardi, L. L. Fillbrook, W. A. Donald, J. E. Beves, *Chem. Eur. J.* **2022**, *28*, e2021044.

DNA mimic foldamers: Tools for Targeting Protein-DNA Interactions

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This contribution presents aromatic oligo-amide DNA mimic foldamers. The structural and functional fidelity of these DNA mimic foldamers hold significant promise for both understanding biological processes and developing potential therapeutics. These DNA mimic foldamers, composed of alternating 8-amino-2-quinoline carboxylic acid (Q) and 8 aminomethyl-2-quinoline carboxylic acid (mQ) building blocks, fold into a single helix in solution.[1] The incorporation of negatively charged side chains enables them to adopt an exo-double helical topology, mimicking the charge distribution of B-DNA. The resulting purely synthetic DNA mimics are much more robust – towards enzymatic cleavage and dissociation –than B-DNA.[1]
Given the essential role of DNA recognition by proteins in various biological processes, DNA mimics are very promising as "decoys" capable of interfering with therapeutically relevant proteins. These foldamers demonstrate the ability to inhibit therapeutically relevant enzymes such as topoisomerase I and HIV-integrase.[1] Furthermore, they exhibit perturbation of chromatin composition and cell cycle progression *in vivo*.[2] The structural investigation of a complex formed between a DNA mimic and a non-sequence-selective DNA binding protein – Sac7d – is also presented.[3] Moreover, to facilitate binding to sequence-selective proteins, a foldamer-DNA conjugate will be introduced.

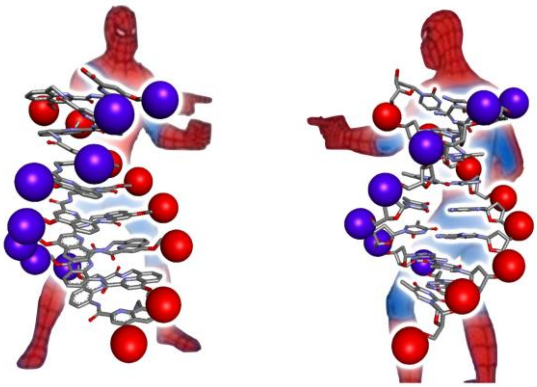

Figure 1. Structures of synthetic DNA mimic foldamer (on the left) and of B-DNA (on the right).

Acknowledgements

We acknowledge financial support from the Deutsche Forschungsgemeinschaft (DFG, CRC1309-C7) and from the European Research Council (ERC, No. ERC-2021-ADG-320892).

References

[1] Ziach, K.; Chollet, C.; Parissi, V.; Prabhakaran, P.; Marchivie, M.; Corvaglia, V.; Bose, P. P.; Laxmi-Reddy, K.; Godde, F.; Schmitter, J.-M.; Chaignepain, S.; Pourquier, P.; Huc, I. *Nat. Chem.* **2018**, *10* (5), 511–518.
[2] Kleene, V.; Corvaglia, V.; Chacin, E.; Forne, I.; Konrad, D. B.; Khosravani, P.; Douat, C.; Kurat, C. F.; Huc, I.; Imhof, A. *Nucleic Acids Res.* **2023**, *51* (18), 9629–9642.
[3] Deepak, D.; Corvaglia, V.; Wu, J.; Allmendinger, L.; Huc, I. ChemRxiv November 3, **2023**.

Competitive exclusion in self-replicating fibres

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Self-replication, i. e. the ability of a chemical or biological entity to promote its own production, is one of the key features of life.[1] Our group has developed synthetic, purely chemical self-replicators which consist of simple building blocks (an aromatic dithiol headgroup and a short peptide) that form cyclic oligomers which ultimately assemble into fibres. Mechanical stress (i. e. stirring) leads to fibre breakage and thus to more growing fibre ends, allowing for exponential growth.[2]

In this work,[3] we show an example that exhibits competitive exclusion,[4] which is an important motor for another key feature of life: Darwinian evolution. In a two-building-block system, two different replicators – either hexamer or octamer rings – emerge (Fig. 1a). Starting from libraries with various hexa-/octamer ratios, placing an aliquot of those into fresh precursors in a repetitive way (Fig. 1b) leads ultimately to the extinction of the hexamer replicator (Fig. 1c). Mechanistic studies showed that this is not due to the octamer simply growing faster: two replicator fibres were found to interact and to influence each other's access to precursors, resulting into different growth behaviours. The occurrence of this phenomenon is highly dependent on the reaction conditions, to the point that it can be completely absent with the two replicators exhibiting similar, unhindered growth.

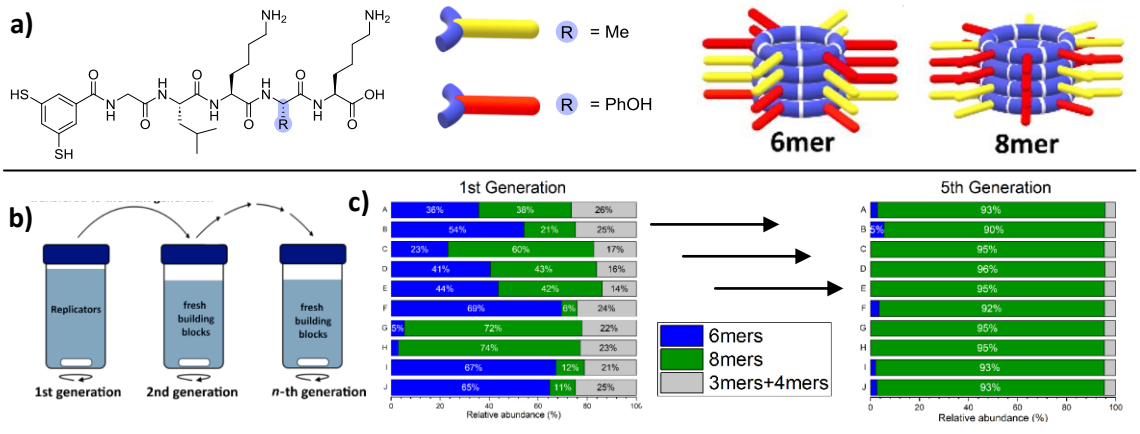

Fig. 1. a) Scheme of the two building blocks (red and yellow) that assemble to self-replicator fibres, b) schematic representation of the serial transfer, c) libraries with different hexa-/octamer proportions that evolve towards 100% octamer when subjected to serial transfer.

References:

1. P. Adamski *et al., Nat. Rev. Chem.* **2020**, *4*, 386–403.
2. S. Otto, *Acc. Chem. Res.* **2022**, *55*, 145–155.
3. M. J. Eleveld, Y. Geiger[+], J. Wu[+], A. Kiani, G. Schaeffer, S. Otto, *Manuscript under revision.*
4. G. Hardin, *Science* **1960**, *131*, 1292–1297.

Design and synthesis of molecular hosts cryptophanes-application in imaging

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Cryptophanes (Crs) are cage-like host molecules composed of two molecular crowns, cyclotriveratrylene (CTV) units usually connected by three ether linkers. These molecular hosts are known since decades to be able to encapsulate many different entities, in particular they are well suited for xenon. [1] Then, the development of Cr-based biosensors has been tremendously studied for applications in hyperpolarized xenon magnetic resonance imaging (MRI) in biological systems. Several works have demonstrated their applicability and relevance, in particular in cells assays, but to date, no application of such a bioprobe has been reported *in vivo*. [2] Indeed, the complex preparation of Cr-monosubstituted derivatives and the poor solubility of these molecules in biocompatible media precludes the obtention of an efficient xenon based bioprobe. The synthetic schemes to produce such derivatives have not evolved so much, leading to minor modifications of the whole backbone of cryptophanes, then narrowing their potential others applications.

Our group has recently described a new synthetic approach, based on the preparation of C_1-symmetrical CTV using an iterative synthetic strategy, [3] and allowing, among other things, the preparation of a CTV with a nitrogen atom in place of the methylene bridges. This new aza-CTV led to the preparation of the first aza-containing cryptophane, and then a new family of compound named cryptophazane [4].

In this communication, the work of our group on the conception and the evaluation of cryptophazane will be detailed. Our recent work on the use of these derivatives in hyperpolarized xenon MRI will be also discussed.

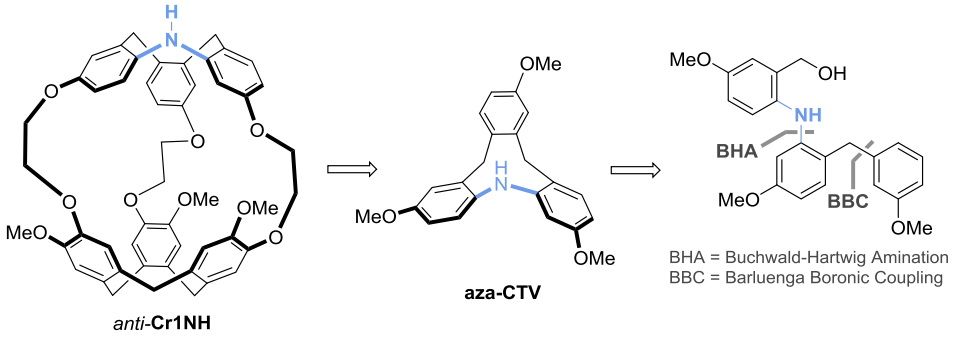

Figure1. Retrosynthesis of cryptophazane.

References

[1] Brotin, T.; Dutasta, J.-P. *Chem. Rev.* **2009**, 88–130. doi 10.1021/cr0680437.

[2] Zemerov, S.D.; Dmochowski, I.J. *RSC Adv.* **2021**, 7693–7703. doi 10.1039/D0RA10765D.

[3] Vigier,C.; Fossé, P.; Fabis,F.; Cailly, T.; Dubost, E. *Adv. Synth. Catal.* **2021**, 3756–3761. doi 10.1002/adsc.202100547.

[4] Vigier,C.; Fayolle, D.; El Siblani, H.; Sopkova – de Oliveira Santos, J.; Fabis, F.; Cailly, T.; Dubost, E. *Angew. Chemie Int. Ed.* **2022**. doi 10.1002/anie.202208580.

AGGREGATION OF PLATINUM LUMINOPHORES: FROM STIMULI-RESPONSIVE EMISSION TO THROUGH SPACE SENSITIZATION

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Rich photophysical properties of square planar Pt(II) complexes bearing aromatic ligands reflect their tendency for self-assembly, which is driven by intermolecular metal···metal and π–π stacking interactions and results in a drastic decrease of the optical band gap, i.e. lower energy of the absorption and emission.[1] Formation of these aggregates is defined by the interplay of weak non-covalent contacts and open wide opportunities to attain diverse responsive molecular materials, optical characteristics of which are sensitive to external perturbation (temperature, mechanical force, organic volatiles etc.) with potential use in chemosensing, imaging, and memory devices.[1]

Combining two or more chromophore motifs in one molecular entity can introduce new photophysical features by creating alternative pathways for energy transfer, increase intermolecular connectivity and impact the aggregation processes. Recently, we have shown that bimetallic compounds composed of two cyanide-bridged cycloplatinated motifs demonstrate higher intensity of phosphorescence and enhanced ability for association vs their conventional mononuclear relatives; the latter is efficiently regulated by the properties of the surrounding medium including solvent polarity.[2] Lately, we investigated the photophysical and aggregation behavior of hetero-chromophoric species comprising different metals and organic blocks. Notably, linking the platinum(II) and rhenium(I) centres via the cyanide or thiocyanate has little detrimental effect on the intensity of photemission, but produces in the materials with distinct mechano-, thermo- and vapochromic chromic features. Furthermore, tailoring a polyaromatic hydrocarbon fragment to a pincer platinum(II) unit in tweezer-like architechture represents a new strategy to realize through space triplet energy transfer and induce low energy phosphorescence from organic dyes by using simple organometallic fragments. These insights in inter-chromophore interactions broaden the scope of optical dynamic behavior and functionalities of molecular materials composed of Pt(II)-based components.

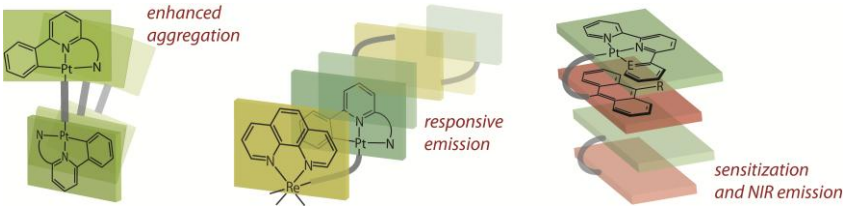

Figure 1. Illustration of Pt(II)-based bichromophore aggregates studied in our work.

Acknowledgements

We thank the Academy of Finland and Deutsche Forschungsgemeinschaft for financial support.

References

[1] K. Li et al., *Chem. Sci.*, **2016**, *7*, 1653–1673; A. K.-W. Chan, V. W.-W. Yam, *Acc. Chem. Res.*, **2018**, *51*, 3041-3051; M. Yoshida, M. Kato, *Coord. Chem. Rev.*, **2020**, *408*, 213194.

[2] V. V. Khistiaeva et al., *Chem. Sci.*, **2024**, DOI: 10.1039/d3sc06941a.

INVESTING IN ENTROPY: THE STRATEGY OF CUCURBIT[*n*]URILS TO ACCELERATE THE INTRAMOLECULAR DIELS-ALDER CYCLOADDITION REACTION OF TERTIARY FURFURYL AMINES

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Cucurbit[*n*]urils (CB[*n*]s), renowned for their host-guest chemistry, are becoming versatile biomimetic receptors.[1] Herein, we disclose that cucurbit[7]uril (CB[7]) accelerates the intramolecular Diels-Alder (IMDA) reaction for previously elusive and unreactive tertiary *N*-methyl-*N*-(homo)allyl-2-furfurylamines up to 4 orders of magnitude under mild conditions. Using ^{1}H NMR titrations and ITC experiments, we characterize the dissimilar thermodynamic and kinetic properties of the complexes. We also determine the activation parameters ($\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$) leading to the transition state of the IMDA reactions, both in the bulk and included in CB[7], to shed light on the key role of the receptor on the acceleration observed. CB[7] acts as an "entropy trap" utilizing guest binding to primarily pay the entropy penalty for reorganizing the substrate in a high-energy reactive conformation that resembles the geometry of the highly ordered transition state required for the IMDA reaction. This study underscores the potential of cucurbit[*n*]urils as artificial active sites, emulating specific aspects of enzymatic catalysis.

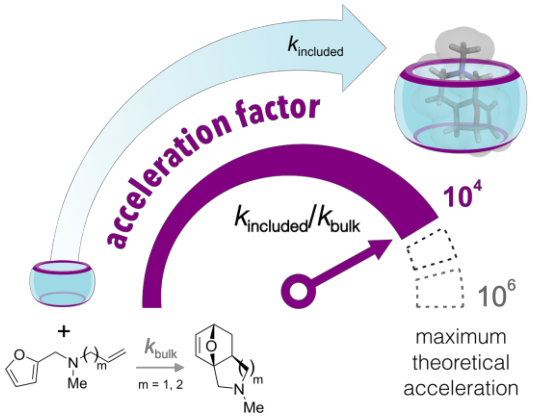

Figure 1. CB[*n*]-mediated intramolecular Diels-Alder reaction of tertiary furfuryl amines.

Acknowledgements

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References

[1] a) F. N. Tehrani, K. I. Assaf, R. Hein, C. M. E. Jensen, T. C. Nugent, W. M. Nau, *ACS Catalysis* **2022**, *12*, 2261-2269. b) A. Palma, M. Artelsmair, G. Wu, X. Lu, S. J. Barrow, N. Uddin, E. Rosta, E. Masson, O. A. Scherman, *Angew. Chem. Int. Ed.* **2017**, *56*, 15688-15692.

Molecular tweezers for multifunctional switchable organogels

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Organogels are a special class of gels that result from the self-assembly of low molecular weight gelators (LMWGs) into three-dimensional networks that entrap a solvent. This new type of soft materials has attracted great interest due to their potential applications as stimuli responsive materials.[1] The recent development of molecular machines, including molecular switches, has allowed the design of controlled dynamic multi-state molecular systems, which we aim to exploit to develop multifunctional switchable organogels.[2]

In recent years, we have reported stimuli-responsive molecular tweezers composed of a terpyridine switching unit and M-salen functional units with properties dependent on the complexed metal ion. The coordination-induced closing-opening motion of the system has been used to modulate different physico-chemical properties (luminescence, catalysis, magnetism, ...) with remarkable versatility.[3-6] This work presents a new class of luminescent molecular tweezers functionalised by long alkyl chains capable of acting as LMWGs. In the open state, these tweezers self-assemble into a fibrillar supramolecular polymer network and form organogels in aromatic solvents. The closing motion results in a drastic conformational change, leading to disassembly of the network and loss of organogelation properties. We have demonstrated that this system performs a reversible sol-gel transition by modulating the intermolecular interactions between the tweezers depending on their conformation (Figure 1). We report here the synthesis of these platinum(II) salphen-based molecular tweezers and the study of their reversible gelation properties.

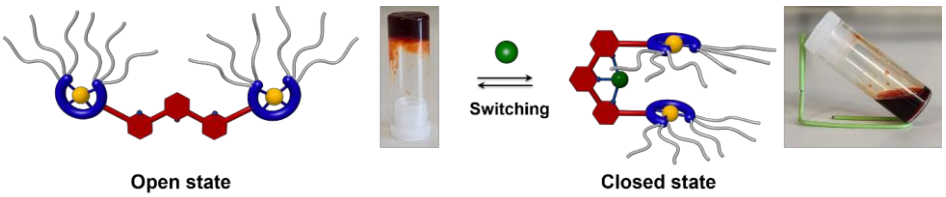

Figure 1. Reversible gelation by mechanical switching of the platinum tweezers in toluene

Acknowledgements

The authors thank G. Clodic and C. Przybylzki (IPCM) for the MALDI-TOF analysis, S. Casale (LRS), F. Ben Romdhane and D. Montero (FCMat) for the SEM and TEM imaging.

References

[1] M.-O. M. Piepenbrock, G. O. Lloyd, N. Clarke and J. W. Steed, *Chem. Rev.*, **2010**, *110*, 1960–2004.
[2] A. S. Lubbe, T. van Leeuwen, S. J. Wezenberg and B. L. Feringa, *Tetrahedron*, **2017**, *73*, 4837–4848.
[3] B. Doistau, A. Tron, S. A. Denisov, G. Jonusauskas, N. D. McClenaghan, G. Gontard, V. Marvaud, B. Hasenknopf and G. Vives, *Chem. Eur. J.*, **2014**, *20*, 15799–15807.
[4] B. Doistau, J.-L. Cantin, L.-M. Chamoreau, V. Marvaud, B. Hasenknopf and G. Vives, *Chem. Commun.*, **2015**, *51*, 12916–12919.
[5] B. Doistau, L. Benda, J.-L. Cantin, L.-M. Chamoreau, E. Ruiz, V. Marvaud, B. Hasenknopf and G. Vives, *J. Am. Chem. Soc.*, **2017**, *139*, 9213–9220.
[6] L. Benda, B. Doistau, C. Rossi-Gendron, L.-M. Chamoreau, B. Hasenknopf and G. Vives, *Commun. Chem.*, **2019**, *2*, 1–11.

Design of Rotaxane-based Molecular Machines for Regulation of Dynamic Photon Up-Conversion

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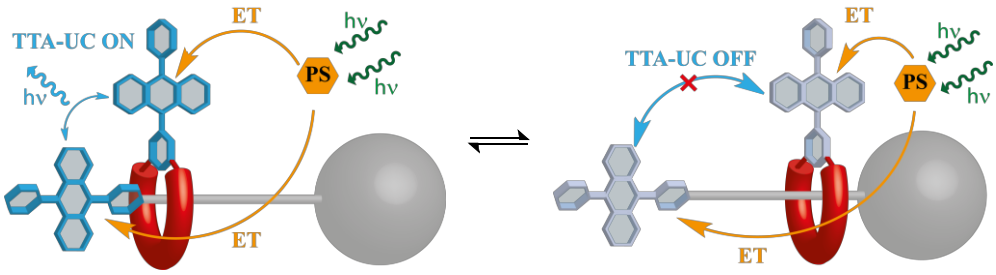
Rotaxanes are mechanically-interlocked molecules (MIMs), where the intrinsic mechanical bond assures structural integrity of their architectures and limits amplitude of spontaneous motion of their non-covalently interlocked components, especially suited to develop molecular machines.[1] Such structurally well-defined multicomponent structures represent versatile platforms to study a range of fundamental processes, including light-matter interactions and fast intramolecular collisions. In this context, we turn our attention to *triplet-triplet annihilation photon up-conversion* (TTA-UC), which is a process where absorption of light of long wavelength will ultimately lead to the emission of photons of higher energy.[2] This is achieved in three steps: 1) photoexcitation of *photosensitizers* (PS), followed by 2) energy transfer (ET) to dye molecules (*annihilators*), and 3) encounter of two excited annihilators promoting triplet fusion to populate a higher energy emissive state. Using well-defined macrocycle trajectories in rotaxanes, we are investigating the intramolecular control of a dynamic TTA-UC process within a MIM incorporating sensitizers and annihilators, through biasing the kinetics and amplitude of sub-component motion.

Herein we present the syntheses and preliminary spectroscopic analyses of prototypes of rotaxanes integrating 9,10-diphenylanthracene annihilators on the macrocycle and the axle, in the presence of an external photosensitizer, to induce the TTA-UC process. Modifications of the nature and length of the axle were accomplished to afford information about the intramolecular TTA-UC process depending on the dynamic nature of ring movement.



Scheme. Schematic representation of a [2]rotaxane containing 9,10-diphenylanthracene annihilators displaying dynamic TTA-UC (i.e., green-to-blue light conversion) tuned by the mechanical bond.

Acknowledgements

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Funded by the European Union

References

[1] M. Xue, Y. Yang, X. Chi, X. Yan, F. Huang, *Chem. Rev.*, **2015**, *115*, 7398-7501; D. Sluysmans, J.F. Stoddart, *Trends in Chemistry*, **2019**, *1*, 195-197.

[2] T.N. Singh-Rachford, F.N. Castellano, *Coord. Chem. Rev.*, **2010**, *254*, 2560-2573.

Switching dynamic covalent reactions of CO_2 capture using host-guest chemistry

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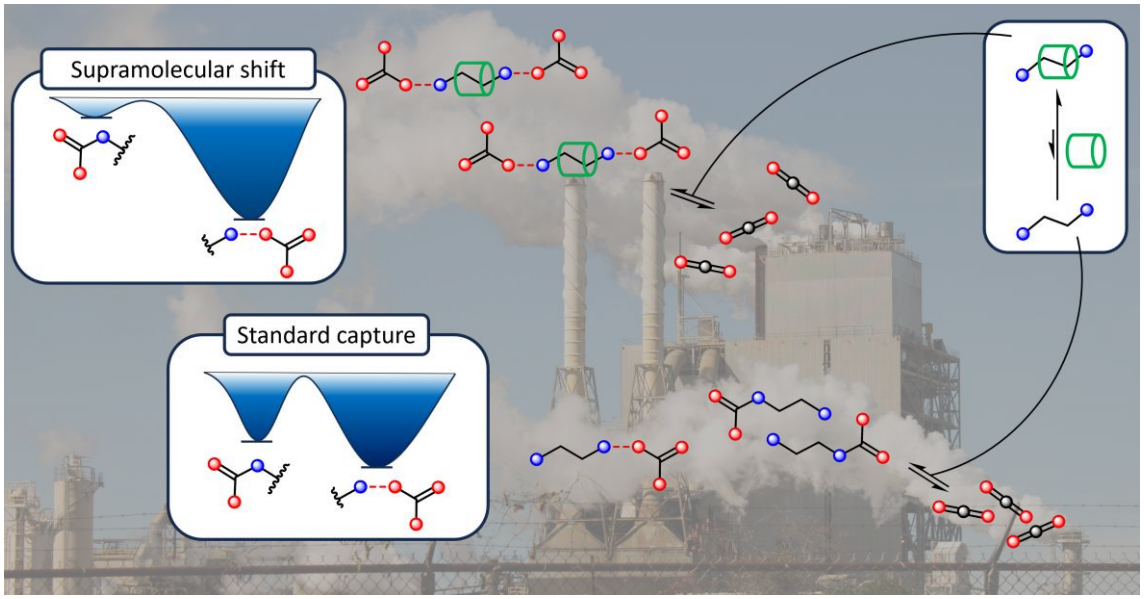
In 2015, the world unanimously decided that humanity must reduce its CO_2 emissions for the good of all.[1] To reduce these emissions, it is possible to capture the CO_2 produced by chemical plants. The only industrial CO_2 capture process is based on the reaction of simple amines with flue gas CO_2 to generate dynamic combinatorial libraries of a majority of ammonium carbamates and a minority of ammonium carbonates adducts.[2,3] Over the past decade, our laboratory has reported that a new class of cavitands - namely dyn[n]arenes - are exquisite receptors for linear poly-ammoniums to form [2]-pseudorotaxanes in water at neutral pH.[4,5] We demonstrate here that this formation of [2]-pseudorotaxanes shifts the equilibrium of CO_2 capture by polyamines in water towards the quasi-exclusive formation of carbonate adducts. In addition, this supramolecular approach to CO_2 capture exhibits enhanced capture efficiency compared to polyamines alone.[6]



References

[1] : https://unfccc.int/process-and-meetings/the-paris-agreement

[2] : F.Marocco Stuardi, F. MacPherson and J. Leclaire, *Curr. Opin. Green and Sustain. Chem.*, **2019**, *16*, 71–76

[3] : J. Septavaux, C. Tosi, P. Jame, C. Nervi, R. Gobetto and J. Leclaire, *Nat. Chem.*, **2020**, *12*, 202–212.

[4] : L. Vial, F. Perret and J. Leclaire, *Eur. J. Org. Chem.*, **2022**, e202101274

[5] : E. Jeamet, J. Septavaux, A. Héloin, M. Donnier-Maréchal, M. Dumartin, B. Ourri, P. Mandal, I. Huc, E. Bignon, E. Dumont, C. Morell, J.-P. Francoia, F. Perret, L. Vial and J. Leclaire, *Chem. Sci.*, **2019**, *10*, 277–283.

[6] T. Chetot, F. Marocco Stuardi, A. Forot, M. Ducreux, A. Baudouin, E. Chefdeville, F. Perret, L. Vial, and J. Leclaire, *ChemRxiv*, **2024,** 10.26434/chemrxiv-2024-t3pml

Bis-porphyrin metallacycles: the role of the metal fragment

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(Metallo)porphyrins play a fundamental role in major biochemical enzymatic functions and in natural processes for electron and energy transfer, light harvesting and oxygen transport; in the artificial realm the metal-mediated assembling approach has afforded a variety of spectacular 3D discrete arrays of porphyrins with new functions, ranging from molecular recognition to (photo)catalysis.[1] The vast majority of these arrays are homoleptic systems built on naked metal ions, while examples containing different type of porphyrins are quite rare. We show here how the simple choice of different 90° metal fragments (in terms of type of metal and ancillary coordination sphere) allows for the obtainment of bis-porphyrin metallacycles with dramatically distinct geometries (two examples are reported in the Figure).[2] Solution and solid state X-ray data are in perfect agreement, and exclude the presence of interconversion between conformers. Additionally, we illustrate how the *inert/labile* characteristic or the *ligand coordination* preference of the metal fragments may be successfully exploited to produce diverse heteroleptic bis-porphyrin metallacycles.[2]

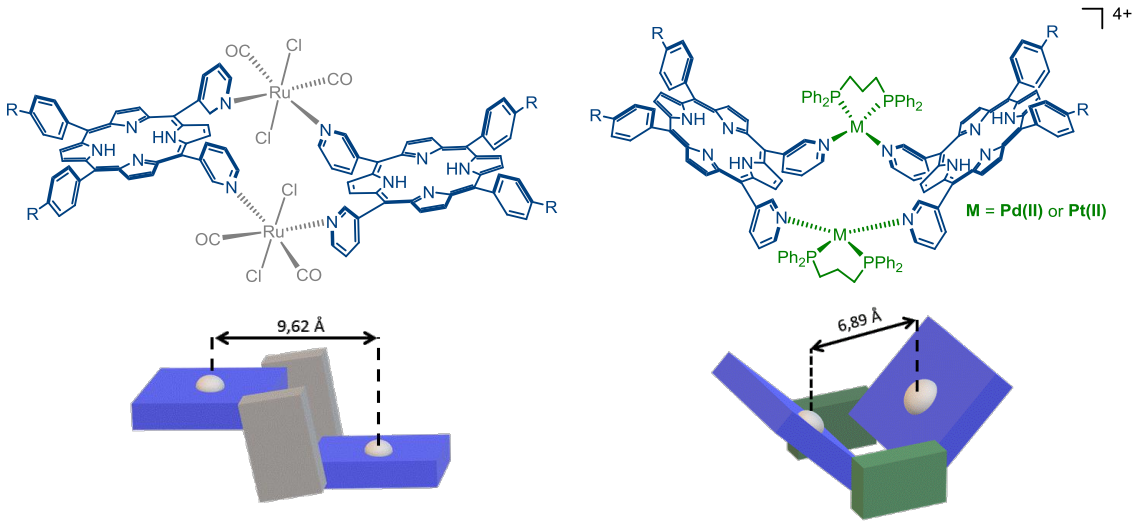

Figure. Schematic structures of two homoleptic bis-porphyrin metallacycles obtained with different 90° metal fragments in combination with the same porphyrin unit.

Acknowledgements

This work was supported by the European Union - Next Generation UE P2022ZSPWF PRIN Project.

References

[1] a) E.G. Percástegui, V. Jancik *Coord. Chem. Rev.* **2020**, *407*, 213165; b) S. Durot, J. Taesch, V. Heitz *Chem. Rev.* **2014**, *114*, 8542.

[2] a) E. Iengo, P. Cavigli, D. Milano, P. Tecilla, *Inorganic Chimca Acta* **2014**, *417*, 59; b) A. Vidal, F. Battistin, G. Balducci, E. Iengo, E. Alessio *Inorg. Chem.* **2021**, *60*, 11503; c) A. Vidal, D. Rossato, E. Iengo, G. Balducci, E. Alessio, *Chem. Eur. J.* **2023**, *29*, e202300893; d) S. Simionato, C. Mucignato, E. Zangrando, G. Balducci, G. Fogar, E. Iengo, *unpublished results*.

Self-Assembly and Mixed-Valence Species of Pentannulated BisAzaCoronene Diimide

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Carbon-based semiconductors are experiencing a growing interest in the past decades due to their unique properties. [1] A particular effort is being made for the synthesis of original conjugated systems, such as nanographenes, conjugated polymers, star shaped or curved architectures, which display interesting features for applications in organic electronics. [2] Additionally, the self-assembly processes of these structures and the resulting molecular packing have direct impacts on the properties and performances of devices. [3]
Regarding organic semiconductors, chemists have focused on p-type structures (electron-rich/hole transporter) at the expense of n-type structures (electron-poor/electron transporter). In this context, the exploration of n-type semiconductors with original architectures is necessary along with the study of their supramolecular behavior. [4]

This work focuses on the development of electron-deficient bisazacoronene diimide (BACD) nanographenes obtained in two steps: a light-mediated benzannulation[5] and an ortho C–H activation reaction on a perylene diimide (PDI) core. This synthetic route was used to build extended π-conjugated structures displaying strong self-assembly properties allowing the formation of dimeric supramolecular mixed-valence species with radical anions and neutral molecules. This strategy was further employed for the preparation of helically chiral compounds.

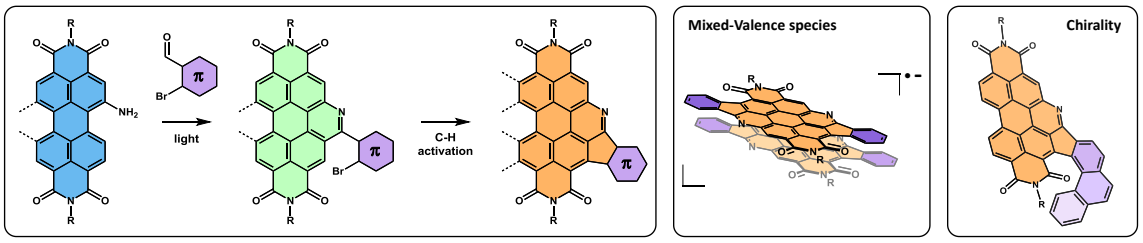

Figure 1. Synthetic strategy and structures of pentannulated bisazacoronene diimide.

Acknowledgements

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References

[1] A. Borissov, Y. K. Maurya, L. Moshniaha, W.-S. Wong, M. Żyła-Karwowska, M. Stępien, *Chem. Rev.* **2022**, *122*, 565–788
[2] X.-S. Zhang, Y.-Y, Huang, J. Zhang, W. Meng, Q. Peng, R. Kong, Z. Xiao, J. Liu, M. Huang, Y. Yi, L. Chen, Q. Fan, G. Lin, Z. Liu, G. Zhang, L. Jiang and D. Zhang, Angew. Chem. Int. Ed. 2020, 59, 3529-3533.
[3] Q. Li and Z. Li, *Acc. Chem. Res.* **2020**, *53*, 962–973
[4] Q. He, P. Kafourou, X. Hu and M. Heeney, SN Appl. Sci.,**2022**, *4*, 247

Mechanistic Insights into High Activity Cage Catalysis

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The development of biomimetic cage catalysts that use the principles of supramolecular chemistry to encapsulate substrates and promote subsequent product formation is a significant academic challenge.[1,2,3] Previous research has shown that the simple cage presented here is an effective catalyst for Michael Addition (MA), exploiting only weak noncovalent interactions to achieve high activity and efficient turnover across a wide substrate scope.[4] Here, we present an insight into the mechanism of this reaction using kinetic modelling, facilitated by the detection of identifiable catalyst intermediates. In conjunction with computational investigations and other experimental analysis, we show that the cage can achieve remarkable rate enhancements of 10^8, facilitated by both pronucleophile acidification alongside preorganization of the substrates.

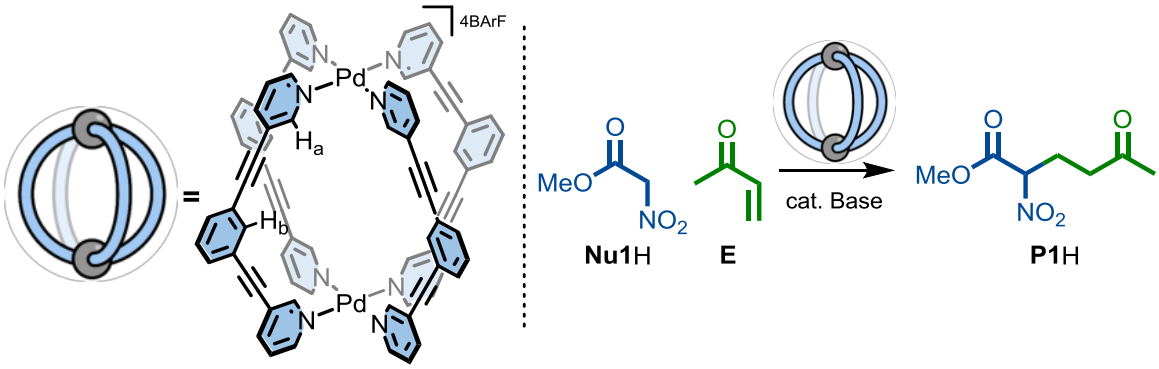

Figure 1. Cage catalysed Michael Addition.

Acknowledgements

We thank the EPSRC for funding (EP/W009803/1) for funding.

References

[1] *Chem. Soc. Rev.*, **2019**, 48, 4707-4730.

[2] *Coord. Chem. Rev,* **2021**, 430, 213656.

[3] *Chem, Sci.,* **2023**, 14, 11300-11331.

[4] *J. Am. Chem. Soc.* **2020**, 142, 41, 17743–17750.

In search of elusive species: the paramagnetic pimers of viologens

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The π-dimerization or pimerization capabilities of π-conjugated organic compounds have been the subject of increasing interests over the last decade. π-dimers and pimers are commonly accepted trivial denominations designating sandwich-like, multicentre-bonded, dimeric entities featuring sub-van der Waals intradimer separation distances. In π-dimers, the non-covalent "chemical bonding" arises from the orbital overlaps occurring between two SOMOs centred on two identical radical ions or neutral species, whereas pimers, which are in essence the mixed-valence analogues of π-dimers, involve orbital overlaps between an organic π-conjugated system with its own radical.[1] Pimers and π-dimers complexes are for instance commonly observed with NDIs,[2a] TTFs[2b] or oligothiophenes[2c] derivatives. Conversely, viologen-based derivatives only form π-dimers[3a,b] and the only cases of pimers mentioned so far in the literature concern studies carried out in the solid state[3c] or on highly constrained structures.[3d]

Our project aimed to understand this unique behavior and develop strategies to stabilize mixed-valence dimers of viologens.[4] We will describe in this presentation a novel synthetic approach towards π-extended viologens and show that such structural modification has a significant effect on their pimerization capabilities. Our presentation will first focus on the photocylization reactions used to access the targeted molecules. Then, their pimerization/π-dimerisation capabilities will be discussed on the ground of electrochemical, spectroelectrochemical and spectroscopic (ESR, Abs/Fluo) measurements supported by DFT calculation.

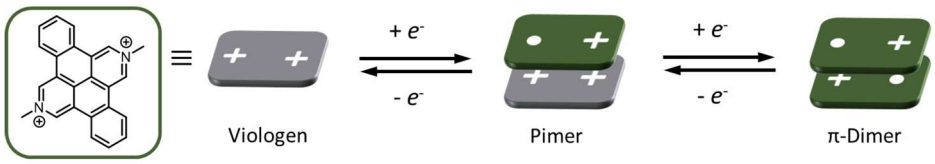

Figure 1. Schematic representation of pimerization of π-extended viologen molecules.

Acknowledgements

We thank the ANR for funding (ANR-21-CE06-0020-01).

References

[1] C. Kahlfuss, E. Saint-Aman, C. Bucher, in *Organic Redox Systems: Synthesis, Properties, and Applications*, T. Nishinaga, Wiley, New-York, **2016**.
[2] a) M. Takeuchi *et al.*, *Angew. Chem. Int. Ed.*, **2013**, *52*, 9167-9171. b) T. Sugarawa *et al.*, *Mol. Cryst. Liq. Cryst.*, **1994**, *255*, 17-26. c) J. T. López Navarrete *et al.*, *J. Am. Chem. Soc.*, **2008**, *130*, 14028-14029.
[3] a) R. G. Wilkins *et al.*, *J. Am. Chem. Soc.*, **1986**, *108*, 3380-3385. b) S. Tazuke *et al.*, *J. Electroanal. Chem.*, **1988**, *243*, 143-160. c) N. Mercier *et al.*, *Chem. Commun.*, **2013**, *49*, 10272-10274. d) J. F. Stoddart *et al.*, *Science*, **2013**, *339*, 429-433.
[4] Article in preparation.

Tuning self-assembly of hydrophilic polymers in water through an aromatic supramolecular structure directing unit (SSDU)

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The self-assembly of hydrophilic polymers in water can be driven using different strategies, the most common being the introduction of hydrophobic end-groups to the polymer chain[1]. Different supramolecular structure directing units (SSDU) have been used in the literature to drive the polymeric assembly towards anisotropic structures[2]. Previously, our team demonstrated that the incorporation of a bis-urea SSDU into a RAFT agent can trigger homopolymer self-assembly in water into nanofibers, via unidirectional hydrogen-bonding[3].

The objective of our work was to use a simple and direct pathway to obtain anisotropic nano-objects in water driven by directional supramolecular π-π interactions of an aromatic sticker incorporated at the core of polymer chains. Surprisingly, simple addition of water to the polymer powder was sufficient to dissolve all polymers synthesized. For one of the polymers, nanoribbons were obtained as results of the combination of two types of aggregates (H- and J-type). The formation of these 2D assemblies was followed over time by a combination of cryo-TEM and UV/VIS absorption spectroscopy. These techniques enabled us to identify the different types of aggregates present in the assemblies as a result of the characteristic absorption bands observed. Finally, a (reversible) transition between ribbons and fibers was observed upon temperature increase, due to a change in aggregation of the aromatic SSDU.

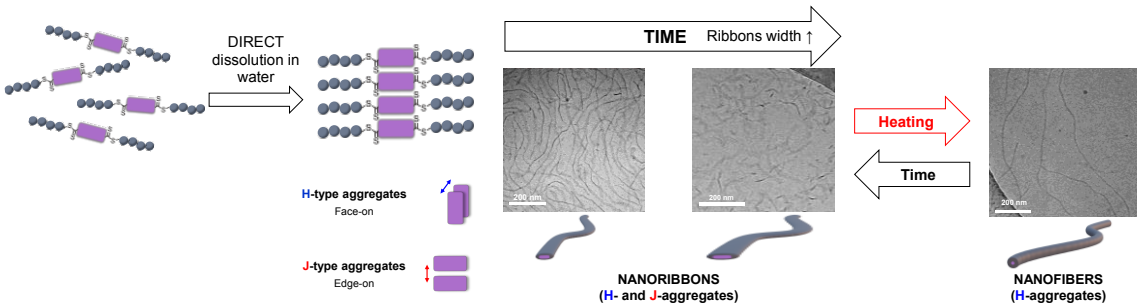

Figure 1. Overview of this work. Direct dissolution in water of hydrophilic polymers bearing an aromatic SSDU in their core. Cryo-TEM images realized at 10 g/L in water.

Acknowledgements

Jean-Michel Guigner (cryo-TEM analyses), ED 397 (Funding).

References

[1] J. Zhang, et al. *Chem. Commun.* **2015**, *51*, 11541–11555.

[2] (a) T. Klein, et al. Polym. Chem. 2020, 11, 6763 6771.; (b) P. Rajdev, et al. *ACS Macro Lett.* **2021**, *10*, 1467–1473.

[3] G. Mellot, et al. *Macromolecules* **2018**, *51*, 10214–10222.

ENDERGONIC ADAPTIVE BEHAVIOR

UPON FUELING OF DYNAMIC COVALENT NETWORKS

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In this contribution, I will demonstrate how the principles of molecular machines can be exploited for purposes different than motion. Suitably engineered chemical reaction networks can, for example, harvest energy to afford the formation of high-energy species.[1],[2] I will discuss our recent efforts[3] – in addition to new unpublished results – in driving Diels-Alder reactions away from equilibrium by exploiting the exergonic carbodiimide hydration.[4] 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]

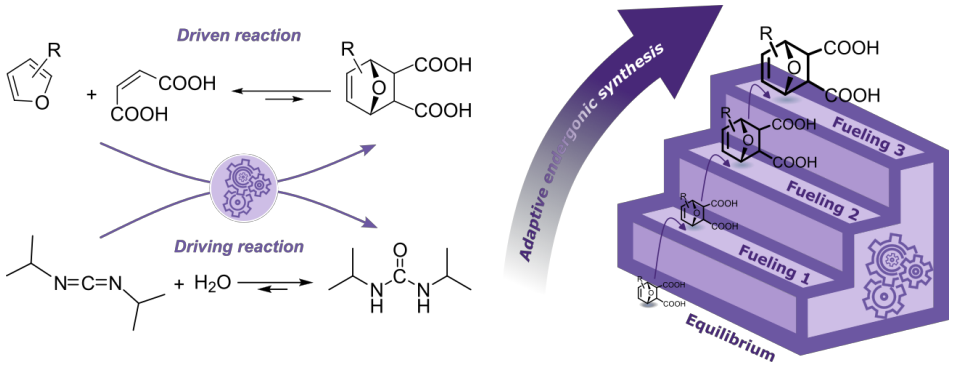

Figure 1. A dynamic covalent network shows adaptive response upon sequential chemical fueling which affords the accumulation of high-energy Diels-Alder adducts.

References

[1] S. Borsley, J. M. Gallagher, D. A. Leigh, B. M. W. Roberts, *Nat. Rev. Chem.* **2024**, *8*, 8–29.

[2] T. Sangchai, S. Al Shehimy, E. Penocchio, G. Ragazzon, *Angew. Chem. Int. Ed.* **2023**, *62*, e202309501.

[3] S. Al Shehimy, H.-D. Le, S. Di Noja, S. Amano, L. Monari, G. Ragazzon, **2024**, DOI 10.26434/chemrxiv-2024-4krgj.

[4] M. Tena-Solsona, B. Rieß, R. K. Grötsch, F. C. Löhrer, C. Wanzke, B. Käsdorf, A. R. Bausch, P. Müller-Buschbaum, O. Lieleg, J. Boekhoven, *Nat. Commun.* **2017**, *8*, 15895.

[5] A. Walther, *Adv. Mater.* **2020**, *32*, 1905111.

Structural transformations of metal-organic cages through tetrazine-alkene reactivity

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The assembly of metal-organic cages follows rules based on the coordination preferences of metal ions and the geometries of their typically rigid and planar precursor ligands. Pd_nL_{2n} metal-organic cages are amongst the most structurally diverse with subtle differences in the metal-ligand coordination vectors giving rise to drastically different assemblies, however almost all rely on the rigidity of aromatic linker groups to avoid the formation of intractable mixtures of structures. We exploit the inverse electron-demand Diels-Alder (IEDDA) reaction between tetrazine linker groups and alkene reagents to trigger structural changes induced by post-assembly modification. The structure of the 1,4-dihydropyridazine produced by IEDDA (often an afterthought in click chemistry) is crucial, with the presence of two sp^3 centers leading to a greater degree of flexibility and non-planarity in this ligand. This drastically changes the range of accessible metal-ligand coordination vectors, triggering an initial Pd_4L_8 tetrahedral cage to transform into different Pd_2L_4 lantern cages, with both the extent (thermodynamics) and rate (kinetics) of this transformation dependent on the alkene dienophile selected. With cyclopentene, the unsymmetrical 1,4-dihydropyridazine ligands undergo integrative sorting in the solid state, with both head-to-tail orientation selection and enantiomer selection, leading to a single lantern isomer from the 39 possible. This preference is rationalized through entropy, symmetry, and the extent of hydrogen bonding. Subsequent oxidation of the 1,4-dihydropyridazine to the aromatic pyridazine rigidifies the ligands and imparts planarity again. The oxidized ligands can no longer fit in the lantern structure, inducing further structural transformations into Pd_4L_8 tetrahedral cages and Pd_3L_6 double-walled triangles. The concept of controllable addition of limited additional flexibility and then its removal through well-defined reactivity we envisage being of great interest for those interested in structural transformations of any class of supramolecular architecture.

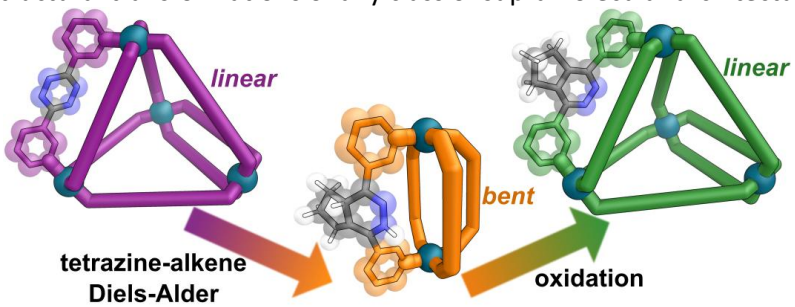

Figure 1. An initial transformation to Pd_2L_4 lanterns is driven by the enhanced flexibility in the 1,4-dihydropyridazine intermediates, with the further transformation to Pd_4L_8 tetrahedra driven by the restoration of aromaticity upon reoxidation to pyridazines.

Acknowledgements

I would like to thank Martin Black, Soumalya Bhattacharyya, and Stephen Argent for work on this project and the Royal Society, EPSRC, and Diamond Light Source for funding.

References

[1] Martin R. Black, Soumalya Bhattacharyya, Stephen P. Argent, and Ben S. Pilgrim, *Manuscript Submitted* 10.26434/chemrxiv-2024-2h48p

[2] Pilgrim, B. S., Champness, N. R. *ChemPlusChem* **2020**, *85,* 1842-1856.

Controlled Activation of Supramolecular Catalysts via Chemical and Electrochemical Redox-Switching

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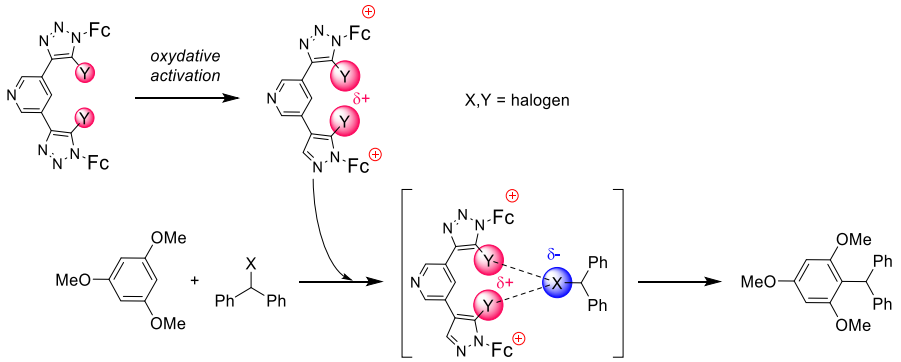
Every year, numerous research efforts are dedicated to exploring the supramolecular Lewis acid & base interactions and its subcategories such as halogen (XB) and hydrogen bonding (HB) among others. Especially in the field of organocatalysis, HB and XB interactions have been employed to catalyze and activate a broad set of organic reactions.[1] Regardless of the presumption of a general weak interactivity exhibited by supramolecular bonding, the scope of reactions keeps expanding. However, in the case of σ-hole interactions such as non-covalent halogen bonding, many aspects are still left unexplored. For instance, the concept of redox-switching of halogen bonding has been established and explored by several groups.[2] However, so far only for molecular recognition and anion detection.

In the present work, we exploit this concept for the activation of a Friedel-Crafts Benchmark reaction via chemical and electrochemical oxidation of HB and XB donors containing redox-active ferrocenyl moieties. The reversibility of the oxidation process and stability of the XB and HB donors in the oxidized state were investigated through cyclic voltammetry and UV-Vis spectroscopy. The reaction kinetics were monitored via ^{1}H NMR spectroscopy. As a result, both catalysts were found to significantly accelerate the Friedel-Crafts reaction upon chemical and also electrochemical oxidative activation. Interestingly, clear differences were observed between the two oxidation approaches. While the chemical oxidation showed higher conversion rates, electrochemical oxidation turned out to be a much milder approach involving the possibility of recovering the respective catalysts.



Scheme 1. Underlying principle for the expected supramolecular activation of the Friedel-Crafts reaction

References

[1] a) D. Bulfield, S. M. Huber, *Chem. Eur. J*. **2016**, *22*, 14434-14450; b) R. L. Sutar, S. M. Huber, *ACS Catal.* **2019**, *9*, 10, 9622-9639; c) S. Akbaba, M. Alvarez, S. Groni, B. Schöllhorn, C. Fave, *Tetrahedron Letters* **2023**, *130*, 154760.

[2] a) J. Y. C. Lim, M. J. Cunningham, J. J. Davis, P. D. Beer *Chem. Commun.*, **2015**,*51*, 14640-14643; b) S. Groni, T. Maby-Raud, C. Fave, M. Branca B. Schöllhorn, *Chem. Commun.*, **2014**, *50*, 14616-14619.

Light-responsive self-assembly of semi-conducting nanoplatelets

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The thickness of CdSe nano-platelets, which are semiconducting nanoparticles, can be manipulated with atomic precision. Consequently, any photogenerated excitons are confined within the well-defined thickness of these quantum wells, and the light they emit is monochromatic. If these nanoplatelets are dispersed in an adequate solvent, they self-assemble into supra-particular polymers, in which their nanoscale shape anisotropy extends to larger structural length scales. [1] However, achieving in-situ and reversible control over the supra-particular polymerization has remained elusive to date. Here, we use light to achieve control over the self-assembly of semiconducting nanoplatelets, in a dynamic nanoparticulate system that integrates light-responsive azobenzene switches as ligands. Upon irradiation with ultraviolet light, the ligands undergo E-to-Z photo-isomerization, leading to a modification of the dipolar moment of the particles and to the formation of micrometer-sized face-to-face stacks. This supraparticular polymerization is reversible. Light-controlled polymerization and depolymerization of quantum wells could have broad implications for the design of neuromorphic networks and other responsive optical systems. [2]

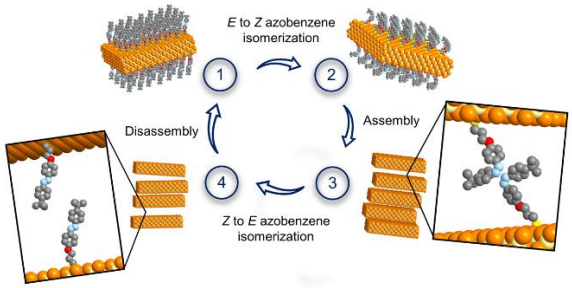

Figure. The supra-particular polymerization of CdSe nanoplatelets can be triggered by light, provided that artificial molecular photo-switches are incorporated as ligands in the system.

Acknowledgements

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References

[1] Abécassis, B.; Tessier, M. D.; Davidson, P.; Dubertret, B. Nano Lett. **2014**, 14

[2] Y. Flores, H. El Said, A. Ryabchun, R. Plamont, J. Smith, L. Curti, H. Huang, N. Katsonis, B. Fleury. **2024**. Light-responsive self-assembly of semi-conducting nanoplatelets. Manuscript submitted for publication.

Tuning the spectroscopic properties of merocyanines through hybridization of foldamers

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Foldamers constitute an interesting class of oligomers that can fold into conformationally ordered architectures.[1] Such compact conformations show structural and functional similarities with biopolymers, mimicking their highly ordered structures and functions, and explaining the intensively growing interest regarding their supramolecular chemistry. A wide variety of building blocks (*e.g.* peptides, ureas,…) have been reported to form foldameric structures through weak intramolecular interactions and have displayed remarkable properties in the context of chiral materials, molecular recognition or catalysis, for instance. While important efforts have been devoted to the study of these dynamic structures and their conformational changes, stimuli-responsive π-functional helical foldamers remain scarce in the literature.[2-3]

On the other hand, it has been shown that the formation of merocyanine dimers modulates their spectroscopics properties, be that in terms of absorption or fluorescence emission (Fig. 1a).[4-5] Herein, the helical foldamers of interest involve an oligoarylamide-based skeleton. This choice appeared relevant, given the predictability and the stability of the corresponding folded structures, as well as their straightforward synthetic access,[6] which allowed the grafting of merocyanines. In this communication, we aim at showing to which extent the single-to-double helix equilibrium can be probed thanks to the unique spectroscopic properties of merocyanines (Fig. 1a). In a reciprocal manner, the influence of merocyanine units over the hybridization equilibrium of this family of foldamers will be underlined.

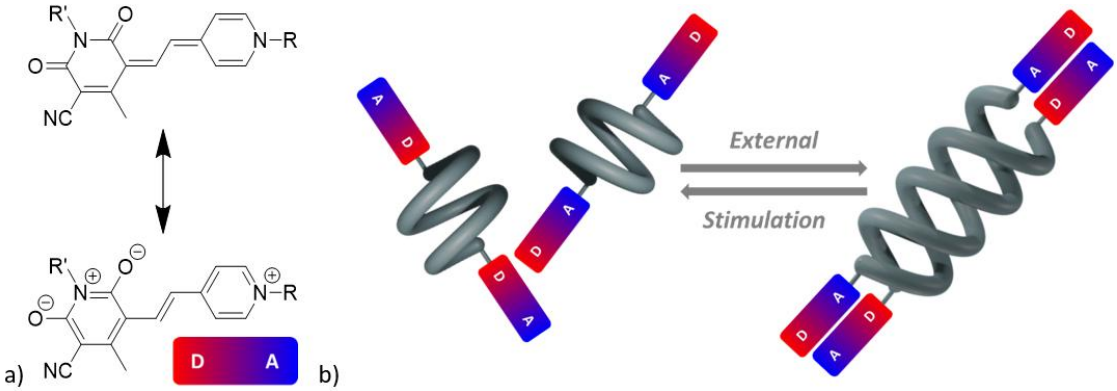

Figure 1. a) Example of synthesized merocyanine, b) Schematic representation of the hybridization process of merocyanine-containing helical foldamers.

References

[1] G. Guichard, I. Huc, *Chem. Commun.*, **2011**, *47*, 5933-5941.
[2] C. Adam, L. Faour, *Chem. Commun.*, **2019**, *55*, 8426-8429.
[3] F. Aparicio, L. Faour, *Chem. Commun.*, **2017**, *53*, 12028-12031.
[4] F. Würthner, S. Yao, *J. Am. Chem. Soc.*, **2002**, *124*, 9431-9447.
[5] X. Hu, A. Schulz, *Chem. Sci.*, **2021**, *12*, 8342-8552.
[6] L. Faour, C. Adam, *Chem. Commun.*, **2019**, *55*, 5743-5746.

Toward new cryptophane analogs: synthesis and encapsulation properties of an unprecedented water-soluble azacryptophane

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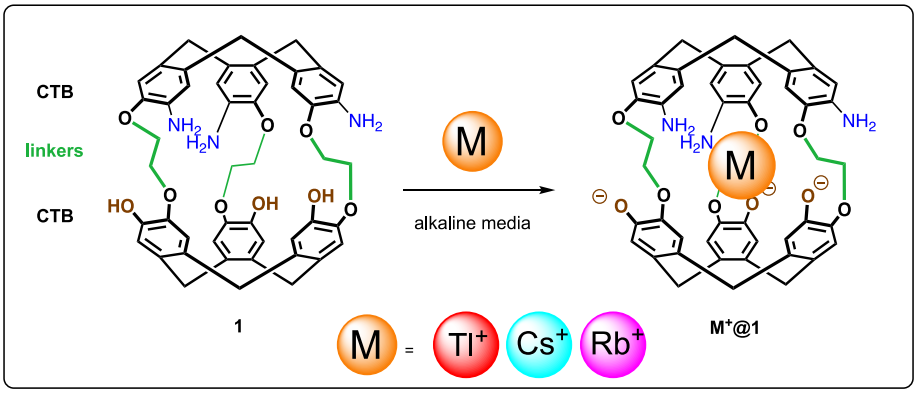
Cryptophanes are hollow molecules, composed of two cyclotribenzylene (CTB) units connected together by linkers whose length and nature can be varied.[1] Since the first synthesis of cryptophane-A in 1981 by A. Collet *et al*., considerable progress has been made in designing cryptophanes that exhibit selective encapsulation properties toward organic and inorganic guests.[2] Despite some progress in this field, the synthesis of cryptophanes, and in particular the introduction of heteroatoms into their structure, remains difficult.

Herein, we report the synthesis of a novel water-soluble cryptophane **1** decorated with three aromatic amine groups and three phenol groups. Then, ability of this compound to bind cationic species such as Cs^+ and Tl^+ in aqueous solution has been assessed by ^{133}Cs NMR and ^{205}Tl NMR. A signal characteristic of the two Cs^+**@1** and Tl^+**@1** complexes has been observed at low frequencies with respect to the free cation dissolved in the bulk. Then, Isothermal Calorimetric Titration experiments enabled us to obtain a complete description of the binding process and to determine the association constants and the thermodynamic parameters of complexation (ΔH^0, ΔS^0 and ΔG^0). Taken together, our results[3] show that *aza*-cryptophane **1** binds very strongly cesium (I) and thallium (I) in aqueous solution under basic conditions. A comparison with other water-soluble cryptophanes[4-6] showing good affinity for cesium (I) and thallium (I) will be discussed.



Scheme. Guest encapsulation by the azacryptophane in aqueous media.

Acknowledgements: ANR JCJC EnaRecAnion (ANR-21-CE07-0006-01)

References

[1] A. Collet, *Tetrahedron,* **1987**, *43,* 5725–5759 ; [2] T. Brotin and J.-P. Dutasta, *Chem. Rev*. **2009**, *109*, 88–130; [3] R. Benchouaia *et al.* , *J. Org. Chem*. **2024, accepted ;** [4] L.-L. Chapellet, J.-P. Dognon, M. Jean, N. Vanthuyne, P. Berthault, T. Buffeteau, T. Brotin, *ChemistrySelect* **2017**, *2*, 5292 – 5300 ; [5] T. Brotin, P. Berthault, D. Pitrat, J.-C. Mulatier, *J. Org. Chem*. **2020**, *85*, 9622-9630 ; [6] a) M. Doll, P. Berthault, E. Léonce, C. Boutin, T. Buffeteau, N. Daugey, N. Vanthune, M. Jean, T. Brotin, N. De Rycke, *J. Org.Chem*. **2021,** *86*, 7648-7658 ; b) M. Doll, P. Berthault, E. Léonce, C. Boutin, E. Jeanneau, T. Brotin, N. De Rycke, *J. Org. Chem.* **2022**, *87*, 2912–2920.

Self-organized mesomorph Donor-Acceptor Hybrid material: from molecular design to device performances

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Mesomorph materials with semiconducting properties are gaining increasin interest in the molecular photonic field. [1] Self-organization of electron donor (D) and acceptor (A) moieties into highly ordered molecular architecture are promising due to specific charge percolation pathways formed by nano-segregated D and A subdomains. Polyoxometalates (POMs) are emerging as alternative molecular electron acceptors, offering remarkable electron reservoir properties[2] for energy conversion/storage and information technology. We're developing hybrid systems that combine POM oxoclusters with π-conjugated mesogenic donors (diaryl benzothiadiazole and pyrene derivatives) decorated with aliphatic chains. This unique molecular architecture results in nanosegregation of both units into layered mesomorphic structures, characterized by distinct regularly alternated D and A subdomains (see Figure 1). [3]
During this presentation, we'll outline the synthetic approach for the synthesis of these hybrid systems, their structural charcterization in solid state, discuss preliminary photophysical investigations, and explore their incorporation into optoelectronic devices.

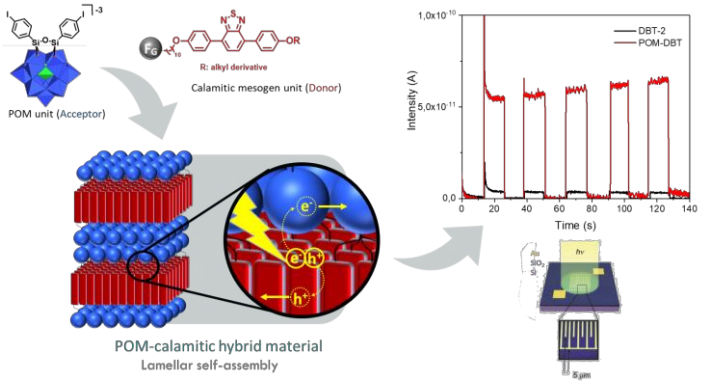

Figure 1. POM-based mesomorph hybrids and their multilamellar nanostructured self-assembly.

Acknowledgements

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References

[1] a) E.-K. Fleischmann, R. Zentel, *Angew. Chem. Int. Ed.* 2013, 52, 8810–8827; b) A. Name, B. Name, *Angew. Chem. Int. Ed.*, **2019**, *16*, 190-195; A. Name, B. Name, *J. Am. Chem. Soc.*, **2020**, *6*, 29-31.
[2] a) G. Toupalas, J. Karlsson, F. A. Black, A. Masip-Sanchez, X. Lopez, Y. Ben M’Barek, S. Blanchard, A. Proust, S. Alves, P. Chabera, I. P. Clark, T. Pullerits, J. M. Poblet, E. A. Gibson, G. Izzet, *Angew. Chem.-Int. Ed.* 2021, 60, 6518–6525; b) S. Amthor, S. Knoll, M. Heiland, L. Zedler, C. Li, D. Nauroozi, W. Tobaschus, A. K. Mengele, M. Anjass, U. S. Schubert, B. Dietzek-Ivansic, S. Rau, C. Streb, *Nat. Chem.* 2022, 14, 321
[3] X. Zhu, C. Hessin, A. Salame, L. Sosa-Vargas, D. Kreher, C. Adachi, A. Proust, P. Mialane, J. Marrot, A. Bouchet, M. Sliwa, S. Mery, B. Heinrich, F. Mathevet, G. Izzet, *Angew. Chem.-Int. Ed.* 2021, 60, 8419–8424

POSTERS

ELECTRON DEFICIENT CAGES HARNESSING ANION-Π INTERACTIONS

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Harnessing non-covalent interactions is one of the focus points of supramolecular chemistry. One of the key aspects of this field is molecular recognition, which refers to the selective binding of a target molecule by a host molecule.

Among the numerous existing interactions, our focus is on anion-π interactions. They can be defined as the interaction between an anion and an electron deficient π-system, and were first described in 2002.[1] Since then, they have garnered growing interest owing to both the crucial role of anions in many biological and chemical processes, as well as the involvement of π-aromatic systems in ions transport and molecular recognition.[2] However, the instability of highly electron-deficient surfaces inherently restricts the strength of anion-π interactions attainable with individual surfaces.[3]

To tackle this issue, our strategy is to design and synthesize supramolecular cages combining several electron deficient surfaces, to increase their π-acidity through synergy.

Among the different supramolecular hosts already described, cryptophanes have an interesting geometry for our purpose. This class of cages is based on two C_3 cyclotriveratrylene units connected by linkers. Cryptophanes are already known for their selectivity in the molecular recognition of small molecules and ions and exhibit interesting chiral properties, which are relevant for our project.[4]

Hence, we will present the synthesis and characterization of cryptophanes possessing three electron deficient linkers. Additionally, the chirality and molecular recognition properties of those cages will be discussed, together with DFT calculations.

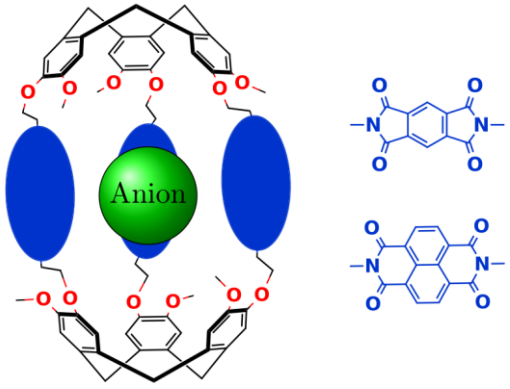

Figure 1. Schematic representation of an encapsulated anion within a cryptophane with electron deficient arms such as benzenediimide and naphthalenediimide.

References

[1] D. Quinonero, C. Garau, C. Rotger, A. Frontera, P. Ballester, A. Costa, P.M. Dey, *Angew. Chem. Int. Ed.*, **2002**, *41*, 3389-3392.

[2] B. Schottel, H. Chifotides, K. Dunbar, *Chem. Soc. Rev.*, **2008**, *37*, 68-83.

[3] Y. Zhao, Y. Cotelle, L. Liu, J. López-Andarias, A.B. Bornhof, M. Akamatsu, N. Sakai, S. Matile, *Acc. Chem. Res.*, **2018**, *51*, 2255-2263.

[4] T. Brotin, J.-P. Dutasta, *Chem. Rev.*, **2009**, *109*, 88–130.

Fuel-Driven Enzymatic Reaction Networks to Program Autonomous Thiol/Disulfide Redox Systems

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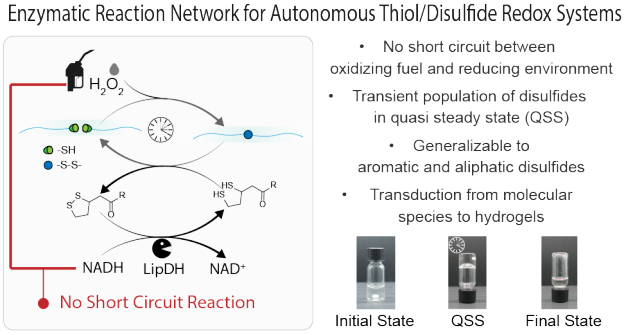
The rational design of chemical reaction networks (CRN) mimicking biological systems is of growing interest in the field of system chemistry. Fuel-driven CRNs with a transient population of a high energy state are one class of particularly relevant CRNs to make autonomous systems with programmable lifetimes.[1] Along this direction, redox-based CRNs hold great promise for their versatility but approaches toward truly autonomous redox-based CRNs remain scarce. Here, we target fuel-driven dissipative formation of disulfide bonds using competing oxidative activation and reductive deactivation processes, which presents a very versatile avenue for autonomous materials design. However, this is challenging to realize because of the direct annihilation of oxidizing fuel and deactivating reducing agent. We overcome this challenge by introducing a redox-based enzymatic reaction network (ERN), enabling dissipative disulfide formation for molecularly dissolved thiols in a fully autonomous manner. Moreover, the ERN allows for programming hydrogel lifetimes by utilizing thiol-terminated star polymers (sPEG-SH). The ERN can be customized to operate with aliphatic and aromatic thiols and should thus be broadly applicable to functional thiols. We further demonstrate how the ERN can be coupled to an upstream enzymatic module, which allowed us to photoinitiate the ERN. We envisage this photoinitiation step will offer enhanced spatiotemporal control for biomedical and soft robotics applications when coupled to materials systems.



Scheme 1. Fuel-driven redox-ERN for molecularly dissolved dissipative thiol/disulfide systems.

Acknowledgements

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References

[1] Merindol, R.; Walther, A. Materials learning from life: concepts for active, adaptive and autonomous molecular systems. *Chem. Soc. Rev.* **2017**, *46*, 5588-5619.

Investigating Self-Constructing Macrocycle Formation via Pulsed-Injection Mass Spectrometry Analysis

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Self-assembly has proven to be a valuable approach for creating large molecular architectures without major synthetic effort. Previous studies have unveiled a family of discrete cyclic macromolecules with stable folded conformations of low symmetry, despite originating from single building blocks. One particular building block, 3,5-bismercaptobenzoic acid, can be decorated with a variety of side-chains (*e.g.* amino acids, nucleotides) exhibiting strong potential for non-covalent interactions as the main driving force for the emergence of remarkably complex macrocyclic foldamers of defined sizes and shapes.[1,2]

To gain deeper insights into the early stages along with the progression of the dynamic combinatorial libraries, we utilized a specially designed experimental setup.[3] A one-pot reaction is performed by combining a dithiol monomer, an oxidizer and a reducing agent in a syringe. Aliquots of the reaction mixture are subsequently injected into an Orbitrap mass spectrometer at specific time intervals. This allows for strikingly precise monitoring of the chemical landscape, including the accumulation and consumption of discrete macrocycles as well as short-chain linear species.

This study demonstrates that macrocyclization via disulfide exchange proceeds more rapidly compared to chain growth and ring closure through oxidation. Further, it shows that each system initially consists of a significant number of macrocycles varying in size, before ultimately converging towards distinct thermodynamic products.

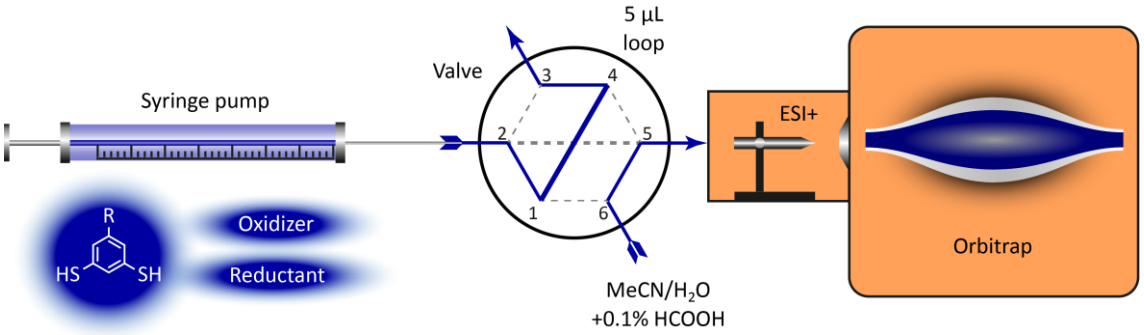

Figure 1. Experimental setup of a one-pot reaction including a 3,5-bismercapto benzoate, oxidizer (H_2O_2) and reductant (TCEP) with pulsed injection setup into an Orbitrap mass spectrometer.

References

[1] C. G. Pappas, P. K. Mandal, B. Liu, B. Kauffmann, X. Miao, D. Komáromy, W. Hoffmann, C. Manz, R. Chang, K. Liu, K. Pagel, I. Huc, S. Otto, *Nat. Chem.* **2020**, *12*, 1180–1186.

[2] B. Liu, C. G. Pappas, E. Zangrando, N. Demitri, P. J. Chmielewski, S. Otto, *J. Am. Chem. Soc.* **2019**, *141*, 1685–1689.

[3] O. Trapp, S. Lamour, F. Maier, A. F. Siegle, K. Zawatzky, B. F. Straub, *Chem. Eur. J.* **2020**, *26*, 15871–15880.

Metal-Peptidic Cages –Synthetic Modularity of Oligoprolines for Tuning Self-Assembly

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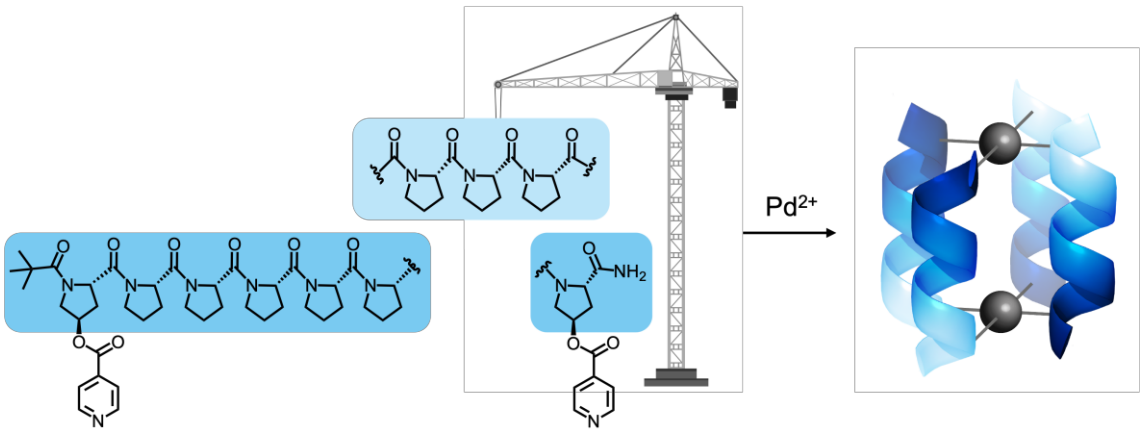
The self-assembly of metal-organic cages enables the rapid creation of three-dimensional, nanoscale architectures reminiscent of proteins.[1] We recently reported the synthesis of a new class of cages - metal-peptidic cages - which utilise water-soluble, chiral and helical oligoproline strands of varying sizes to rapidly form Pd_2L_4 cages from 1 to 4 nm in length, and see emergent isomer control in the generation of a single cage structural isomer.[2,3]

Herein, we disclose our latest results, exploring how the the modularity of the oligoproline helix can be exploited in the design of metal-peptide cage systems. We show how chirality (both point and helical), length, register and pyridine substitution affects the outcome of self-assembly reactions and utilise these design principles to synthesise novel Pd_3L_4 metal-peptide cages.



References

[1] C. T. McTernan, J. A. Davies and J. R. Nitschke, *Chem. Rev.*, 2022, **122**, 10393–10437.

[2] P. Wilhelm, B. Lewandowski, N. Trapp and H. Wennemers, *J. Am. Chem. Soc.*, 2014, **136**, 15829–15832.

[3] B. E. Barber, E. M. G. Jamieson and L. E. M. White and C. T. McTernan, doi.org/10.26434/chemrxiv-2023-89mz0.

Stepwise functionalization of a pillar[5]arene-containing [2]Rotaxane with pentafluorophenyl ester stoppers

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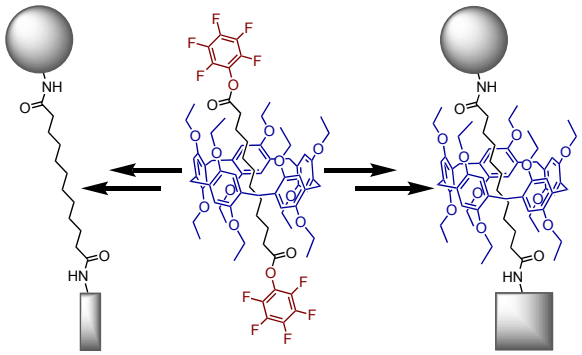
The direct preparation of rotaxanes from pillar[5]arene-based inclusion complexes is highly dependent on the nature of the reagents even when similar reactions are used for their synthesis and yields are often quite moderate.[1] To solve this problem, our group has developed the preparation of pillar[5]arene-containing [2]rotaxane building blocks allowing their efficient post-modification by a stopper exchange reaction.[2] Very recently, we have also shown that the reactivity of symmetrical pillar[5]arene-based building block is affected by the presence of the macrocyclic subunit.[3] Indeed, the first stopper exchange reaction is fast while the second always significantly slower thus allowing selective mono-functionalization of the rotaxane building block in high yields. Introduction of a second stopper is then possible to generate dissymmetrical rotaxanes or axles in high yields. Moreover, we have also shown that the pillar[5]arene moiety can act as a protecting group allowing the efficient synthesis of unsymmetrically substituted compounds particularly difficult to prepare from a bifunctional starting material lacking the macrocyclic moiety.



Acknowledgements

Financial support from the ANR (projects FastGiant ANR-17-CE07-0012-01 and Pillar ANR-19-CE06-0032) and the *Fondation Jean-Marie Lehn* is gratefully acknowledged.

References

[1] R. Milev, A. Lopez-Pacheco, I. Nierengarten, T. M. N. Trinh, M. Holler, R. Deschenaux, J.-F. Nierengarten, *Eur. J. Org. Chem*. **2015**, 479-485.

[2] a) I. Nierengarten, E. Meichsner, M. Holler, P. M. Pieper, R. Deschenaux, B. Delavaux-Nicot, J.-F. Nierengarten, *Chem. Eur. J.* **2018**, *24*, 169-177; b) I. Nierengarten, J.-F. Nierengarten, *ChemistryOpen* **2020**, *9*, 393-400. c) M. Rémy, I. Nierengarten, B. Park, M. Holler, U. Hahn, J.-F. Nierengarten, *Chem. Eur. J.* **2021**, *27*, 8492-8499.

[3] N. Becharguia, E. Wasielewski, R. Abidi, I. Nierengarten, J.-F. Nierengarten, *Chem. Eur. J.* **2024**, *30*, e202303501.

Controlling self-sorting in dynamic assembly: stimuli-responsive multi-cage systems

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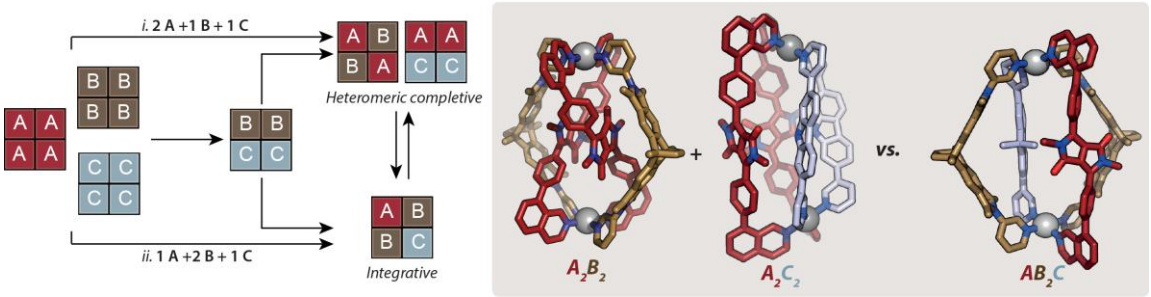
Heteroleptic coordination cages are self-assembled nano-objects composed of multiple organic ligands associating in a discrete assembly through integrative self-sorting. We have recently pushed integrative self-sorting of Pd(II) cages to its limit by bringing four distinct building blocks in a unique 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.



References

(1) Kai Wu, **Elie Benchimol**, Ananya Baksi and Guido H. Clever. *"Non-statistical Assembly of Multicomponent [Pd$_2$ABCD] Cages"*, *Nat. Chem.*, 2024
https://doi.org/10.1038/s41557-023-01415-7

(2) **Elie Benchimol**, Irene Regeni, Guido H. Clever. "*Heteromeric completive self-sorting in coordination cage systems"*, *J. Am. Chem. Soc.*, accepted
https://doi.org/10.1021/jacs.3c14168

MULTIVALENT GLYCOSYL-CYCLODEXTRINS AS SELECTIVE INHIBITORS OF α-GLUCOSIDASES.

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In carbohydrate/protein interactions, the supramolecular multivalent effect is now well known. As recently studied and reviewed by Garcia-Fernandez and coll., multivalent effect can both improve inhibition of glycosidases and interactions with lectins.[1] Siriwardena et al.[2] reported the first examples of nanodiamond particles bearing unmodified monosaccharides as efficient inhibitors of glucosidases at low micromolar IC_{50} (1.3 µM<IC_{50}<22 µM). It was demonstrated that even with non-matching natural substrate/enzyme couples, the inhibition probably occurred by a mixed inhibition mode. Drawing on this result, we described the first strong inhibitors of α-glucosidase based on cyclodextrins (CDs) bearing unmodified saccharides[3] (32<IC_{50}<132 µM). These triazole-linked conjugates are strong non-competitive inhibitors, especially the per-6-α-D-mannopyranosyl-γ–cyclodextrin and the per-6-α-D-glucopyranosyl-β–cyclodextrin [3]. We synthesized several new CD platforms bearing various monosaccharides (Mannose/Glucosamine/Glucuronic acid), di or trisaccharides, and evaluated their inhibitory effect on α-glucosidase and α-amylase. The multivalent effect was clearly demonstrated in the selective interaction of α–glucosidase [4].

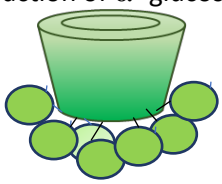

Figure 1. Multivalent glycosyl-cyclodextrins.

Acknowledgements

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References

[1] M. González-Cuesta, C. Ortiz Mellet, J. M. García Fernández, *Chem. Commun.* **2020**, *56*, 5207–5222; M. González-Cuesta, D. Goyard, E. Nanba, K. Higaki, J. M. García Fernández, O. Renaudet, C. Ortiz Mellet, *Chem. Commun.* **2019**, *55*, 12845–12848.

[2]A. Siriwardena, M. Khanal, A. Barras, O. Bande, T. Mena-Barragán, C. O. Mellet, J. M. Garcia Fernández, R. Boukherroub, S. Szunerits, *RSC Adv.* **2015**, *5*, 100568–100578.

[3] U. Alali, A. Vallin, A. Bil, T. Khanchouche, D. Mathiron, C. Przybylski, R. Beaulieu, J. Kovensky, M. Benazza, V. Bonnet, *Org. Biomol. Chem.* **2019**, *17*, 7228–7237.

[4] T. Khanchouch, A. Vallin, U. Alali, M. Benazza, R. Abidi, V. Bonnet, *Helv. Chim. Acta,* **2024**, in press.

COOPERATIVE SELF-ASSEMBLIES BASED ON FUNCTIONALIZED CYCLODEXTRINS AS ANTI-ADHESIVE AGENTS AGAINST SARS-CoV-2

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Our team previously showed that it was possible to form fibers from small oligomers of DNA and cyclodextrins functionalized with an adamantane and ammonium. Hydrophobic interactions initiate small supramolecular polymers, followed by multivalent electrostatic interactions that drive the formation of larger co-assemblies.[1] In 2020, during a CRYO-EM experiment, we unexpectedly observed a SARS-CoV-2 particle near self-assembled cyclodextrins fibers. We thus wondered if we could bring specific interactions between them and trigger this assembly on purpose. This surprising observation encouraged us to explore the ability of cyclodextrin assemblies to cooperatively interact with viruses such as SARS-CoV-2 and use them as anti-adhesive agents to potentially inhibit cell infection. We therefore changed non-specific electrostatic interactions into specific ones, using glycan-based ligands. We will show here how adamantane and glycan-functionalized cyclodextrins demonstrate promising inhibitory activity against SARS-CoV-2 through cooperative interactions.

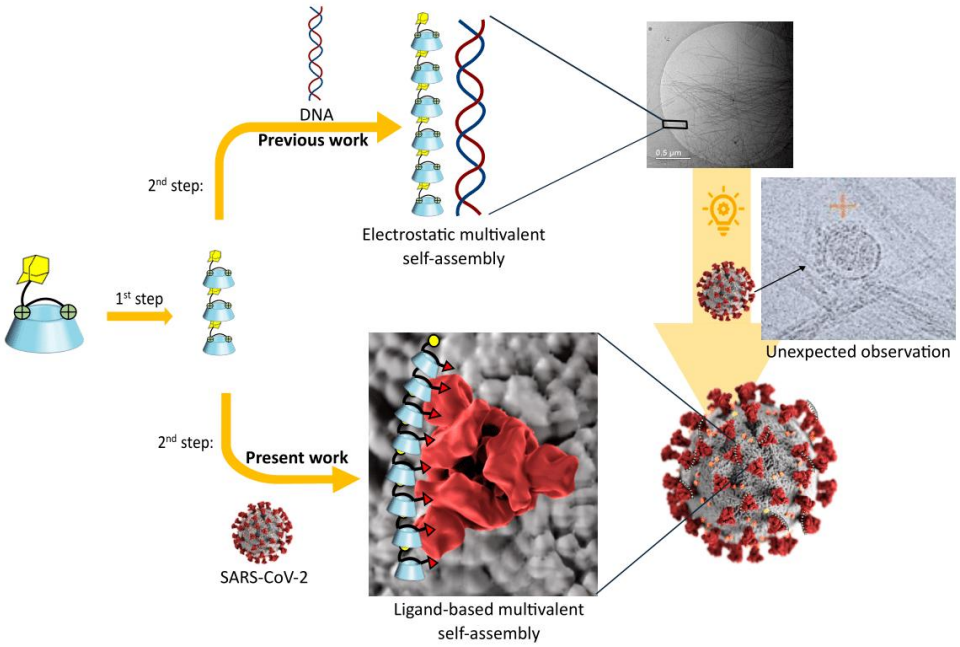

Figure 1. From CDs interactions with DNA to multivalent anti-adhesive agents against SARS-CoV-2

References

[1] Evenou, E; Rossignol; Pembouong, G; Gothland, A; Colesnic, D; Barbeyron, R; Rudiuk, S; Marcelin, A.G; Ménand, M; Baigl, D; Calvez, V; Bouteiller, L; Sollogoub, M; *Angew. Chem. Int. Ed.* **2018**, *57*, 7753-7758.

Synthesis and Applications of Unusual Self-assembled Coordination Architectures

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Biological systems have complex structures and pathways to execute intricate chemical reactions. In attempts to replicate it to study their pathways, chemists have endeavored to craft discreate molecular structures featuring precise nanocavities. Over the last twenty years, there has been a proliferation of those structures achieved through hydrogen bonding and Dynamic covalent chemistry (DCvC). Concurrently, the concept of Supramolecular coordination structures (SCCs) emerged as a powerful tool for the synthesis of visually appealing 2D and 3D discrete architectures.[1]

In literature, pyridyl moieties with generally rigid structures have been extensively studied. However, my primary objective was to investigate the use of flexible building blocks for creating discrete structures through metal-ligand coordination. This approach is anticipated to yield unique and nontrivial structures. We explored flexible tetratopic pyridyl donors through introducing flexibility via an alkyl spacer. A simple such donor led to the formation of an unconventional molecular boat structure. This structure was then utilized for the selective separation of physiochemically similar isomers, specifically phenanthrene from a mixture of anthracene. [2] Subsequently, by elongating the ligand, we aimed to unveil the complexity it could generate, resulting in the creation of an intertwined, unusual A-type cube. The rigid analogue of that building block showed regular but rare triangular orthobicupola. [3]

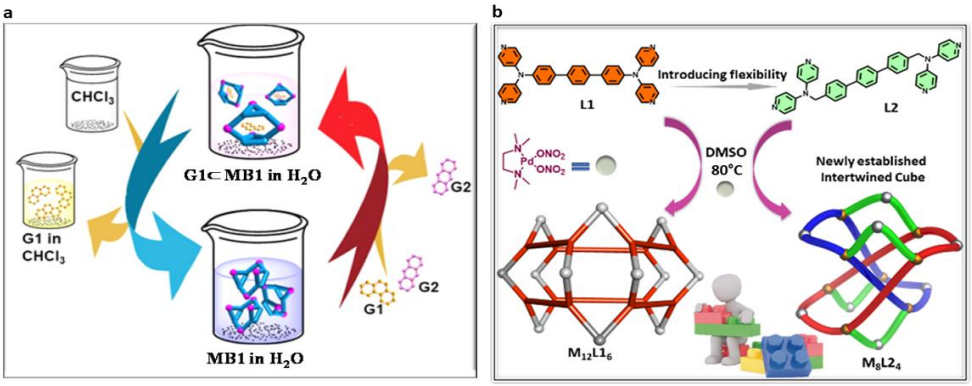

Figure. Molecular boat (MB1) used for selective separation of Phenanthrene from equimolar mixture of Phenanthrene and anthracene, (b)Synthesis of Unique water soluble A type Intertwined cube.

References

[1] Saha, R.; Mondal, B.; Mukherjee, P. S. *Chem. Rev.* **2022**, *122*, 12244.

[2] Sainaba, A. B.; Venkateswarulu, M.; Bhandari, P.; Arachchige, K. S. A.; Clegg, J. K.; Mukherjee, P. S. *J. Am. Chem. Soc.* **2022**, *144*, 7504.

[3] Sainaba, A. B.; Venkateswarulu, M.; Bhandari, P.; Clegg, J. K.; Mukherjee, P. S. *Angew. Chem., Int. Ed.*, **2024**, e202315572.

WEAVING COORDINATION POLYMERS INTO DYNAMIC SUPRAMOLECULAR GELS

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Intelligent supramolecular nanomaterials capable of self-organization are of the utmost interest in the molecular materials community, especially if they can be further endowed with switchable elements to exert an external control.[1,2] Here we report supramolecular coordination polymers formed between metal ions and polyoxometalate hybrids bearing two terpyridine ligands in a linear geometry (Figure 1).[3–5] Upon complexation, the polymeric chains self-assemble in fibers, on account of the electrostatic forces between the negatively charged polyoxometalate cores and the positively charged metal nodes. Eventually, the fibers physically cross-link and confer to the material a gel structure. Through SAXS and TEM experiments, supported by molecular dynamics, we were able to infer the molecular-level arrangement of the polymers in the fibers. Furthermore, thanks to their intrinsically dynamic nature, these gels exhibit mechano- and thermo-responsive properties, such as birefringence or spin-crossover, and can self-heal after breaking to restore the hierarchical organization from the molecular to the macroscopic level.

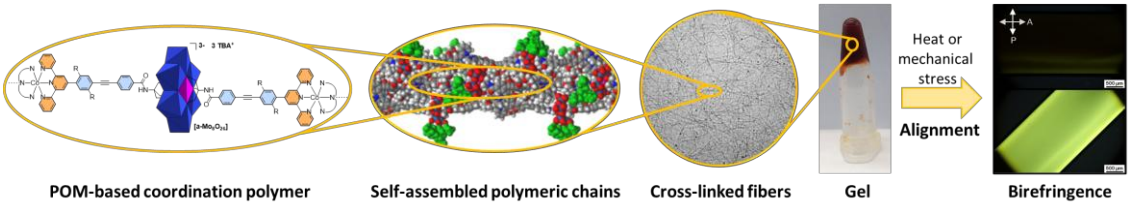

Figure 1. Self-organization from the molecular to the material level.

Acknowledgements

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References

[1] M.-O. M. Piepenbrock, G. O. Lloyd, N. Clarke, J. W. Steed, *Chem. Rev.* **2010**, *110*, 1960–2004.
[2] C. D. Jones, J. W. Steed, *Chem. Soc. Rev.* **2016**, *45*, 6546–6596.
[3] M. S. Centellas, M. Piot, R. Salles, A. Proust, L. Tortech, D. Brouri, S. Hupin, B. Abécassis, D. Landy, C. Bo, G. Izzet, *Chem. Sci.* **2020**, *11*, 11072–11080.
[4] M. Piot, B. Abécassis, D. Brouri, C. Troufflard, A. Proust, G. Izzet, *Proc. Natl. Acad. Sci. U.S.A.* **2018**, *115*, 8895–8900.
[5] G. Izzet, B. Abécassis, D. Brouri, M. Piot, B. Matt, S. A. Serapian, C. Bo, A. Proust, *J. Am. Chem. Soc.* **2016**, *138*, 5093–5099.

Dynamic Covalent Synthesis of Size-controlled Linear and Macrocyclic Graphene Nanoribbons

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Extensive research has been conducted on graphene, leading to its widespread use as a material renowned for its captivating electronic, optical, and mechanical characteristics.[1] Graphene Nanoribbons (GNRs) or nanographenes are the graphene strips of well-defined size, structure and composition.[2] There is significant activity in the field of n-type graphene nanoribbons (GNRs) and nitrogen-doped acenes. However, rylene diimide ribbons appeared as a promising candidate for the elaboration of electron deficient (n-type) materials.[3] The synthesis of large size rylene imides-based GNRs often involves multi-step processes and use of toxic reagents and precious metals, which remain critical issue in the exploration of GNRs.
With this objective in mind, our group have developed a two steps dynamic covalent synthetic approach subsequently "locked" by visible light which is very efficient for the synthesis of electron deficient materials for organic electronics (Fig. A).[4] Herein, we will be presenting the synthesis of BisAzaCoroneneDiimide (BACD)-based linear as well as macrocyclic GNRs by utilizing this locked or "frozen" dynamic covalent method (Fig. B). The shape of the GNRs can be easily switched by incorporating substituents at appropriate positions of PDIs and by varying the corresponding aldehyde linkers. The size of the GNRs can be tune by controlling stoichiometry of PDIs and aldehydes. Our targeted GNRs are expected to appear as a promising organic semiconductors.

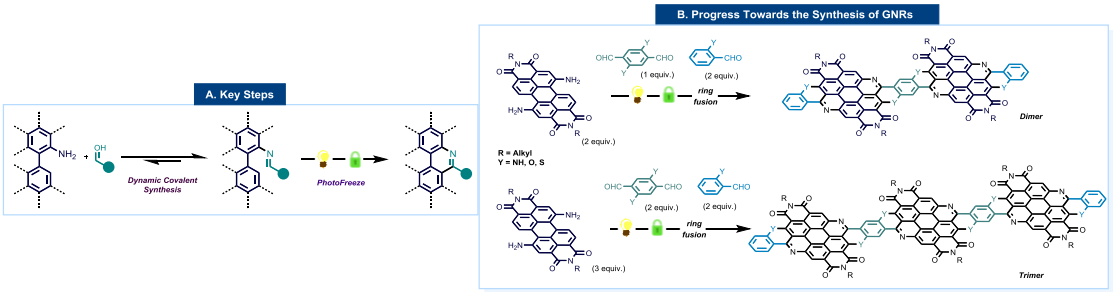

Figure. (A) Dynamic covalent synthetic approach for the synthesizing of (B) GNRs.

Acknowledgements

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References

[1] A. R. Urade, I. Lahiri, K. S. Suresh, *JOM*, **2023**, *75*, 614–630.
[2] Y. Gu, Z. Qiu, K. Müllen, *J. Am. Chem. Soc.* **2022**, *144*, 11499–11524.
[3] F. Saal, F. Zhang, M. Holzapfel, M. Stolte, E. Michail, M. Moos, A. Schmiedel, A.-M. Krause, C. Lambert, F. Würthner, P. Ravat, *J. Am. Chem. Soc.* **2020**, *142*, 21298–21303.
[4] (a) A. Gapin, A. H. G. David, M. Allain, D. Masson, O. Alévêque, T. Ave, L. Le Bras, P. Hudhomme, A. Goujon, *Chem. Eur. J.* **2023**, *29*, e202300652 ; (b) A. H. G. David, D. Shymon, H. Melville, L.-A. Accou, A. Gapin, M. Allain, O. Alévêque, M. Force, A. Grosjean, P. Hudhomme, and L. L. Bras, A. Goujon, *J. Mater. Chem. C*, **2023**, *11*, 14631-14640.

P-12

Light Driven Dynamic covalent Synthesis of deficient Semiconducting Polymer

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Over the past years, in the field of organic electronics, conjugated materials have captured significant attention due to their potential for flexible, lightweight, and cost-effective electronic devices.[1] Current research is concentrated on synthesizing new conjugated materials to enhance optoelectronic properties, especially for diversifying n-type organic semiconductors. This expansion of possibilities represents a major and crucial challenge in the field of organic electronics. The synthesis of conjugated polymers typically involves precious metal-catalyzed cross-coupling reactions between halogenated components and toxic stannylated reagents or sensitive borylated derivatives, often with additional additives.[2] However, these synthetic approaches face various limitations, including batch-to-batch variation and side reactions.
In this context, we are investigating a novel synthetic methodologies based on dynamic covalent chemistry to thermodynamically control the preparation of polyimines.[3,4] These polyimines can then be locked using visible-light irradiation through a photocyclization reaction. By varying the reactant stoichiometry, the reaction conditions, a certain control on the polymer population molecular weight can be obtained.

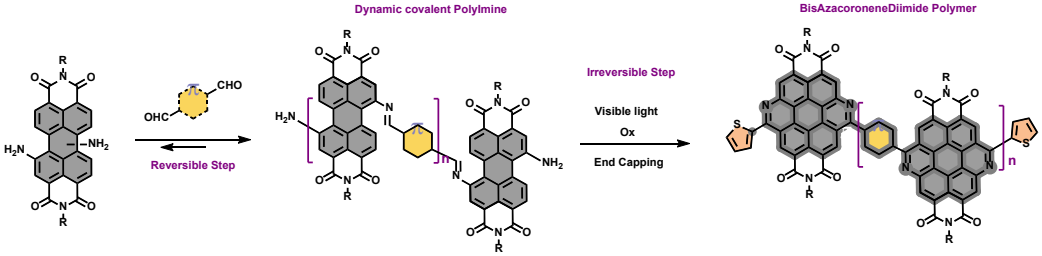

Figure 1: Light-driven polymerization of DiaminoPeryleneDiimide with ditopic aldehydes.

Specifically, we are investigating the *one-pot* condensation of DiaminoPeryleneDiimide with various ditopic aldehyde motifs to synthesize a new library of BisAzacoronenDiimide polymers. By varying the nature of the bis-aldehyde, conjugated polymers showing a low LUMO and a tuneable strong visible-light absorption were prepared. Such materials have a strong potential as active materials of organic solar cells, photodetectors, organic field-effet transistors and more. Their study in devices in ongoing.

Acknowledgements

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References

[1] C. Lee, S. Lee, G.-U. Kim, W. Lee, B. J. Kim, *Chem. Rev.* **2019**, *119*, 8028–8086.
[2] H. Jia, T. Lei, *J. Mater. Chem. C* **2019**, *7*, 12809–12821.
[3] R. El-Berjawi, L. Rocard, A. Goujon, T. Cauchy, P. Hudhomme, *J. Org. Chem.* **2020**, *85*, 12252–12261.
[4] A. Gapin, A. H. G. David, M. Allain, D. Masson, O. Alévêque, T. Ave, L. Le Bras, P. Hudhomme, A. Goujon, *Chem. Eur. J.* **2023**, *29*, e202300652.

A sensitive paper-based sensor for fluoride detection in water using Tb^{3+} photoluminescence

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Fluoride ions are important for bone growth, but a higher intake of fluoride leads to dental and skeletal fluorosis and nephrolithiasis and inhibits the biosynthesis of neurotransmitters in fetuses.[1],[2] Several dry regions in the world contain higher than permissible limits of fluoride (1.5 ppm) in groundwater.[3],[4] Thus, it is important to design and synthesize molecular probes for the selective detection of fluoride without the aid of sophisticated equipment.

Lanthanides (Ln^{3+}) are well known for their sharp, line-like emission, large pseudo-Stokes shift, and long excited-state lifetimes, allowing the recording of the emission in the time-gated mode.[5] Compound **1** is one of the sensitizers for enhancing Tb^{3+} luminescence in terbium cholate hydrogel, which does not need any multi-step synthesis.[6] We developed a strategy of fluoride-triggered desilylation of *pro*-sensitizer **2**, releasing sensitizer **1**. In the optimized assaying conditions, *pro*-sensitizer **2** exhibited a selective response to fluoride ions even in the presence of 7-fold higher concentrations of other interfering anions. The detection be completed in 40 min with the limit of detection estimated to be **27 ppb**, which is well below the permissible limit recommended by WHO. As the protocol is simple, reasonably fast, and selective, we developed a paper-based detection protocol and fluoride detection in real-life samples (e.g., toothpaste and groundwater).[7]

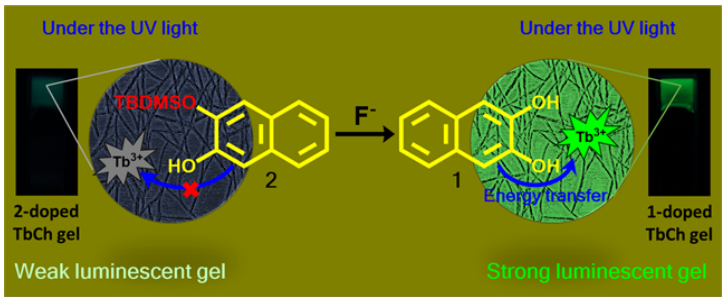

Figure 1. Schematic of fluoride detection using the Tb^{3+} luminescence in the hydrogel matrix.

Acknowledgments

UM thanks the Science and Engineering Research Board (SERB) India for funding and the J. C. Bsoe fellowship. PKC thanks the CSIR and Ministry of Education (Govt. of India) for the awards of JRF and PMRF research fellowships. PKC also thanks Mr. Divy Meena (IISc, Bangalore) for his generous help in arranging the water samples. We also thank Mr. Manish Sharma and Prof. Ragini Gupta (MNIT, Jaipur, India) for ISE measurements.

References

[1] R. M. Duke, E. B. Veale, F. M. Pfeffer, P. E. Kruger, T. Gunnlaugsson, *Chem. Soc. Rev.*, **2010**, *39*, 3936.
[2] P. D. Beer, P. A. Gale, *Angew. Chem. Int. Ed.*, **2001**, *40*, 486–516.
[3] Y. S. Solanki, M. Agarwal, A. B. Gupta, S. Gupta, P. Shukla, *Sci. Total Environ.*, **2022**, *807*, 150601.
[4] M. X. Mu, X. Ke, W. Cheng, J. Li, C. D. Ji and M. Z. Yin, *Anal. Chem.* **2022**, *94*, 11470−11475.
[5] J. -C. G. Bünzli, *Acc. Chem. Res.*, **2006**, *39*, 53−61.
[6] S. Bhowmik, S. Banerjee, U. Maitra, *Chem. Commun.*, **2010**, *46*, 8642–8644.
[7] P. K. Chaturvedi, U. Maitra, Sens. Diagn. (*accepted manuscript*).

Cesium-template oligomerization of allenylpyridine into chiral polyaza-allenophanic receptors

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The synthesis of new macrocycles with unusual topologies continues to be a growing and interesting field, but also challenging.[1,2] We developed a one-pot synthetic methodology enabling the synthesis of three distinct allenophanes[3] in a single reaction with good overall yields. The use of Cs^+ as a template significantly improved the yield and altered the proportion between the obtained allenophanes, increasing the formation of the smaller allenophane **2** while completely inhibiting the formation of the larger **4**. Taking advantage of their structural differences, allenophanes **2** and **3** have been employed as synthetic receptors. Allenophane **2** has proven effective in complexing small, neutral organic molecules containing two hydrogen-bond donating groups, with particular selectivity for catechol derivatives. On the other hand, allenophane **3** was suitable for hosting ammonium cations such as choline, with dependence on their R substituents $(NR_4)^+$.

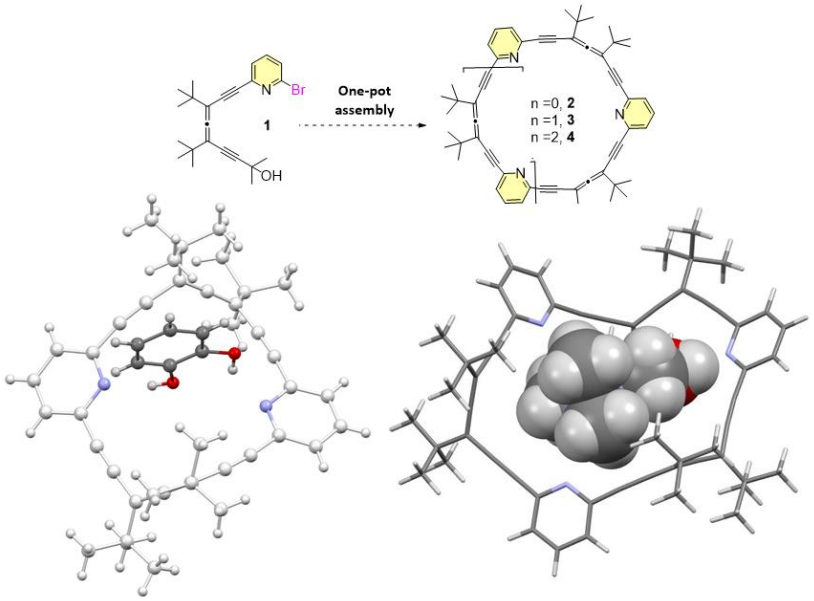

Figure 1. Top) Representation of a one-pot synthesis of 3 allenophanes from the same monomer. Bottom) Crystal structure of the complex [2·catechol] and computational model of the complex [3·choline].

Acknowledgements

We thank Dr. Berta Covelo for her commitment with X-ray studies. Financial support from Ministerio de Economia y Competitividad of Spain (PID2021-128057NB-I00) and Xunta de Galicia (EC431C 2021/41)

References

[1] Han, X. N.; Han, Y.; Chen, C. F. Recent Advances in the Synthesis and Applications of Macrocyclic Arenes. *Chem. Soc. Rev.* **2023**, *52* (9), 3265-3298.

[2] Liu, Z.; Nalluri, S. K. M.; Fraser Stoddart, J. Surveying Macrocyclic Chemistry: From Flexible Crown Ethers to Rigid Cyclophanes. *Chem. Soc. Rev.* **2017**, *46* (9), 2459-2478.

[3] Miguez, S., Cid, M.M; *Synthesis* **2017,** 49(18): 4111-4

Aqueous Hydrazone-based Self-Sorting of a Pseudo[1]rotaxane

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In recent years, advances in the fields of host–guest chemistry and supramolecular switches have highlighted the intrinsic challenge of developing new receptors that implement stimuli-responsiveness or constitutional dynamism. These new hosts are of particular interest when they are capable of recognizing interesting substrates in aqueous media or biological milieu. Consequently, synthetic strategies for the preparation of highly functional macrocyclic hosts, such as integrative self-sorting, are of great interest.

In this context, we have prepared a new series of pyridinium-based cyclophanes, the "fun boxes", based on the previously reported red box"[1] and "red cage"[2]. These new receptors exhibit high hydrolytic stability and can act as supramolecular hosts by including electron-rich polyaromatic guests, such as dihydroxynaphatalene derivatives, in their cavities. Moreover, the starting materials with a mismatched number of reactive centers allow the introduction of an additional aldehyde or hydrazine group into the structure. We explored the *exo*-functionalization of the macrocycles and combined it with their supramolecular host nature for the preparation of an intramolecular pseudo[1]rotaxane, which can self-assemble into "daisy chain" structures. Interestingly, we also achieved the one-pot synthesis of this new pseudo[1]rotaxane from the mismatched starting materials by means of a unique hydrazone-based self-sorting process.[3]

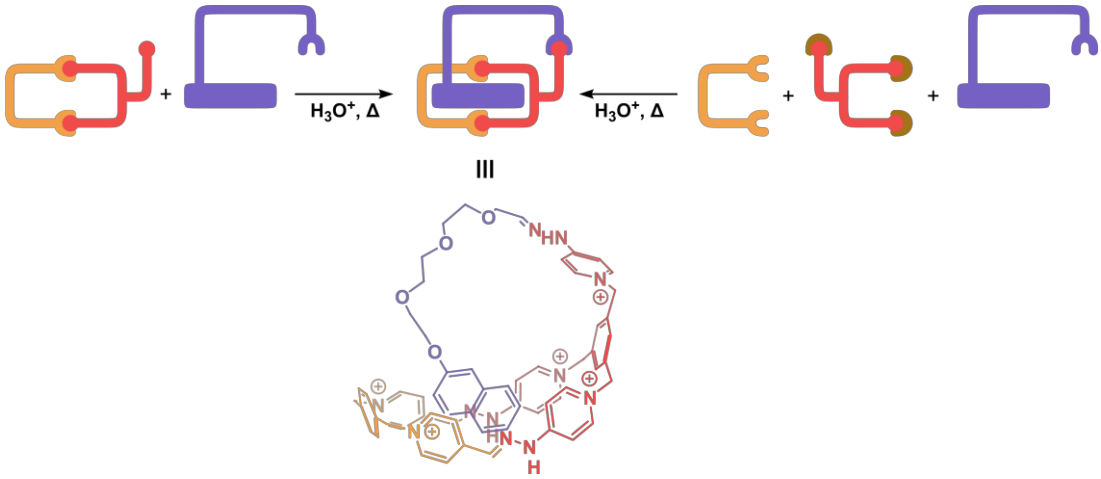

Figure 1. **Top.** Schematic representation of the synthesis of the pseudo[1]rotaxane, achieved both by exo-functionalization of a "fun box" receptor and by a one-pot self-sorting process. **Bottom.** Chemical structure of the pseudo[1]rotaxane.

References

[1] A. Blanco-Gómez, I. Neira, J. L. Barriada, M. Melle-Franco, C. Peinador, M. D. García, *Chem. Sci.*, **2019**, *10*, 10680-10686.

[2] P. Cortón, H. Wang, I. Neira, A. Blanco-Gómez, E. Pazos, C. Peinador, H. Li, M. D. García, *Org. Chem. Front.*, **2022**, *9*, 81-87.

[3] P. Cortón, N. Fernández-Labandeira, M. Díaz-Abellás, C. Peinador, E. Pazos, A. Blanco-Gómez, M. D. García, *J. Org. Chem.*, **2023**, *88*, 6784-6790.

ELECTRON DEFICIENT HEMICRYPTOPHANES

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Hemicryptophanes are covalent molecular cages based on a cyclotriveratrylene (CTV) unit and an additional C_3 symmetrical moiety. Such architectures allow for the recognition of anions, cations and zwitterions thanks to their ditopic character. [1] In order to increase the affinity of hemicryptophanes for negatively charged species anion-π interactions are highly promising while still being underrecognized. Benzene triimides are aromatic electron deficient units -with a strong positive quadrupolar moment- and have a C_3 symmetry axis matching the topography of CTVs which makes them good candidates to endow hemicryptophanes with strong anion-π interactions. [2]

Hereby, we will describe the synthesis and characterization of receptors with either electron rich or electron poor linkers between CTV and BTI units, which modulate the affinity for charged guests. Finally, the control of the CTV configuration within the hemicryptophane is made possible by the use of (achiral) solvents. The characterization of the chiral switch as well as calculations will be presented. [3]

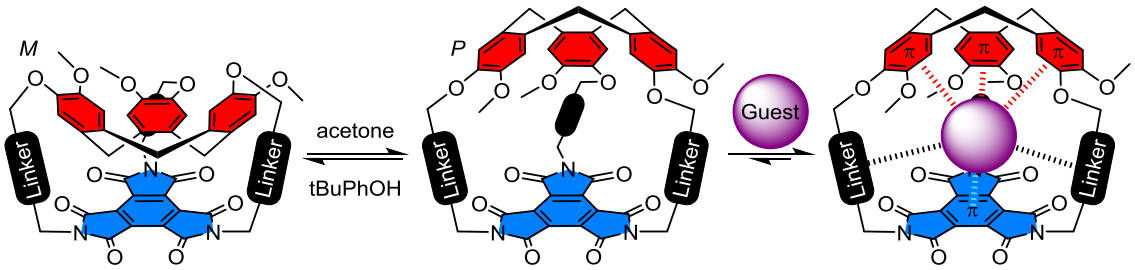

Figure 1. Schematic representation of benzene triimides hemicryptophanes and their ability to recognize guests through multiple π-interactions or to switch configuration depending on the solvent.

Acknowledgements

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References

[1] D. Zhang, A. Martinez, J.P. Dutasta, *Chem. Rev.*, **2017**, *117*, 4900–4942.

[2] D.-H. Tuo, Y.-F. Ao, Q.-Q. Wang, D.-X. Wang, *Org. Lett.*, **2019**, *21*, 7158-7162.

[3] L. Miton, E. Antonetti, D. García-López, P. Nava, V. Robert, M. Albalat, N. Vanthuyne, A. Martinez, Y. Cotelle, *Chem. Eur. J.*, e202303294

Hexaphyrin-Cyclodextrin Hybrids: Switching between Möbius and Hückel Aromatic Systems in Chiral Environment

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Hexaphyrins offer a versatile platform for aromaticity switching through multiple stimuli (redox, coordination, protonation, temperature, polarity and conformational constraints).[1a-c] Remarkably, we recently showed that the association of an hexaphyrin to a doubly-linked chiral cyclodextrin unit (HCD) provides us with two 28π diastereomeric Möbius systems with opposite bridging pattern. Focusing on a dynamic strategy, metalation of these Möbius hexaphyrin with Zn(II) shows chirality transfers between the cyclodextrin, the bridging pattern and the hexaphyrin, tuning the *P/M* twist stereoselectivity up to 60% *de*.[2] Following a different approach, Osuka group achieved metalation with Pd(II) binap salt, resulting in 23% *ee* and further enabling chiral separation.[3] In order to obtain potentially resolvable diastereomers, metal coordination with Pd(II) was done on HCD systems which gave us two *pseudo* enantiomeric monometallic complexes (PdHCD) F1 and F2 with highly efficient chiral communication from the bridging pattern to the Möbius twist. These conformationally stable isomers allow to easily switch between Möbius and Hückel aromatic systems to develop new applications using planar chirality for chiral guest recognition and chiral sensing material.

28π Möbius aromatic PdHCD conjugates showed intense ECD (Electronic Circular Dichroism) spectra. The 28π PdHCD F1 and F2 pseudo enantiomers which show the same ECD spectra with opposite Cotton effects and large Δε attributed to the strong aromaticity, is interesting in view of their potential application as chiral sensors. Redox tuning of chiroptical properties was achieved both with chemical and electrochemical oxidation, to form 26π Hückel aromatic PdHCD conjugates. The 26PdHCD shows weaker ECD spectra for both F1 and F2. The stability of the chiroptical response between Möbius and Hückel aromatic systems allowed us to switch between these states up to 25 cycles. These promising results suggest to further investigate these systems with the redox process, chiral properties, host guest chemistry within confined space and further.

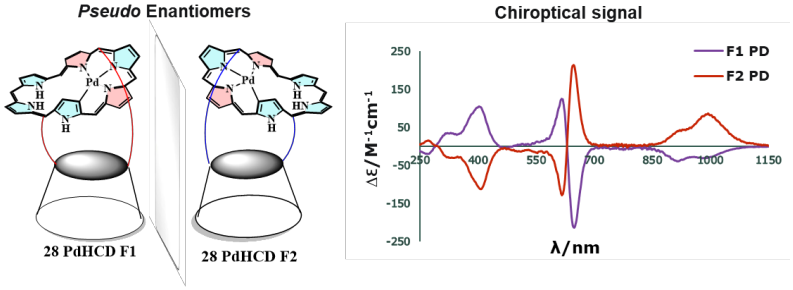

Figure 1. Circular dichroism of PdHCD F1 and F2.

References

[1] a) M. Stępień, B. Szyszko, L. Latos-Grażyński, *J. Am. Chem. Soc.,* **2010**, 132, *9*, 3140; b) S. Xue, D. Kuzuhara, N. Aratani, H. Yamada, *Angew. Chem. Int. Ed*., **2019**, *58*, 12524; c) H. Ruffin, A. Fihey, B. Boitrel, S. Le Gac, *Angew. Chem. Int. Ed*. **2022**., *61*, e202113844.

[2] R. Benchouaia, N. Cissé, B. Boitrel, M. Sollogoub, S. Le Gac, M. Ménand, *J. Am. Chem. Soc*., **2019**, 141, *29*, 11583.

[3] T. Tanaka, T. sugita, S. Tokuji, S. Saito, Osuka, A. *Angew. Chem. Int. Ed*. **2010**., *49*, 6619.

Supramolecular Engineering of Acceptor-Donor-Acceptor π-Conjugated Molecules Prone to J-Aggregation

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In the past few decades, the development of organic solar cells (OSCs) has been considerably growing.[1] A way to obtain remarkably efficient OSCs is to increase their open-circuit voltage (V_{oc}), which will, then, improve the power conversion efficiency of the OSCs. The improvement of the V_{oc} can be partially linked to the packing of the donor and acceptor materials of the photoactive layer of the OSCs. Slip-stacked J-aggregate materials[2] have been found to minimize energetic disorder and achieve good energetic alignment between the acceptor and donor materials, which enhance the V_{oc}.[3] In this context, the development of strategies leading to new π-conjugated molecules showing J-aggregation is of high interest. Here, we present the synthesis of a series of thiophene-based ADA π-conjugated compounds, combining electron-donating (D) and electron-accepting (A) building-blocks, functionalized with central bulky groups of different sizes. The impact of the latter on the supramolecular organization has been analyzed by X-ray diffraction and UV-Vis spectroscopy.

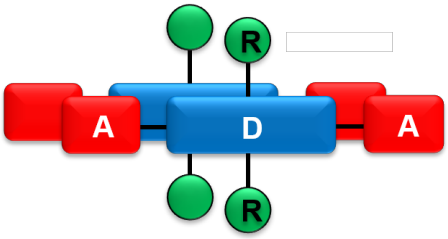

Figure 1. Illustration of ADA systems functionalized with central bulky side chains prone to J-aggregation.

Acknowledgements

This work is associated with the STEEP UP project within the EU M-ERA.NET 2022 program (http://www.m-era-steepup.eu/the-project/) and funded by the Agence Nationale de la Recherche (ANR-23-MER3-0006-01).

References

[1] a) T. Sharma, P. Mahajan, M. Adil Afroz, A. Singh, Yukta, N. Kumar Tailor, S. Purohit, S. Verma, B. Padha, V. Gupta, S. Arya, S. Satapathi, *ChemSusChem*, **2022**, *15*, e202101067. b) D. Luo, W. Jang, D. D. Babu, M. S. Kim, D. H. Wang, A. K. K. Kyaw, *J. Mater. Chem. A*, **2022**, *10*, 3255-3295.

[2] J. H. Kim, T. Schembri, D. Bialas, M. Stolte, F. Würthner, *Adv. Mater.*, **2022**, *34*, 2104678.

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PORPHYRIN CAGES FOR HOST-GUEST CHEMISTRY

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In *Nature*, there is an omnipresent family of molecules (**porphyrinoids**) involved in most (photo)chemical events that transform solar energy into chemical energy, by consuming and regenerating O_2, H_2O, CO_2, H_2 in a closed cycle.[1] **Porphyrins** are π-conjugated macrocycles responsible for executing many of the essential life processes, such as oxygen transport/storage (*hemoglobin* and *myoglobin*), electron transfer (*cytochrome b5*), enzymatic oxidation/oxygenation (*cytochromes P450, peroxidases*), and convert sunlight in photosynthetic systems (*chlorophylls*).

Moreover, porphyrins reactivity and symmetry enable their functionalization in different positions which provide high versatility in self-assembly processes. Therefore, numerous examples of organic molecular cages based on porphyrins have been published showing their exceptional ability to host different kind of molecules as well as their interesting (photo)catalytic properties.[(2,3)]

Here we show the formation of a molecular cage by means of the connection of two porphyrins via four linkers through **dynamic imine bonds** (**Figure 1**). According to the organization of these imine bonds two **conformations** are possible for the cage: **extended** and **compact**. Furthermore, the **host-guest chemistry** of this system was studied to determine its capability to host a wide range of ligands, observing a chelate cooperative effect in most of the guest tested due to a mutual conformational adaptation (**Figure 1**).

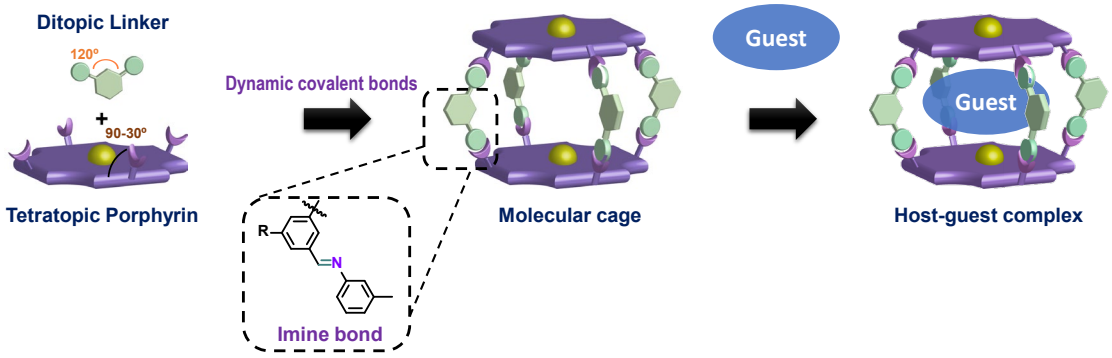

Figure 1. Schematic representation of molecular cage self-assembly and host-guest complex formation.

Acknowledgements

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References

[1] IPCC Climate Change. The physical science basis. **2013**, *1535*.

[2] Guilard, R.; Kadish, K. M.; Smith, K. M.; Guilard, R., *The porphyrin handbook*. Academic Press New York: **2003**; Vol. 18.

[3] Durot, S.; Taesch, J.; Heitz, V. J. C. R. *Chem. Rev*. **2014**, *114*, (17), 8542.

Unforeseen Catalytic Reactivity of Nitrostyrene Derivatives via Supramolecular Catalysis

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Non-covalent interactions have emerged as pivotal tools in the design of ligands for diverse asymmetric catalytic systems. Our group is particularly interested on benzene-1,3,5-tricarboxamides (**BTAs**)[1], disk-like molecules featuring hydrogen bonding groups, which self-assemble into stable threefold hydrogen-bonded helices. Thanks to efficient chirality induction and amplification processes, BTAs appended with intrinsically achiral phosphine copper complexes demonstrated good efficacy in asymmetric catalysis, providing good enantioselectivities for well-established hydrosilylation and hydroamination reactions[2,3]. Leveraging this supramolecular catalytic copper hydride system, we probed the reactivity of nitrostyrene derivatives. While 3-nitrostyrene (3NS) followed the classical expected hydroamination pathway, 2- and 4-nitrostyrene (2NS, 4NS) derivatives underwent an unexpected diastereo- and enantioselective dimerization reaction leading to 1,2-diaryl-1,2-dimethyl ethane derivatives in excellent yields (**Figure 1**). Furthermore, our investigation highlights higher chemo, diastereo and enantioselectivity with supramolecular helical catalysts relatively to conventional ligands. This underscores the distinct advantages of supramolecular catalysis in facilitating unconventional reactivity pathways.

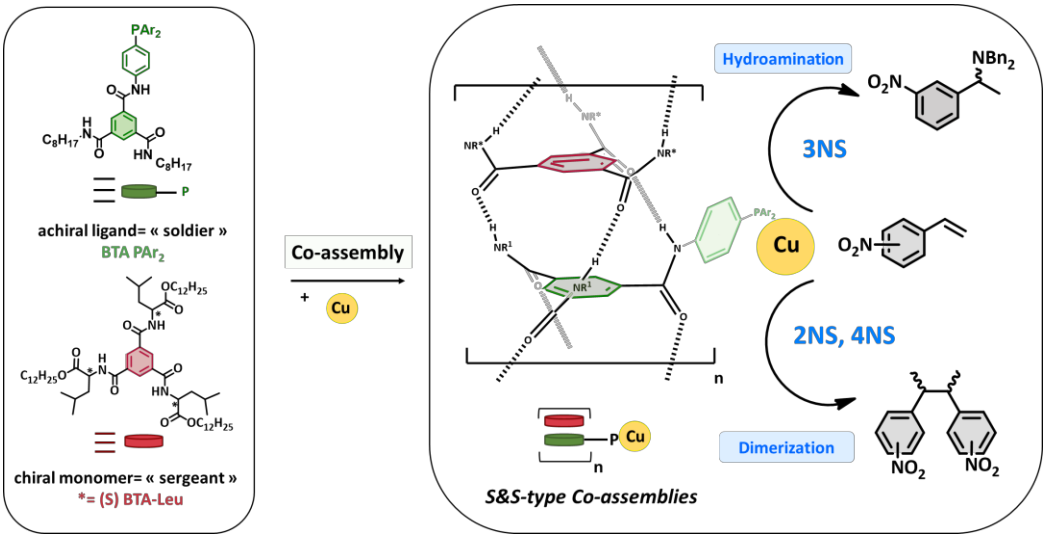

Figure 1. Reactivities of nitrostyrene derivatives with supramolecular helical copper catalysts.

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Omar Khaled for the training (chiral GC and HPLC), The French Agence Nationale de la Recherche is acknowledged for funding the project AdECat (ANR).

References

[1] M. Raynal and al., *J. Am. Chem. Soc.* **2016**, *138,* 14, 4908–4916.
[2] Y. Li and al., *J. Am. Chem. Soc.,* **2020**, *142*, 5676.
[3] P. Aoun and al., Catal. Sci. Technol., **2022**, *12*, 834–842.

Transient switching of molecular tweezers by a chemical fuel

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During the past thirty years chemists have designed, constructed and investigated a large variety of molecular devices and machines by exploiting chemical, photochemical and electrochemical stimuli to transform appropriately designed supramolecular systems. This research has led to the design of diverse molecular machines inspired by nature or their macroscopic counterparts such as molecular motors, switches, cages and tweezers. [1] A significant, yet challenging goal is the development of systems whose actuation is triggered by cooperative or coordinated actions.

We have recently developed switchable molecular tweezers[2] that can be controlled by metal coordination. Our system is based on a terpyridine ligand functionalized by metal salphen complexes. The open tweezers adopt "W" shaped conformation that can be switched to a closed "U" conformation, bridging the two functional salphen complexes into proximity. [3] We aim to combine the mechanical conformation switching of our system with a chemical fuel to enable an autonomous operation.[4] Herein, we report multicomponent switching cascades based on terpyridine molecular tweezers, tren(Zn) complex and carboxylic acids that slowly decompose over time as chemical fuels (Figure 1). This system allows transient out of equilibrium closing of the tweezers with a precise temporal control depending on the acid and its concentration. We will present the detailed kinetics studies of these out-of equilibrium multicomponent systems and their impact on the conformation and properties of luminescent tweezers.

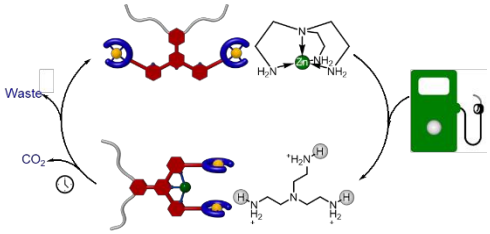

Figure 1. Chemical fuel-driven multicomponent cascade switching system.

Acknowledgements

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References

[1] S. Erbas-Cakmak, D. A. Leigh, C. T. McTernan, A. L. Nussbaumer, *Chem. Rev.,* **2015**, *115*, 10081-10206.

[2] P. Msellem, M. Dekthiarenko, N. Hadj Seyd, G. Vives, *Beilstein J. Org. Chem.,* **2024**, *20*, 504-539.

[3] A. B. Doistau, A. Tron, S. A. Denisov, G. Jonusauskas, N. D. Mcclenaghan, G. Gontard, V. Marvaud, B. Hasenknopf, G. Vives, *Chem. Eur. J.,* **2014**, *20*, 15799-15807; B. L. Benda, B. Doistau, C. Rossi-Gendron, L.-M. Chamoreau, B. Hasenknopf, G. Vives, *Comm. Chem.,* **2019**, *2*, 144.

[4] A. B. Doistau, L. Benda, J.-L. Cantin, L.-M. Chamoreau, E. Ruiz, V. Marvaud, B. Hasenknopf, G. Vives, *J. Am. Chem. Soc.,* **2017**, *139*, 9213-9220; B. A. Ghosh, I. Paul, M. Schmittel, *J. Am. Chem. Soc.,* **2019**, *141*, 18954-18957; C. L. Wimberger, J. Andréasson, J. E. Beves, *Chem. Commun.,* **2022**, *58*, 5610-5613.

P-22

Design and synthesis of foldamers that can self-assemble in water to form a supramolecular structure

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The complex functions of proteins are intimately linked to their three-dimensional structures. Inspired by the folding modes of these biomolecules, and seeking to mimic their functions, chemists have developed unnatural oligomers that fold into architectures mimicking the secondary structures of these biomolecules: foldamers. Our laboratory has been developing the knowledge and tools for the design and synthesis of such compounds for several years. Their preparation and characterization are now well established, however the construction of more complex architectures resulting from the assembly of several secondary elements to obtain tertiary and quaternary structures, necessary for the emergence of functions, remains a challenge. Here we describe our strategy to build quaternary structures from synthetic oligomers by hybridization in multiple helices.

Our strategy rely on the particular property of helical fluoroquinoline oligoamide foldamers to form stable antiparallel double helices (Fig. 1). Two of these oligomers will be connected through a designed linker that will orient the helices with an angle of 90° so that, upon hybridization, four subunits will join together to form a square-shaped structure (Fig. 2). Once obtained, side chains of the oligomers located towards the interior of the assembly can modified to create interaction zones in the centre of the structure.

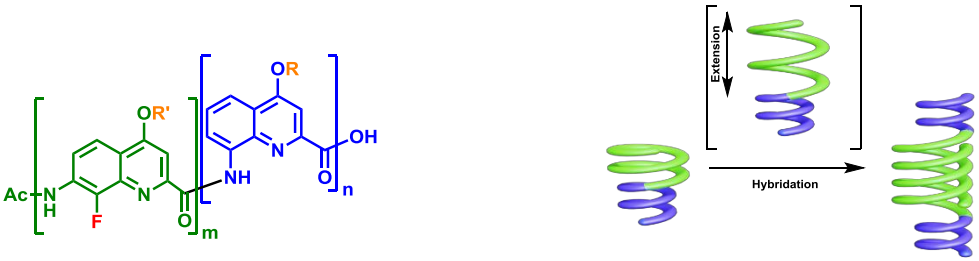

Figure 1 : Quinolines sequence on the left and scheme of the hybridization in water on the right

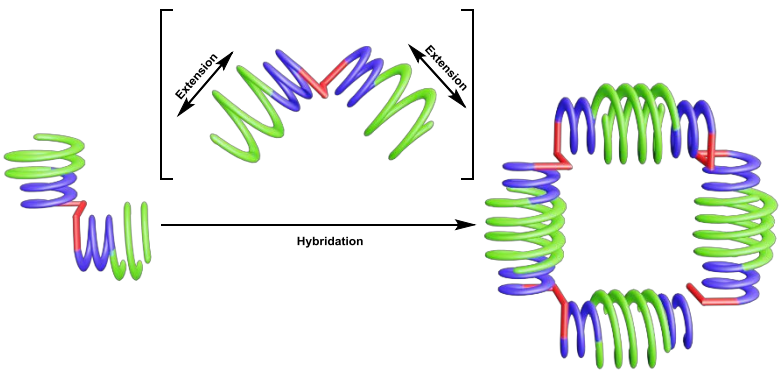

Figure 2 : Scheme of the hybridization in square of for subunits

SELF-ASSEMBLY OF PRECISION MACROMOLECULES FORMING A SUPRAMOLECULAR CATALYST: INSIGHTS FROM MOLECULAR DYNAMICS SIMULATIONS

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Sequence-defined macromolecules, inspired by the sequence control in biopolymers such as proteins and DNA, are now accessible through various synthetic pathways.[1] Previous studies by our group and collaborators have shown the paramount importance of the sequence order in short catalytic oligomers.[2,3] In view of combining the control over monomer sequence and supramolecular interactions, a new system was designed **(Figure 1)**. The precision macromolecules, oligomer A (O_a) and oligomer B (O_b), are able to bind through complementary nucleobase derivatives pairs **G**-**C** and **T**-**D** (see colored units in **Figure 1**). The formation of the O_a/O_b complex brings all five necessary catalytic subunits (**M**, 2 **P**, **I**, **I'**) close to each other, a mandatory step to enable catalytic activity. The model reaction studied here is the aerobic oxidation of benzyl alcohol into benzaldehyde. Molecular dynamics (MD) simulations are utilized to decipher the mechanisms of assembly at the atomistic level. Overall, our analyses of simulations, including original representations in network and modules, showed the formation of a very flexible, compact and globular duplex, in which the interactions between the complementary nucleobase derivatives play an important role but are not the only contribution to the binding.[4]

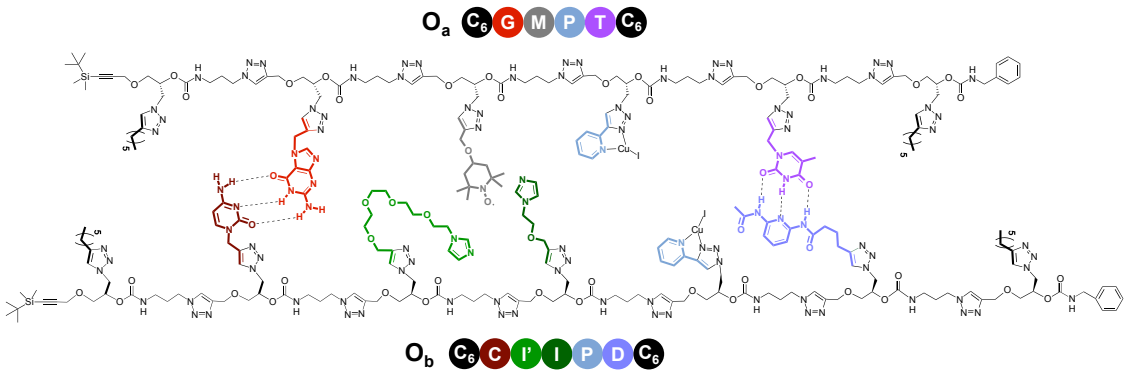

Figure 1. Chemical structure of the O_a/O_b self-assembled catalytic system

Acknowledgements

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References

[1] S. C. Solleder, R. V. Schneider, K. S. Wetzel, A. C. Boukis, M. A. R. Meier, *Macromol. Rapid. Commun.* **2017**, *38,* 1600711.
[2] P. Chandra, A. M. Jonas, A. E. Fernandes, *J. Am. Chem. Soc*. **2018**, *140*, 5179-5184.
[3] J. Li, Q. Qin, S. Kardas, M. Fosséprè, M. Surin, A. E. Fernandes, K. Glinel, A. M. Jonas, *ACS Catal.* **2022**, *12*, 2126-2131.
[4] Q. Qin, J. Li, D. Dellemme, M. Fosséprè, G. Barozzino-Consiglio, I. Nekkaa, A. Boborodea, A. E. Fernandes, K. Glinel, M. Surin, A. M. Jonas, *Chem. Sci.* **2023**, *14*, 9283-9292.

Tuning Supramolecular Units and Block Copolymers Organization within Polymer Matrices through Macromolecule Functionalization

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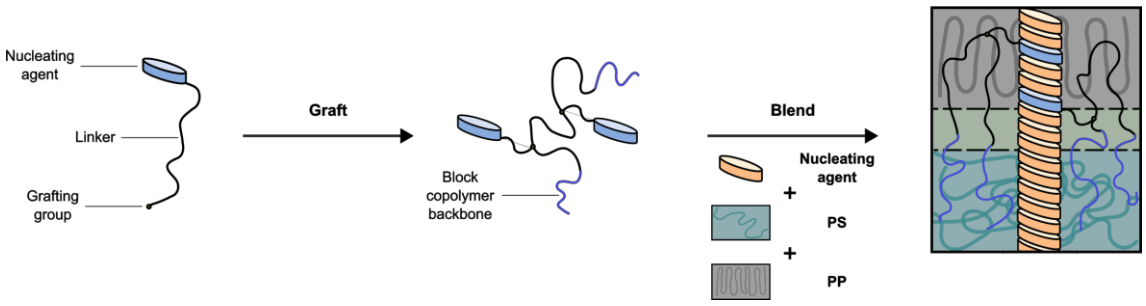
Mixtures of post-consumer plastics are difficult to sort and recycle, thus representing a major challenge for achieving a circular plastics economy.[1] The utility of such materials is limited because of the incompatibility of most commercial polymers, which leads to coarse phase separation, weak interfaces, and ultimately poor mechanical properties. Many solutions have been reported, such as the use of block copolymers as compatibilizers, but there still remains a great demand for innovative strategies for improving the properties of blends of incompatible polymers. A promising approach is to develop new (supra)macromolecular tools for finely controlling the structure and properties at the interface of incompatible polymers. In this context, we have explored the hierarchical assembly of block copolymers and supramolecular polymers in a polypropylene matrix with a polystyrene minor phase. A series of increasingly complex compositions were targeted, ranging from a simple blend of PS and PP to a blend of these polymers compatibilized with a polystyrene-*block*-poly(ethylethylene)-*block*-polystyrene block copolymer bearing pendant supramolecular motifs. These materials were prepared in the melt by extrusion, and they were studied using a comprehensive set of analytical techniques, including variable temperature FTIR spectroscopy, SAXS, WAXS, XRD, DSC, POM, TEM, and SEM. We have uncovered intriguing non-orthogonal assembly behavior between the supramolecular polymer, the unfunctionalized block copolymer, and grafted derivatives of the block copolymer, giving rise to striking consequences to the structure of the final materials.



References

[1] Plastics – The Facts 2022. PlasticsEurope, 2022. https://plasticseurope.org/knowledge-hub/plastics-the-facts-2022/ (accessed 2024−02−27)

[2] Xu, J.; et al. *Macromolecules* **2018**, *51*, 8585

Design of Self-Assembled Metallocages: Recognition, Luminescence and Chirality

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Over the past two decades, considerable efforts have been devoted to the rational design of metallocages possessing nanocavities thanks to the emergence of synthetic supramolecular chemistry methodologies.[1] These architectures possess tailored cavities which makes them attractive for applications, such as gas sorption/separation, catalysis and sensing.[2] Thus ligands constitute a powerful tool for the construction of such functional supramolecular assemblies with tunable properties. In this context, we have first developed the use of a semi-rigid bidentate ligand to construct a variety of appealing structures including nanocages of type M_2L_4 based on Co(II) and Cu(II).[3] Subsequently, the use of rigid luminescent bis(ethynylpyridine)aniline and bis(ethynylpyridine)benzene based ligands has led to the formation of nanocapsules of type M_2L_4 (M = Pd, Pt), [3] whose cavities are able to accommodate neutral organic molecules and/or anionic organometallic complexes guests. Finally the use of a new semi-rigid bidentate ligand including a chiral 1,1'-biphenyl type unit in its racemic form to coordinate Zn(II) and Co(II) has been studied.[4]

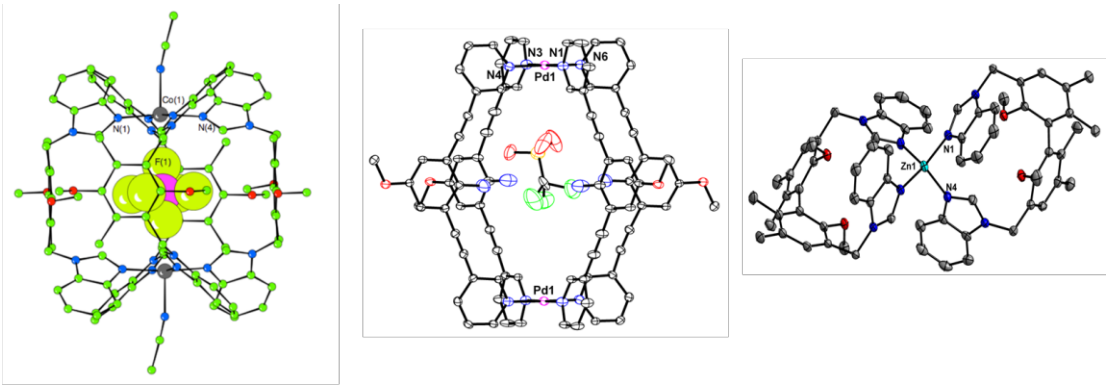

Figure 1. a) Co-based metallocages b) Pd-based metallocages c) Zn-based chiral loop

References

[1] For selected recent review articles see: D. B. Bokotial, K. Acharyya, A. Chowdhury, P. S. Mukherjee, Angew. Chem. Int. Ed., **2024**, e202401136; C. T. McTernan, J. A. Davies, J. R. Nitschke, *Chem. Rev*. **2022**, *122*, 10393; D. Tripathy, N. B. Debata, K. C. Naik, H. S. Sahoo, Coord. Chem. Rev., **2022**, *456*, 214396; J. Dong, Y. Liu, Y. Cui, *Acc. Chem. Res*., **2021**, *54*, 194; H.-Q. Yin, X.-B. Yin, *Acc. Chem. Res*., **2021**, *53*, 485; S. Pullen, J. Tessarolo, G. H. Clever *Chem. Sci.*, **2021**, *12*, 7269; A. J. Gosselin, C. A. Rowland, E. D. Bloch, *Chem. Rev*., **2020**, *120*, 8987; H. Sepehrpour, W. Fu, Y. Sun, P. J. Stang, *J. Am. Chem. Soc.*, **2019**, *141*, 14005.

[2] H. Amouri, C. Desmarets, J. Moussa, *Chem. Rev.* **2012**, *112*, 2015.

[3] E. Puig, C. Desmarets, G. Gontard, M.-N. Rager, A. L. Cooksy, H. Amouri, Inorg. Chem., **2019**, *58*, 3189; C. Desmarets, G. Gontard, A. L. Cooksy, M.-N. Rager, H. Amouri, *Inorg. Chem.*, **2014**, *53*, 4287; C. Desmarets, T. Ducarre; M.-N. Rager, G. Gontard, H. Amouri, *Materials*, **2014**, *7*, 287.

[4] H. Soudry, C. Desmarets, G. Gontard, T. Edgington, A. L. Cooksy, H. Amouri, *Dalton Trans.*, ***2017***, *46,* 10240.

Encapsulation triggered emission enhancement of PCP-cyanine red emitter

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The green fluorescent protein provides insights and bio-inspiration towards tuning of photophysical properties by the modification of the supramolecular environment around a chromophore. The latter emissive moiety embedded in the protein displays emission which can be shifted on a 100 nm scale upon solely modification of the surrounding protein structure.[1]

So inspired by nature, we aim to enhance the red emission of a [2,2]paracyclophanyl cyanine cationic organic chromophore by its encapsulation in an self-assembled hexameric resorcin[4]arene-based capsule known for hosting cations, in particular coordination complexes.[2] Harnessing chiral guest in the latter chiral capsule provides chiral bias that triggers chirality induction from the [2,2]paracyclophanyl cyanine to the capsule. Such interaction opens a route towards encapsulation triggered chiroptic tuning with prospective Cotton effect modification and CPL tuning.

The encapsulation studies and its effect on emission will be presented as well as the first chiroptic results.

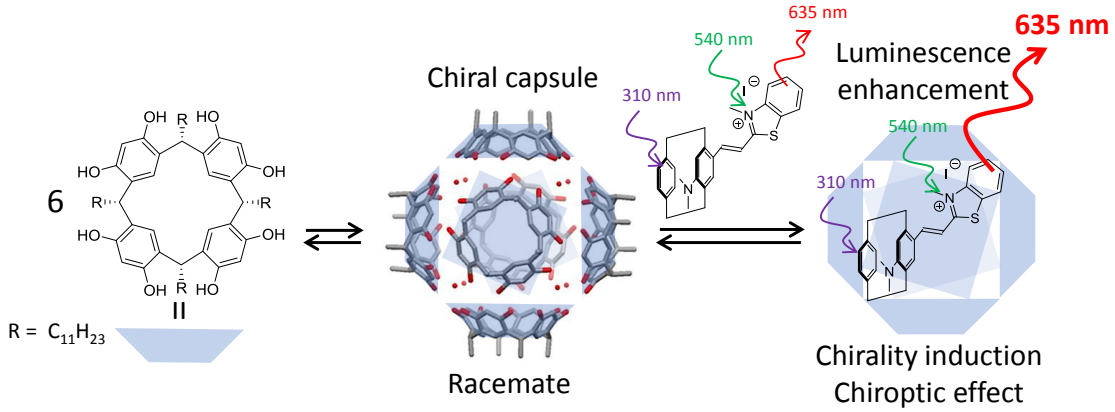

Figure 1. Encapsulation triggered PCP-cyanine emission enhancement.

Acknowledgements

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References

[1] M. Drobizhev, P. R. Callis, R. Nifosì, G. Wicks, C. Stoltzfus, L. Barnett, T. E. Hughes, P. Sullivan & A. Rebane, *Sci. Rep.,* **2015,** *5,* 13223.

[2] T. Zhang, L. Le Corre, O. Reinaud, B. Colasson, *Chem. Eur. J.*, **2021**, *27*, 434-443.

CESIUM SALT EXTRACTION AND DEPOSITION BY A PHOTOSWITCHABLE CALIX[4]PYRROLE RECEPTOR

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Selective removal of cesium salts from wastewater remains a significant challenge in industry. Calix[4]pyrrole macrocycles are promising extracting agents as they show high binding affinity and selectivity towards anions and cesium ion pairs.[1] Nevertheless, while very high affinity is desired for efficient extraction, it hampers recyclability and recovery of the subbstrate. An effective strategy to overcome this issue, [2] recently developed in our group, is to introduce a photoresponsive strap such that low-affinity and high-affinity states can be addressed by light.[3] A drawback of the current system is the use of damaging UV light and low photo-stationary state ratios, which hamper its efficiency as an extractant. To address these issues, we have introduced *Z*-diazocine as a bridging unit. Here, we present two diazocine-strapped calix[4]pyrrole receptors, which can be switched over multiple cycles between high and low binding affinity states using visible light irradiation. Both *Z*-isomers strongly bind chloride and bromide anions in 1:1 stoichiometry. Exposure of the host-guest complexes to 405 nm, leading to formation of the respective *E*-isomer, results in anion release. The receptor with a longer spacer is shown to function as an effective extractant of cesium bromide. This work opens up a new photo-modulable approach to extraction and deposition of cesium salts, which eventually will help to reduce the volume of waste streams.

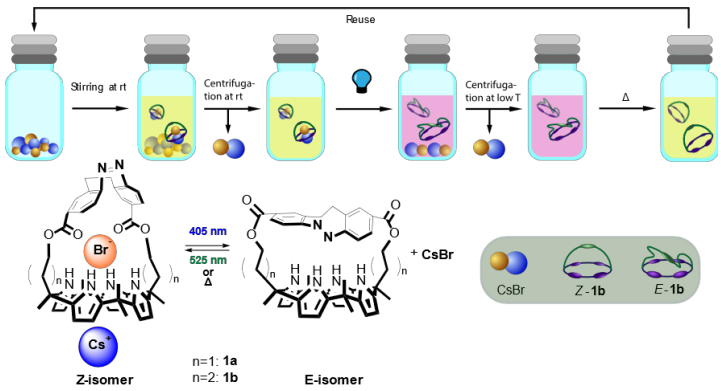

Figure 1. Cesium bromide extraction by Z-diazocine strapped calix[4]pyrrole receptor.

Acknowledgements

We thank the Dutch Research Council (NWO-M1 OCENW.M20.306) for financial support.

References

[1] D. S. Kim and J. L. Sessler, *Chem. Soc. Rev.*, **2015**, *44*, 532–546.
[2] J. de Jong, J. E. Bos and S. J. Wezenberg, *Chem. Rev.*, **2023**, *123*, 8530-8574.
[3] D. Villarón, M. A. Siegler and S. J. Wezenberg, *Chem. Sci.*, **2021**, *12*, 3188-3193.

π-Basic $Au_3(pyrazolate)_3$ complexes as building blocks for the construction of molecular cages

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Cyclic trinuclear complexes (CTCs) are known for their tunable π-basicity and interesting optical properties. However, there are limited examples of incorporating these motifs into molecular cages.[1] In order to construct cages with CTC building blocks, we synthesized pyrazole-based ligands with substituents suitable for further reaction. One tetrahedral cage and two trigonal prismatic cages were obtained by an imine condensation reaction between gold CTCs with peripheral aldehyde groups and commercially available amines. The tetrahedral cage can encapsulate C_{60} (**Figure 1a**) and C_{70}.[2] Furthermore, we synthesized two metalloligands with pyridine donor groups: a triotopic ligand and a ditopic ligand. The reaction between the first ligand and Pd^{II} ions formed a spherical $Pd^{II}_6Fe^{II}_{24}Au^{I}_{24}$ coordination cage with a diameter of ~ 4.1 nm and a molecular weight of 21 kDa (**Figure 1b**), while the second ligand formed a $Pd^{II}_2Fe^{II}_8Au^{I}_{12}$ cage in the same conditions.

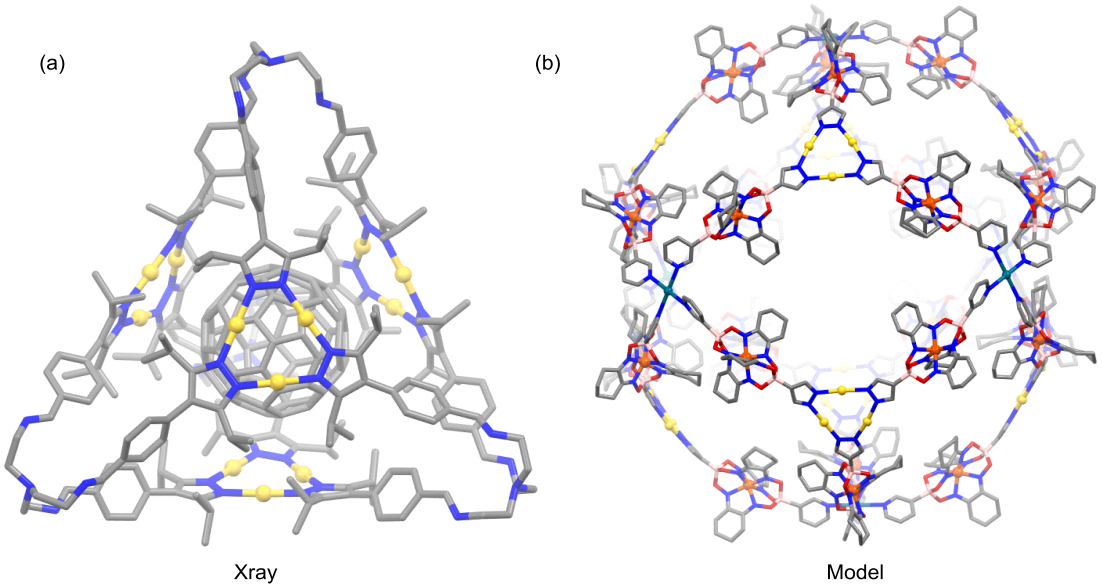

Figure 1. **a)** Structure of the host-guest complex of a tetrahedral cage with C_{60}, and **b)** A $Pd^{II}_6Fe^{II}_{24}Au^{I}_{24}$ coordination cage.

References

[1] J. Zheng, Z. Lu, K. Wu, G. Ning, D. Li, *Chem. Rev.* **2020**, *120*, 9675-9742.
[2] N. Eren, F. Fadaei-Tirani, R. Scopelliti and K. Severin, *Chem. Sci.*, **2024,** *15*, 3539.

Comparative Study of Novel Supramolecular Structures Involving Anions and Squaramide-bis(triazolium) Receptors

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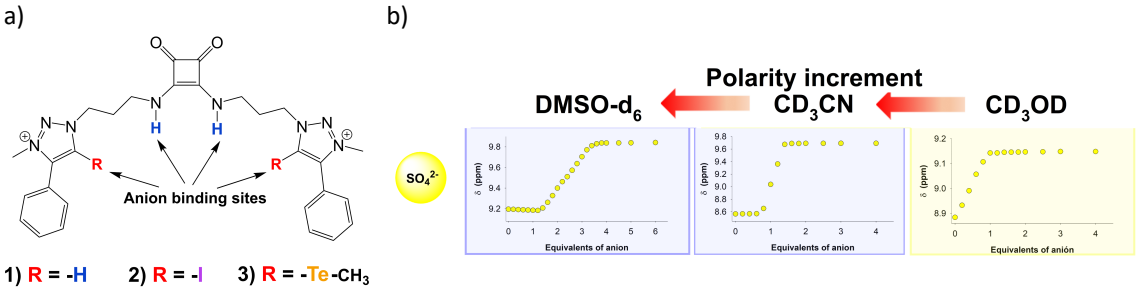
Anion recognition is a thriving and well-established field within supramolecular chemistry.[1] On the other hand, anion-induced supramolecular polymers represent a relatively understudied class of materials, characterized by the self-assembly of one or more molecular components.[2,3] In both scenarios, hydrogen bonding (HB) has been the most commonly employed non-covalent interaction.[1] Nevertheless, in the last decade, σ-hole interactions such as halogen (XB) and chalcogen bonding (ChB) have also gained significant attention.[4]

In this work, the comparative study of novel supramolecular structures induced by anions is presented, based on receptors bearing one squaramide unit and proto (HB), iodo (XB) or tellurium (ChB) bis(triazolium) groups as extra anion binding sites (**Figure 1a**). The addition of increasing amounts of SO_4^{2-} anions in DMSO-d_6 and CD_3CN solution, did not promote any shifts in the ^1H NMR spectra of receptor **1**, subsequent additions induced significant downfield shifts, suggesting the formation of supramolecular polymers. In contrast, the addition of anions in CD_3OD solution resulted in a classical behavior for an anion-receptor complex (**Figure 1b**). All of these supramolecular structures were also identified by ^1H NMR, ^{125}Te NMR, UV-Vis spectroscopy, Dynamic Light Scattering and DOSY ^1H NMR experiments.



1) R = -H 2) R = -I 3) R = -Te-CH_3

Figure 1. a) Structure of the receptors, **b)** ^1H NMR titration profiles for the receptor **1** during the increasing addition of SO_4^{2-} anions.

Acknowledgements

This work was supported by Ministerio de Ciencia e Innovación of Spain and FEDER project PID2020-113483GB-I00 and Fundación Séneca Región de Murcia (CARM) Project 21956/PI/22.

References

[1] P. A. Gale, E. N. Howe, X. Wu, *Chem.* **2016**, *1*, 351−422.
[2] F. Zapata, L. González, A. Bastida, D. Bautista, A. Caballero, *Chem. Comm.* **2020**, *56*, 7084-7087.
[3] E. Navarro-García, B. Galmés, J.L. Esquivel, M.D. Velasco, A. Bastida, F. Zapata, A. Caballero, A. Frontera, *Dalton Trans.* **2022**, *51*, 1325-1332.
[4] J. Y. C. Lim, P. D. Beer, *Chem.* **2018**, *4*, 731-783.

CHIRAL PLASMONIC WATER SOLUBLE POLY(PHENYLACETYLENES)@AGNPS HYBRID MATERIALS AS A TOOL OF METAL IONS DETECTION

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We present new stimuli-responsive hybrid materials by employing water-soluble poly(phenylacetylene)s (PPAs) with primary amines as chiral protecting agents[1] for silver nanoparticles (AgNPs).[2] The selected PPA with ammonium groups in its pendant poly-(*S*)-**1** enhances solubility in aqueous media and provides specific interaction sites for AgNPs. This interaction mechanism was explored through experimental and DFT calculations.

Moreover, the nanocomposites demonstrate pH-dependent nanostructuration, resulting in varied sizes of the hybrid material and distributions of silver nanoparticles (AgNPs). This hybrid material exhibits response to the oxidation state of silver in the ECD. The pH modulation applied to the final AgNP@poly-(*S*)-**1** produce a switchable system with the ability to aggregate and precipitate under alkaline conditions, followed by self-healing properties upon acidification. The materials show potential for sensing applications due to their chiroptic and optic responses after the addition of various cations.

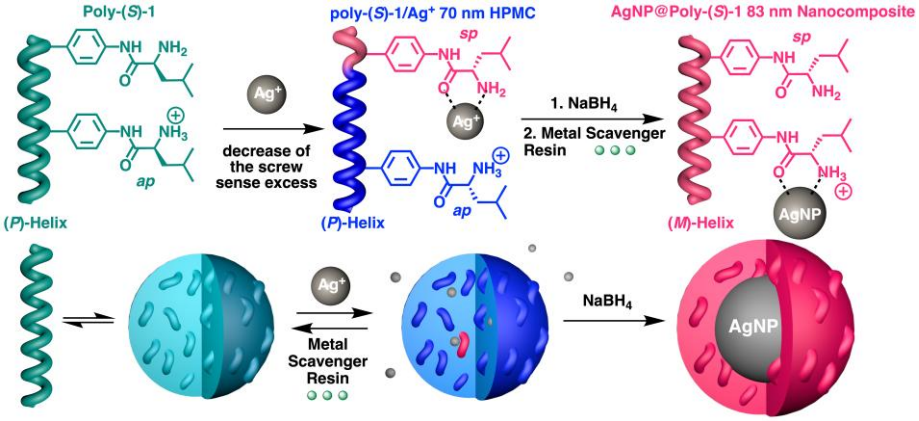

Figure 1. Schematic representation of the chemical reduction at pH=1 of poly-(*S*)-**1**/Ag^+ Helical Polymer Metal Nanoparticle (HPMC) to AgNP@poly-(*S*)-**1** nanocomposite.

Acknowledgements

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References

[1] S.-P Esteban, Q. Emilio, R. Ricardo, F. Félix, *Chem. Matter.*, **2018**, *30*, 6908-6914.

[2] N.-M Manuel, A. Sandra, Q. Emilio, R. Ricardo, F. Félix, *Chem. Matter.*, **2021**, *33*, 4805-4812.

Dyn[n]arenes: One Ring to Rule Them All !

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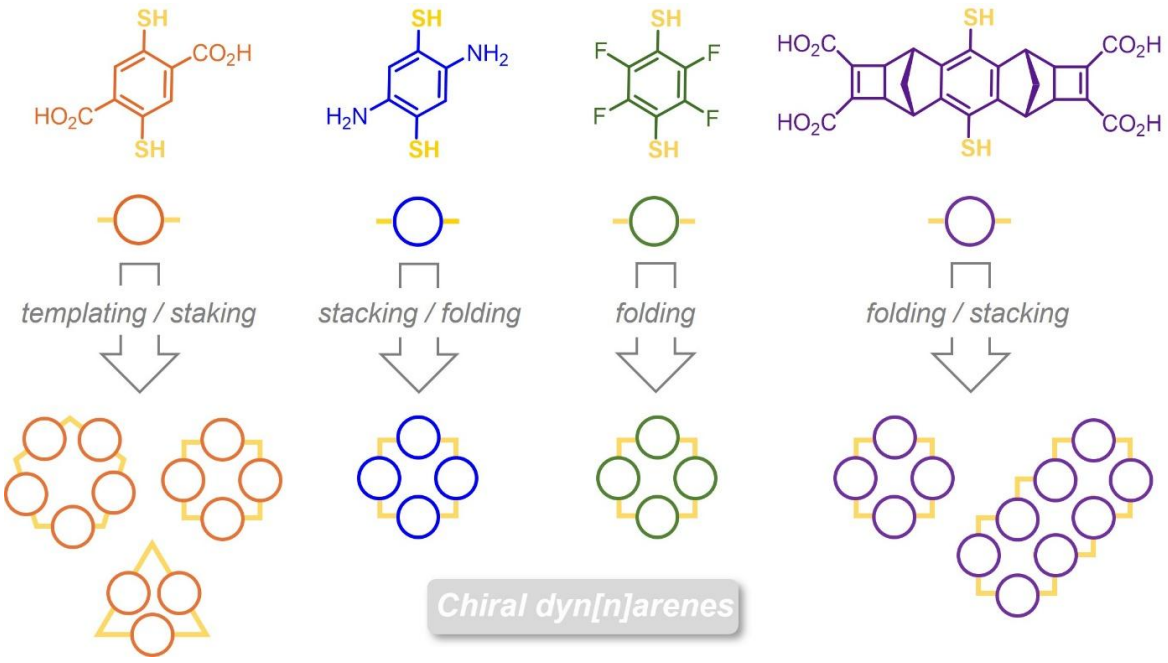
If blockbuster cavitands such as cucurbit[n]urils, pillar[n]arenes, cyclodextrins, calix[n]arenes are synthetically very accessible and robust, they suffer from limitations: not only their harsh assembling conditions generally rules out the use of the famous template effect, but also their synthesis procedures generally deliver unfunctionalized architectures that imply further post-functionalization steps.

Dyn[n]arenes are the strict polydisulfide-based analogues of pillar[n]arenes.[1] Although less famous than their static homologues, these dynamic cavitands are self-assembled in water at physiological pH and possess unique stereo-chemical features. Here, we show that the covalent assembling process can be guided by supramolecular interactions with or without a targeted partner. As a result, not only can the size and functions be chosen on demand, but the stereochemical features can be precisely controlled by careful choice on the building blocks and the assembling conditions.[2]



References

[1] L. Vial, F. Perret, J. Leclaire *Eur. J. Org. Chem.* **2022**, e202101274.

[2] Y. Zhang *et al. Chem. Sci.* **2023**, 13, 7126-7135; M. Dumartin *et al. Chem. Sci.* **2020**, *11*, 8151-8156; M. Donnier-Maréchal *et al. Org. Lett.* **2018**, *20*, 2420-2423; P.-T. Skowron et al. *J. Org. Chem.* **2016**, *81*, 654-661.

Cyclodextrin-based Photosensitive Bimetallic Complexes for Catalysis

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Ruthenium (Ru) complexes have been developed as photosensitizers due to their light-responsive property [1,2]. For catalysis, except functioning as the catalytic center directly, Ru complexes are widely adopted as the light-triggered stimuli responsive moiety within a bimetallic catalyst system [3, 4, 5].

Previously our group reported series of catalysts based on NHC-bridged mono-metallic cyclodextrins (CD) and verified their stereoselectivity, which derives from the different CD size. Furthermore, we prepared bimetallic CD complexes. It is assumed that in these CD-based bimetallic complexes, electron communication between two metals (outside & inside the CD cavity) that linked together by a conjugated part could influence the catalytic process happened on the transition metal situated inside the CD cavity.

Thus, combining the photosensitivity of Ru complex and the steric selectivity of the CD, several bimetallic complexes have been designed and synthesized to verify if the stereoselectivity and stimuli controllability can yield a single product in a competitive multi-product generated reaction. There are only few reports in this field and none of the synthesized complexes have been reported. Through two dimensions (light presence and CD cavity size) of catalytic efficiency evaluation and electrochemistry research, the mechanism how the electron communication and light-triggered process enable or boost the catalysis could be revealed.

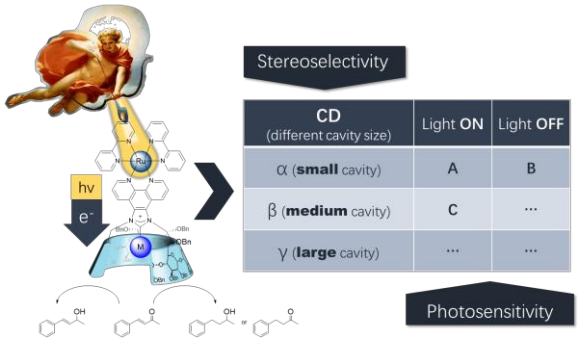

Figure 1. Module of the photosensitive bimetallic complexes.

Acknowledgements

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References

[1] S Rau, J. G. Vos et al, *Angew. Chem. Int. Ed.* **2006**, *45*, 6215 –6218.
[2] A. K. Mengele, S. Rau et al, *Angew. Chem. Int. Ed.* **2022**, e20211484.
[3] S-H. Fan, K-Z Wang et al, *Inorg. Chem* **2010**, *49*, 3752–3763.
[4] S. Tschierlei, B. Dietzek et al, *Angew. Chem. Int. Ed.* **2010**, *49*, 3981 –3984.
[5] M. Scholl, R. H. Grubbs et al, *Org. Lett.* **1999**, *6*, 953–956.
[6] P. Zhang, M. Sollogoub, et al. *Angew. Chem. Int. Ed.* **2017**, *56*, 10821 –10825.
[7] G. Xu, M. Sollogoub et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 7591-7597.

New insights into the self-assembly processes of alkynyl (1,2-dppe) Ru^{II} compounds

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Small molecules self-assembly through non-covalent interactions is ubiquitous and central to achieve high charge transport.[1-2] Self-assembly (SA) occurring in solution may lead to the formation of 1D supramolecular polymers or 2D nanosheets.[3] SA may also appear at the solid state and has been well-developed since the discovery of liquid crystals (mesogens) for display technologies.[4] In those fields, organometallic molecules have shown their superiority compared to purely organic compounds because introducing a metal into the molecular backbone has brought about a wealth of new properties such as (chiral)luminescence,[5] complementary weak metallophilic interactions that have strengthened and guided the supramolecular process[6] to name a few. We recently reported the preparation of a new Ru^{II} bis-acetylides complex equipped with a mesogenic ligand,[7] which was able to form micrometer long ribbons that eventually trapped aromatic solvent molecules to form a gel. Inspired by those outcomes, we have explored new scaffolds and investigated their self-assembly behaviour. While monometallic compounds lead to 1D objects, bimetallic molecules afford 2D nanosheets thanks to an *isodesmic* process (Figure 1).

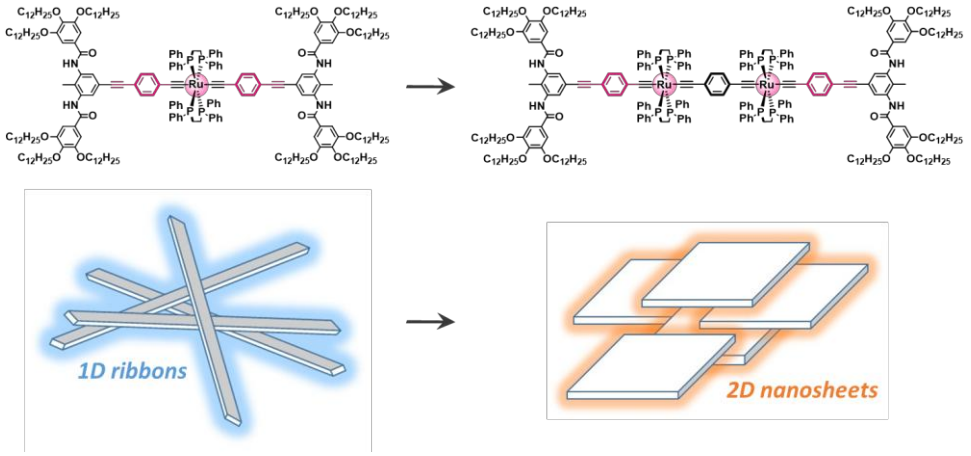

Figure 1. 1D (2D) objects formed by self-assembly of mono(bi)metallic species

References

[1] R. De, S. K. Pal, *Chem. Commun.* **2023**, *59*, 3050.

[2] D. B. Amabilino, D. K. Smith, J. W. Steed, *Chem. Soc. Rev.* **2017**, *46*, 2404.

[3] T. F. A. De Greef, M. M. J. S. Martin Wolffs, A, P. H. J. Schenning, R. P. Sijbesma, E. W. Meijer, *Chem. Rev.* **2009**, *109*, 5687; L. Kleine-Kleffmann, A. Schulz, V. Stepanenko, F. Würthner, *Angew. Chem. Int. Ed.* **2023**, *62*, e202314667.

[4] D. Pucci, B. Donnio, in *Handbook of Liquid Crystals: 8 Volume Set, Second Edition* Wiley-VCH Verlag GmbH & Co. KGaA.: **2014**

[5] Y. Han, Y. Yin, F. Wang, *Angew. Chem. Int. Ed.* **2021**, *60*, 14076.

[6] Q. Wan, X. S. Xiao, W. P. To, W. Lu, Y. Chen, K. H. Low, C. M. Che, *Angew. Chem. Int. Ed.* **2018**, *57*, 17189.

[7] O. Galangau, D. Daou, N. El Beyrouti, E. Caytan, C. Meriadec, F. Artzner, S. Rigaut, *Inorg. Chem.* **2021**, *60*, 11474 ; O. Galangau, E. Caytan, W. T. Gallonde, I. de Waele, F. Camerel, S. Rigaut, *Eur. J. Inorg. Chem.* **2023**, *26*, e202200579.

The Hitchhiker's Guide to Mechanical Isomerism: Isometric motifs and their stereoselective synthesis

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Upon mechanical bond formation, achiral sub-components can be desymmetrised to yield chiral and geometric isomers.[1] When considering the catenation of oriented and/or facially dissymmetric macrocycles (**I** and **II**) and rotaxane formation using the same with bilaterally symmetric axles (**III** and **IV**), seven distinct isomeric motifs can be formed (**V**-**XI**).[2] Of these, only mechanically planar chiral systems (**V** and **VIII**) have been studied significantly and axially chiral rotaxanes **XI** were only discovered in 2022.[3] Here we report a study of the factors controlling the selective synthesis of both of geometric and chiral mechanical isomers and the first direct enantioselective synthesis of a mechanically axially chiral rotaxane. All of the fundamental mechanical stereoisomers can now be synthesised stereoselectively.[4,5]

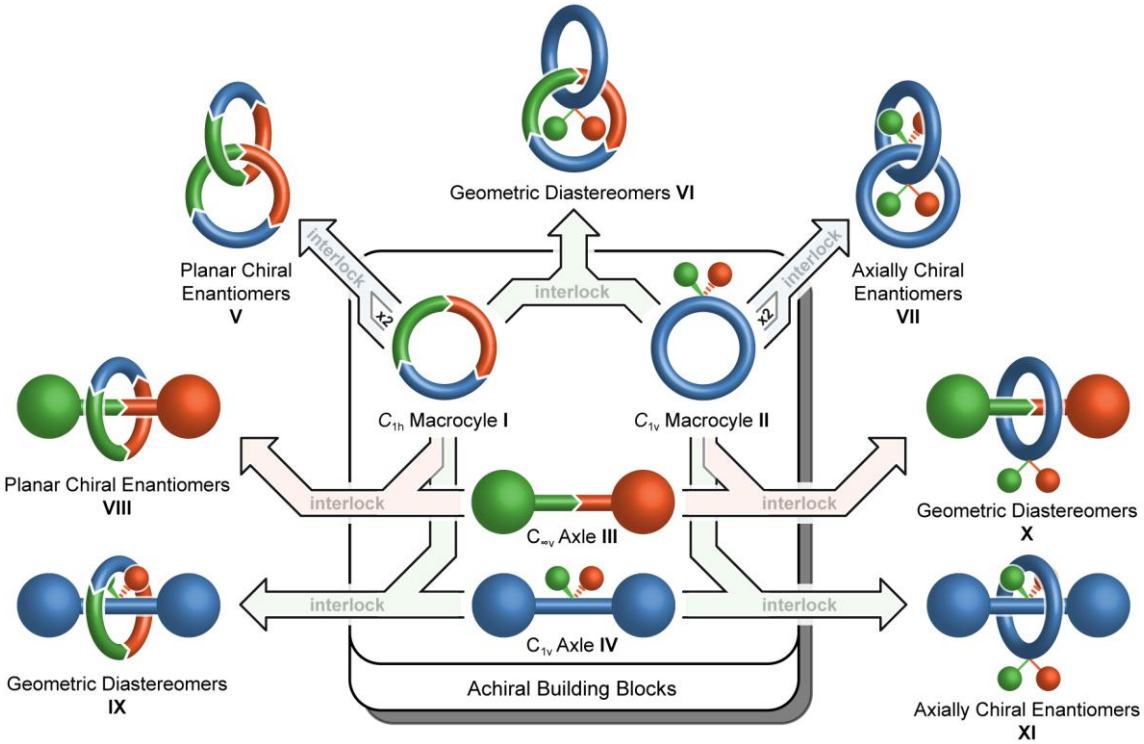

Figure 1. Mechanical isomers of [2]catenanes and [2]rotaxanes through combination of oriented or facially dissymmetric macrocycles **I** and **II** and bilaterally symmetric axles **III** and **IV**.

References

[1] H. L. Frisch and E. Wasserman, *J. Am. Chem. Soc.*, 1961, **83**, 3789–3795.
[2] E. M. G. Jamieson, F. Modicom, & S. M. Goldup, *Chem. Soc. Rev.*, 2018, **47**, 5266-5311.
[3] J. R. J. Maynard, P. Gallagher, D. Lozano, P. Butler & S. M. Goldup, *Nat. Chem.*, **14**, 1038–1044 (2022).
[4] A.Savoini, P. R. Gallagher, A. Saady & S. M. Goldup, 2024, DOI: 10.1021/jacs.3c14594.
[5] P. R. Gallagher, A. Savoini, A. Saady, J. R. J Maynard, P. Butler, G. J. Tizzard & S. M. Goldup, 2024, DOI: 10.1021/jacs.3c14329.

DYNAMIC PORPHYRIN CAGES WITH EXCEPTIONAL FEATURES FOR HOST-GUEST CHEMISTRY

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In recent times, organic molecular cages based on porphyrins have been widely studied due to their exceptional ability to host different kind of molecules into their inner cavities as well as their interesting (photo)catalytic properties. [1,2]

In this communication, novel porphyrin cages were attained by employing the self-assembly strategy and the bottom-up approach, where dynamic covalent bonds were formed by means of the imine condensation reaction in thermodynamic conditions. Two isomeric cages can be achieved depending on whether the amine group is placed in the porphyrin or in the linker, called ***N=C*** and ***C=N*** cages, respectively. Furthermore, according to the arrangement of these **imine bonds**, the molecular cage could present two main conformations: ***extended*** and ***compact***.

Interestingly, the conformational equilibrium can be modified to obtain the less favored conformation through the employment of molecules with different sizes to establish host-guest complexes. As a result, a flexible inner cavity is obtained, and outscoring values of K_a are registered.

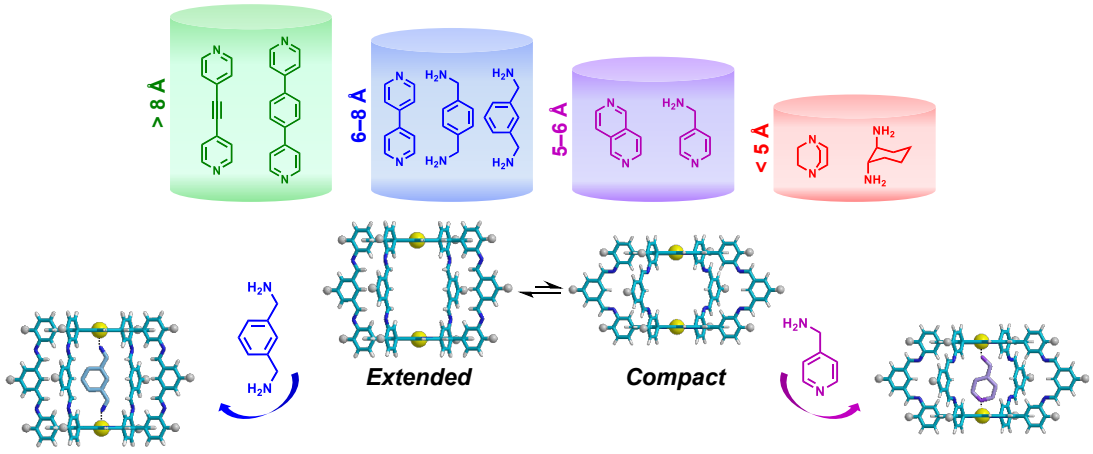

Figure 1. Conformational control in porphyrin cage through host-guest chemistry.

Acknowledgements

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References

[1] Durot, S.; Taesch, J.; Heitz, V. *Chem. Rev*. **2014**, *114*, 8542.
[2] Mukhopadhyay, R. D.; Kim, Y.; Koo, J.; Kim, K. *Acc. Chem. Res*. **2018**, *51*, 2730-2738.

Effect of the dimensionality in [M(*m*-SPhCO$_2$R)]$_n$ (M= Cu, Ag; R= H, Me) Coordination Polymers on the photophysical properties

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The development of new luminescent materials constitutes an active field of research as their application can be very diversified. [1] [2] Among them, we find a lot of luminescent solids made of Critical Raw Materials (CRM), like heavy rare earth. Because the sustainability of these elements is a problem, the use of d^{10} coinage metals, such as Cu and Ag, to design new materials can be a solution, as these metals exhibit good emission efficiency and various luminescent properties. [1] [3] Coordination polymers (CPs), have been reported as a good alternative, and more specifically thiolate-based ligand CPs, due to their ability to form stable compounds thanks to the strong interaction between the sulfur and the d^{10} coinage metal. [3]

In this context, four CPs ([Cu(*m*-SPhCO$_2$H)]$_n$ (**1**), ([Ag(*m*-SPhCO$_2$H)]$_n$ (**2**), [Cu(*m*-SPhCO$_2$Me)]$_n$ (**3**) and, [Ag(*m*-SPhCO$_2$Me)]$_n$ (**4**) have been prepared to understand the effect of the carboxylic acid and the methyl ester in the *meta* position of the thiolate ligands on the dimensionality of the materials and their physical properties.(**Fig. 1**) The four compounds were obtained in solvothermal conditions and the structures were determined by single crystal and powder x-ray diffraction. While (**1**) and (**2**) are 2D lamellar materials and non-luminescent at room temperature, (**3**) and (**4**) have a 1D structure and exhibit intense photoemission. (**Fig. 1**)

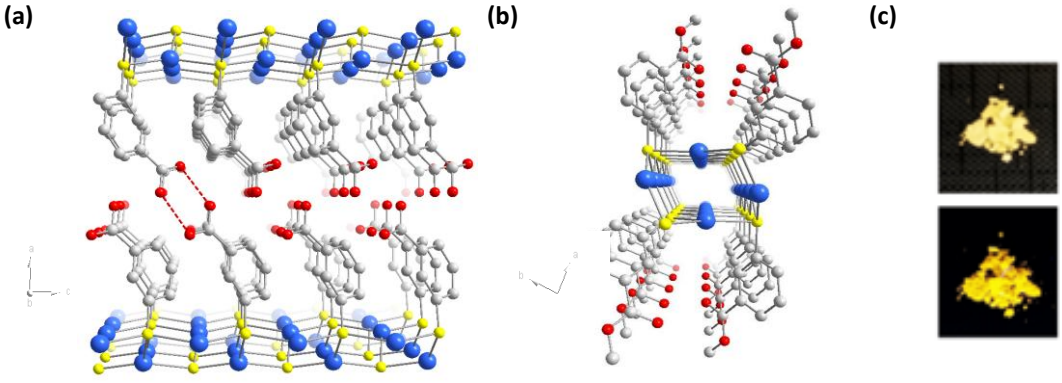

Fig.1 (a) Projection of the 2D lamellar structure of **(2)** and **(b)** projection of the 1D structure of **(4)**. Blue : Ag, yellow : S, grey : C, Hydrogen are omitted for clarity. Hydrogen bonds are represented with red dashed lines. **(c)** Photograph of **(4)** at RT under ambiant light (top) and under UV light (bottom).

References

[1] O. Veselska, D. Podbevšek, G. Ledoux, A. Fateeva, A. Demessence, *Chem. Commun.*, **2017**, 53, 12225.

[2] J-Q. Liu, Z-D. Luo, Y. Pan, A. Kumar Singh, M. Trivedi, A. Kumar, *Coord. Chem. Rev.,* **2020**, 406, 213145.

Self-assembly of triarylamine-based macrocycles

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Triarylamines are a class of organic compounds renowned for their versatile properties in polymer science and organic electronics.[1] Previously, our research group reported the first triarylamine-based conjugated hexaaza[1_6]paracyclophane macrocycle, featuring six lateral amide functions, which made possible the self-assembly of macrocycles into tubular structures with delocalization of charge carriers achieved through bonds in the plane of the macrocycle and through space between macrocycles along the supramolecular stacks.[2]

In this work, we will describe how the substitution pattern of the core macrocycle allows us to tune the properties of the assembled nanotubes. We have expanded our library of hexaaza[1_6]paracyclophane macrocycles by designing and synthesizing a series of substituted triarylamine-based conjugated macrocycles bearing a different number of lateral amide functions. Density functional theory calculations (DFT) provided us with an insight into the geometry of macrocyclic monomer and self-assembled polymer (Figure 1). Using chemical oxidation monitored by UV-Vis-NIR spectroscopy, we observed an increase in the radical cations' localization which is strongly dependent on the oxidation level. Further characterization by (pulse) EPR spectroscopy provided additional insights into the electronic and magnetic properties of these new materials.

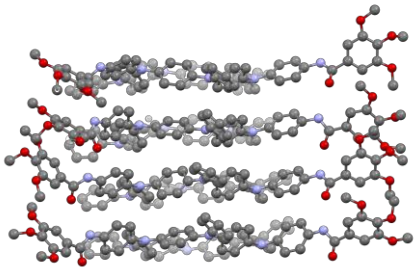

Figure 1. DFT-calculated structure of self-assembled hexaaza[1_6]paracyclophane trisamide.

Acknowledgements

This work was supported by the Interdisciplinary Thematic Institute ITI-CSC via the IdEx Unistra (ANR-10-IDEX-0002) within the program Investissement d'Avenir. A.G. thanks the CSC Graduate School funded by the French National Research Agency (CSC-IGS ANR-17-EURE-0016) for a PhD fellowship.

References

[1] Wang, J.; Liu, K.; Ma, L.; Zhan, X. *Chem. Rev.* **2016**, *116*, 14675–14725.

[2] Picini, F.; Schneider, S.; Gavat, O.; Vargas Jentzsch, A.; Tan, J.; Maaloum, M.; Strub, J.; Tokunaga, S.; Lehn, J.; Moulin, E.; Giuseppone, N. *J. Am. Chem. Soc.* **2021**, *143*, 6498–6504

Calix[n]phyrin condensation: A Tool for the Construction of Flexible Mechanically Interlocked Molecules

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Rotaxanes are mechanically interlocked molecules composed of a bulky-group-stoppered linear axle passing through the macrocyclic ring large enough to accommodate molecular thread. They have found multiple applications due to their capability to perform various types of molecular movements.[1-3] Herein we report the synthesis and reactivity of dipyrromethene-stoppered rotaxanes acting as building blocks for rotaxanes and catenanes. The introduction of porphyrinoid moiety within the architecture allows for observing a new type of dynamic behaviour of the MIM relying on the macrocycle bending.

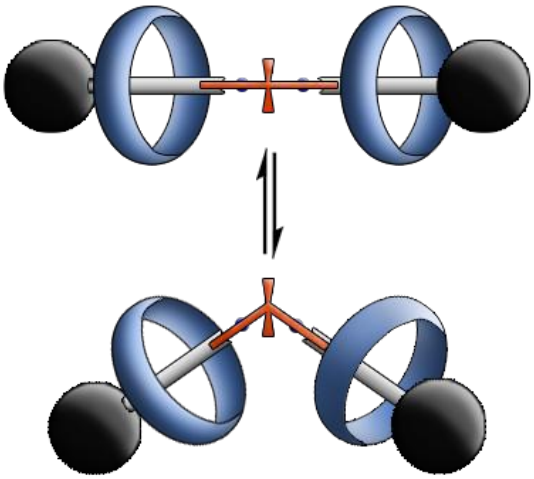

Figure 1. The bending motion observed for porphyrinoid-incorporated [3]rotaxane.

Acknowledgements

This work was supported by the National Science Centre of Poland upon Grant 2020/38/E/ST4/00024.

References

[1] Y. Wu, M. Frasconi, W. G. Liu, R. M. Young, W. A. Goddard III, M. R. Wasielewski, J. F. Stoddart, *J. Am. Chem. Soc.* **2020**, *142, 11835−11846*

[2] T. Kumpulainen, M. R. Panman, B. H. Bakker, M. Hilbers, S. Woutersen, A. M. Brouwer, *J. Am. Chem. Soc* .**2019**, *141, 19118−19129*

[3] H. V. Schröder, A. Mekic, H. Hupatz, S. Sobottka, F. Witte, L. H. Urner, M. Gaedke, K. Pagel, B. Sarkar, B. Paulusa, C. A. Schalley, *Nanoscale,* **2018**, *10, 21425–21433*

PROBING THE SUPRAMOLECULAR ASSEMBLIES OF A TRIAZATRUXENE-BASED CAGE

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The coordination driven self-assembly methodology provides access to discrete three-dimensional structures with high yields thanks to the reversibility and the high directionality of the coordination bond.[1] Most of these polyhedra exhibit a cavity that can be used for host-guest binding, with possible applications in catalysis or drug delivery for instance. In this context, our team has developed molecular hosts which are able to trigger the guest release thanks to a redox stimulation.[2-4] Similarly to the case of macrocycles which allow the construction of [2]-catenanes, the 3D cavity of coordination cages allows access to interpenetrated species, namely interlocked cages, the latter being characterized by a high compactness.[5]
In this context, we have been interested in controlling the self-assembly process of an electron rich triazatruxene-based ligand **L** with an electro-deficient bis-rhodium complex **M**. This association leads, depending on the experimental conditions, to the selective formation of: *i)* a cage (**M_3L_2**), *ii)* two interlocked cages (**$[M_3L_2]_2$**) or *iii)* a host-guest complex (**$2L\subset M_3L_2$**) where the relative location of donating and accepting units is perfectly controlled (Figure 1). Details of their formation, their structure as well as their electronic properties will be presented.

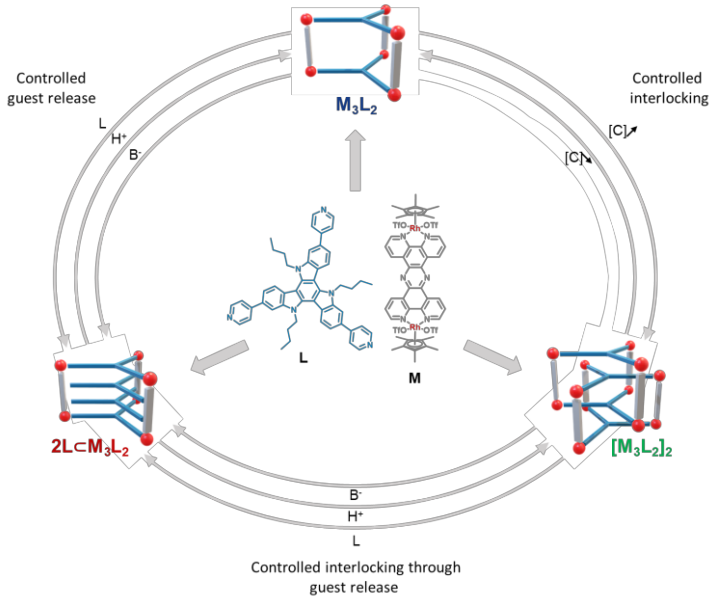

Figure 1. The three structures which are obtained upon self-assembling ligand **L** and complex **M**.

References

[1] R. Chakrabarty, P. S. Mukherjee, P. J. Stang, *Chem. Rev.*, **2011**, *111 (11)*, 6810-918.
[2] V. Croué, S. Goeb, G. Szalóki, M. Allain, M. Sallé, *Angew. Chem. Int. Ed.*, **2016**, *55 (5)*, 1746–1750.
[3] G. Szalóki, V. Croué, V. Carré, F. Aubriet, O. Alévêque, E. Levillain, M. Allain, J. Arago, E. Orti, S. Goeb, M. Sallé, *Angew. Chem. Int. Ed.*, **2017**, *56 (51)*, 16272–16276.
[4] S. Goeb, M. Sallé, *Acc. Chem. Res.*, **2021**, *54 (4)*, 1043–1055.
[5] D. Luo, B. Pan, J. Zhang, C. Ma, Y. Su, Q. Gan, *Chin. Chem. Lett.*, **2021**, *32 (4)*, 1397–1399.

Chiral luminescent iridium(III) metalloligands and their self-assembly into luminescent coordination polymers

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As demonstrated more than a century ago by Alfred Werner,[1] molecular chirality in coordination compounds may originate not only from the ligands but also from the metal atom itself. Quite surprisingly, while several chiral-at-metal complexes have been reported, few cases deal with their use as chiral building blocks for the generation of heterometallic coordination polymers (CP), also known as mixed-metal-organic frameworks.[2] Indeed, in most of the examples employing chiral coordination compounds as metallatectons or metalloligands, the chirality is associated with the presence of asymmetric carbon atoms on the metalloligand scaffold. Furthermore, whereas *tris*-chelate octahedral Iridium complexes have been used to form luminescent CPs,[3] their intrinsic chirality is usually not exploited and those metalloligands are employed as racemates.

Herein, the synthesis of a family of chiral-at-metal *tris*-chelate Iridium complexes that combine chiral and luminescent information and are equipped with peripheral coordination sites will be detailed. Formation of luminescent heterometallic CPs upon self-assembly with Cd atoms will be highlighted.[4]

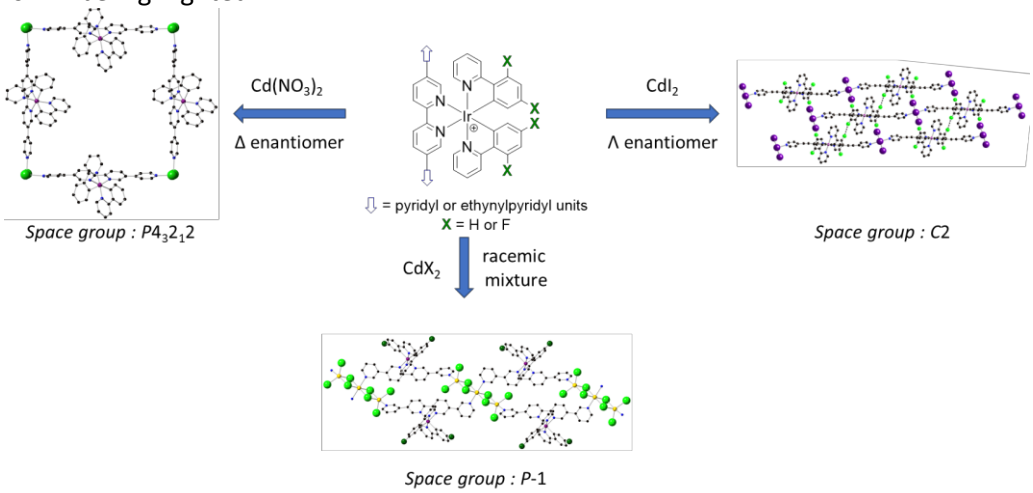

Figure 1. General chemical structure of the iridium metalloligands studied and X-Ray structures of three heterometallic CPs obtained upon self-assembly with Cd(II) metal centres.

References

[1] A. Werner, V. King, *Ber. Dtsch. Chem. Ges.*, **1911**, *44*, 1887-1898.
[2] G. Kumar, R. Gupta, *Chem. Soc. Rev.*, **2013**, *42*, 9403–9453
[3] D. Rota Martir, E. Zysman-Colman, *Coord. Chem. Rev.*, **2018**, *364*, 86-117.
[4] C. Xu, A. Guenet, N. Kyritsakas, J.-M. Planeix, M. W. Hosseini, *Chem. Commun.*, **2015**, *51*, 14785–14788; C. Xu, A. Guenet, N. Kyritsakas, J.-M. Planeix, M. W. Hosseini, *Inorg. Chem.*, **2015**, *54*, 10429–10439; M. Florent, N. Kyritsakas, J.-M. Planeix, A. Guenet, M. W. Hosseini, *Dalton Trans.*, **2021**, *50*, 15924-15934.

Supramolecular assembly of electro- and photoactive π-functional foldamers

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Over the last decades, supramolecular chemistry has allowed major breakthroughs in miscellaneous research and applied fields. In this context, and inspired by naturally-occurring molecules, chemists have dedicated much effort to design oligomers that fold into well-defined conformations and are named foldamers.[1]
In particular, helical foldamers have shown their interest in the fields of catalysis,[2] selective host-guest encapsulation[3], or more recently stimuli-responsive materials.[4-5] Among the diversity of foldamer skeletons, some are able to hybridize and form multiple helices.[6] The latter present different geometrical features and hence, new physicochemical properties, which could be of interest to develop original materials with singular optoelectronic properties.
To this end, helical foldamers grafted with luminescent and electroactive units were designed and synthesized. These entities can organize into supramolecular associations, directing the conformation of foldamers and subsequently impacting their physical and chemical attributes. The presented results will cover supramolecular assembly in solution and the impact on the optical properties of these foldamers.

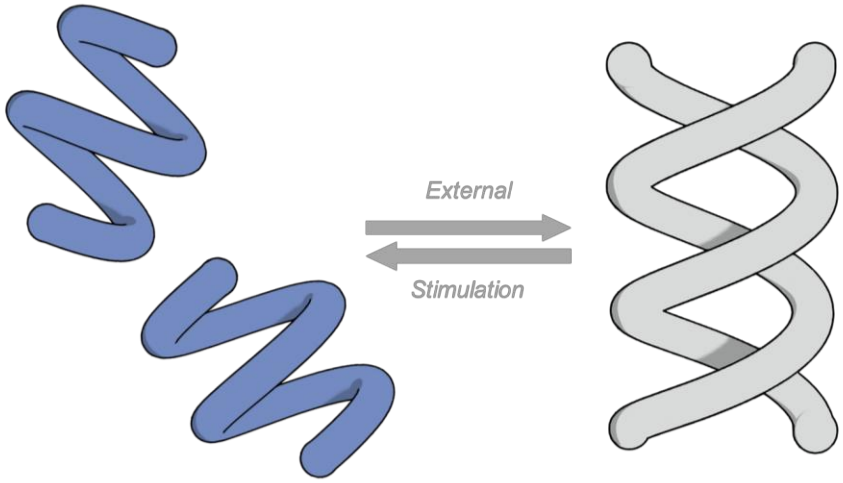

Figure 1. Control of the single-to-double helix equilibrium through external stimulation

References

[1] S.H. Gellman, *Acc. Chem. Res.* **1998**, 31, 173-180
[2] R.A. Smaldone, J.S. Moore, *Chem. Eur. J.* **2008**., 14, 2650-2657
[3] F. Aparicio, L. Faour, M. Allain, D. Canevet, M. Sallé, *Chem. Commun.* **2017**, 53, 12028–12031.
[4] C. Adam, L. Faour, V. Bonnin, T. Breton, E. Levillain, M. Sallé, C. Gautier, D. Canevet, *Chem. Commun*. **2019**, 55, 8426-8429
[5] L. Faour, C. Adam, C. Gautier, S. Goeb, M. Allain, E. Levillain, D. Canevet, M. Sallé, *Chem. Commun.*, **2019**, 55, 5743–5746.
[6] V. Berl, I. Huc, R. G. Khoury, J.-M. Lehn *Chem. Eur. J.* **2001**, 7, 2810–2820

Towards dual light control of a catalytically-driven chemical reaction cycle

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Chemically-fueled chemical reaction networks (CRNs) are key in controlling dissipative self-assembly. Having catalysts gating fuel consumption for both the activation and deactivation chemistry of (assembly-prone) monomers and controlling the catalytic activity with an external stimulus would provide better control over where, when, and how long self-assembled structures can form. Here we achieve light control over monomer activation and subsequent assembly into supramolecular fibers, and partial light control over deactivation and fiber disassembly. Activation proceeds via photoredox catalysis under visible light, whereas deactivation is achieved by organometallic catalysis that relies on a photocaged pre-fuel activated by ultraviolet light. Overall, we show how supramolecular fibers can be formed by visible light and how their destruction is accelerated by ultraviolet light.

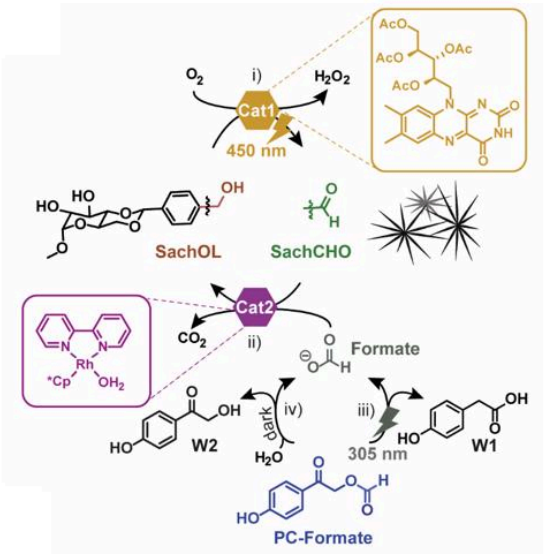

Figure 1. Towards dual wavelength control over a catalytically-driven CRN, forming transient SachCHO fibers. Oxidation of SachOL to SachCHO by using riboflavin tetraacetate (RFTA, **Cat1**) by 450 nm irradiation. Reduction of SachCHO to SachOL by $[Cp^*Rh(Bpy)(H)]^+$, which is generated from $[Cp^*Rh(Bpy)(H_2O)]^{2+}$(**Cat2**) using formate as hydride source. Photocleavage of p-hydroxyphenacyl formate (**PC-Formate**), releases formate with 305 nm light producing p-hydroxyphenylacetic acid (W1) as main by-product. PC-Formate also releases the fuel in the dark at longer times upon hydrolysis, producing α-hydroxyketone (W2) as by-product.

Acknowledgements

Write here your acknowledgements in Calibri 11pt.

References

More details at: https://doi.org/10.26434/chemrxiv-2023-rxm8h-v2

Designing aromatic oligoamide cone-shaped carbohydrate receptors

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Despite the importance of carbohydrates for life, as building blocks or for intercellular communication, their recognition still proves to be a challenge, whether with natural or artificial receptors. The reason for this is that saccharides are isomers including various tautomeric and anomeric forms. The competitive interactions of the saccharide with polar solvents, such as H_2O, and the receptor are also very challenging.[1] Foldamers, a class of artificial receptors for carbohydrates, are helically folded artificial receptors. They fall into three distinct categories based on the accessibility of their appendices: open-ended helices, capsules and cones (Figure 1A).[2]

The aromatic oligoamide capsules demonstrated high selectivity for specific mono- or disaccharides, as they completely segregate the saccharides from their environment.[3] While capsules are effective up to a certain size of oligosaccharides, their utility diminishes beyond this threshold, like for glycoproteins. In these cases, smaller segments could be recognized by cone-shaped receptors.

This work discusses four strategies for creating cones from heterocyclic oligoamide sequences: self-assembly, head-to-head linker, staple and “unimolecular elongation” (Figure 1B). The interactions between these cone structures and different saccharides have been analyzed using 1D and 2D NMR, CD, and X-ray structural techniques.

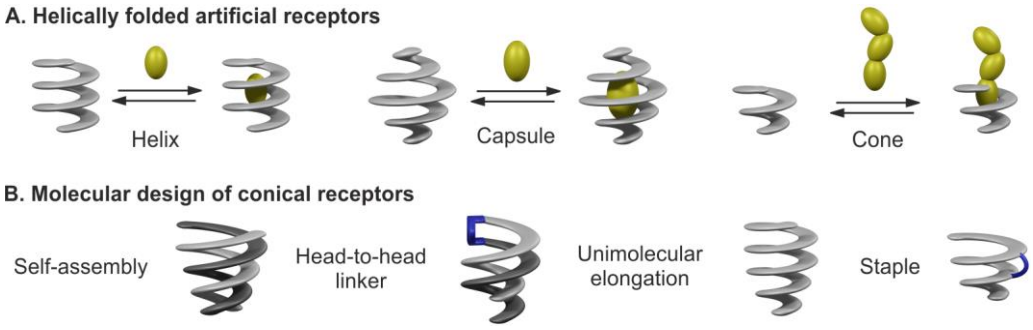

Figure 1. **A**. Schematic representation of the recognition modes of helically folded artificial receptors (grey) and guests (yellow). **B.** Schematic representation of four molecular designs of conical receptors from heterocyclic oligoamide sequences.

References

[1] E. Klein, Y. Ferrand, N. P. Barwell, A. P. Davis, *Angew. Chem. Int. Ed.*, **2008**, *47*, 2693-2696.
[2] Y. Ferrand, I. Huc, *Acc. Chem. Res.*, **2018**, *51*, 970-977.
[3] N. Chandramouli, Y. Ferrand, G. Lautrette, B. Kauffmann, C. D.Mackereth, M. Laguerre, D. Dubreuil, I. Huc, *Nature Chemistry*, **2015**, *7*, 334-341.

From the threading of linear molecules through a macrocycle thanks to boron to the synthesis of a rotaxane.

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Several molecular assemblies containing one or more boron atoms have been reported in the litterature.[1] Boron offers indeed a rich chemistry thanks to its ability to form bonds with many common atoms (C, O, N, S, …) while the lability of these bonds can be very varied. However, the synthesis of interlocked molecules with boron as a gathering atom had never been described in the literature except for a very recent work from Schaufelberger's group.[2] We describe herein our recent efficient method for the threading of macrocycles using boron from BODIPYs and boron diketonates.[3] This work eventually led to the synthesis of a new kind of rotaxane after stoppering and removal of the boron.

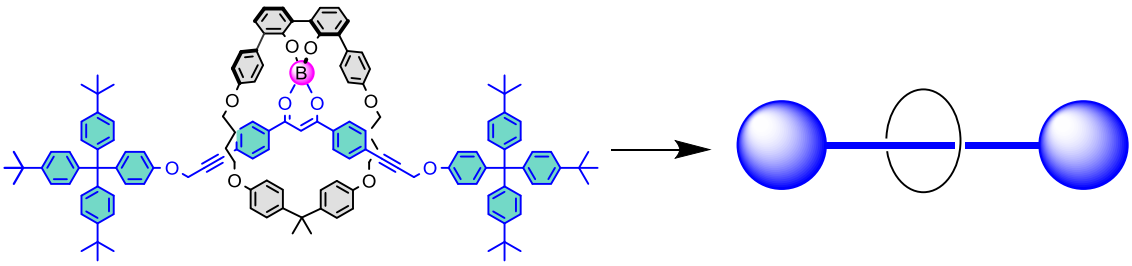

Figure 1. Removal of boron in a boron-threaded and stoppered molecule for the synthesis of a rotaxane.

References

[1] S. Yamamoto, H. Iida, E. Yashima, *Angew. Chem. Int. Ed*, **2013**, *52*, 6849-6853; N. Christinat, R. Scopelliti, K. Severin, *Chem. Commun.*, **2008**, *31*, 3660-3662; B. Nisanci, S. Sahinoglu, E. Tuner, M. Arik, I. Kani, A. Dastana, Ö. A. Bozdemir, *Chem. Commun.* **2017**, *53*, 12418-12421; T. Nakamura, G. Yamaguchi, T. Nabeshima, *Angew. Chem. Int. Ed.* **2016**, *55*, 9606-9609; D. Stoltenberg, S. Lüthje, O. Winkelmann, C. Näther, U. Lüning, *Eur. J. Org. Chem.,* **2011**, 5845-5859.

[2] J. Yu, M. Gaedke, S. Das, D. L. Stares, C. A. Schalley, F. Schaufelberger, **2023**, *ChemRxiv* https:///doi.org/10.26434/chemrxiv-2023-v95p8.

[3] M. Hicguet, L. Verrieux, O. Mongin, T. Roisnel, F. Berrée, A. Fihey, B. le Guennic, Y. Trolez, *Angew. Chem. Int. Ed.*, **2024**, e202318297, https://doi.org/10.1002/anie.202318297.

Effects of Functional Groups on the Adsorption of CO2 in Pillar[5]arenes

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In this study, density functional theory was employed to investigate how varying functional groups at the rim affect CO2 adsorption on P[5]A. Comparing -OH [1], -OCH3, =O, and -OCOH groups, we observed that P[5]A-OCH3 exhibited the highest CO2 adsorption energy due to an increase in hydrogen bonds. This increased adsorption energy is attributed to the formation of more hydrogen bonds between CO2 and P[5]A-OCH3 than in the P[5]A-OH. The top-in configuration exhibits no CO2 adsorption, associated with hydrogen bonds but more robust π-π interactions with P[5]A. In P[5]A-OCOH, CO2 adsorbed on the top and bottom functional groups through weak hydrogen bonds and π-π interactions. A novel configuration involved CO2 situated between two P[5]A functional groups, featuring weak hydrogen bonds and electrostatic interactions. This study sheds light on the diverse CO2 adsorption behaviors of P[5]A based on specific rim functional groups.

Acknowledgements

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References

[1] Q. Duy Ho and E. Rauls, ChemistrySelect 8, e202204215 (2023).

Supramolecular Janus nanocylinders: controlling their characteristics through the process or chemistry

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Janus particles are asymmetric nanoparticles with two faces of different compositions and features. This makes them relevant for applications as sensors, in two-color display panels, in catalysis or as emulsion stabilizers[1]. Janus nanorods (JNR) are very difficult to prepare due to their nanometric dimensions and anisotropic character, but this simultaneously makes them very relevant for applications where high surface areas and high aspect ratios are needed. The only two methods reported prior to our work to prepare JNR rely on self-assembly of copolymers bearing strongly incompatible arms, which limits the range of polymers which can be used on either face of the JNR. Recently, our team reported the first strategy which affords the formation of JNR without relying on the polymer arm incompatibility, but on the self-assembly in solution of two polymers end-functionalized with non-symmetrical and complementary hydrogen bonding stickers (Figure 1) [2,3]. It was however shown that this strategy led to frozen JNR in aqueous medium; which requires to pre-dissolve both polymers in an organic common solvent exhibiting a strong hydrogen bond competing ability and then adding water. The mechanism of their formation was unknown.

Here, we report the investigation of the mechanism of formation of the JNR from the initial state in pure organic solvent prior to water addition. It was shown that the polymers may be either pre-assembled or dissolved as unimers in the organic co-solvent, depending on its nature. This affects the final characteristics of the JNR (length, diameter) upon water addition and therefore affords a convenient kinetic way to control these characteristics[4]. Additionally, the characteristics of the JNR can be affected by varying the degree of polymerization and chemical nature of the polymer arms. This fine degree of control makes the JNR relevant for biomedical applications, which is a topic we are currently investigating.

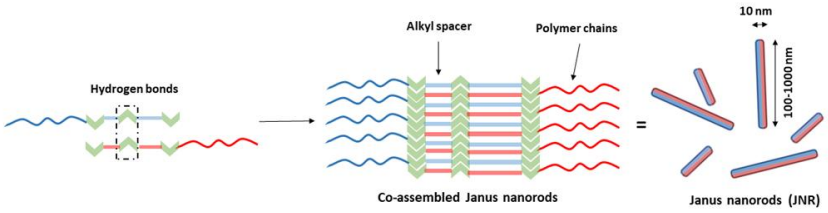

Figure 1. Scheme of supramolecular Janus nanorods co-assembly

Acknowledgements

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References

[1] Walther, A et al, *Soft Matter*, **2008**, 4, 663–668
[2] Choisnet,T et al, *Chem. Commun*, **2019**,55, 9519-9522
[3] Han, S. et al, *Nature Commun*. **2020**, 11, 4760

A Transient Supramolecular Glue for Temporal Regulation of Augmented Biocatalytic Reactions

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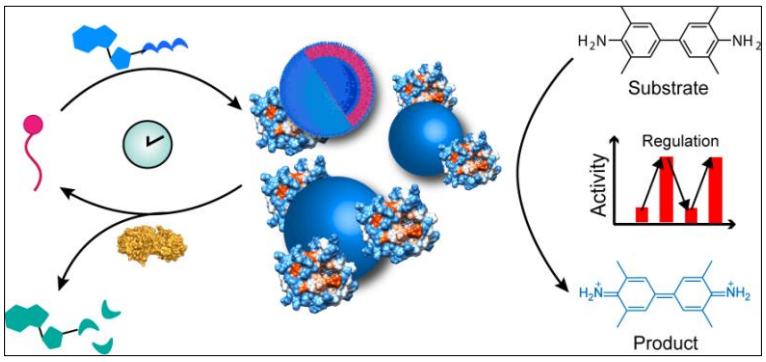
Transient control over biomolecular components is essential for intracellular reaction networks, robust signal transductions, and efficient cell-cell communications.[1] Similarly, the temporal modulation of enzyme activity makes dynamic control of biological transmission and metabolism possible. In this work, I will present synthetic supramolecular systems with multivalent non-covalent interactions, termed “molecular glue”, as biomolecular adhesion to tailor several natural processes. Given the potential of molecular glues yet unexplored for the augmentation and regulation of enzyme catalysis, I would present a vesicular glue system for the amplification of biocatalytic processes. The system forms bilayer vesicle structures by utilizing guanidinium group-bearing surfactants and adenosine triphosphates (ATP), employing ATP's dual role as a structural element and a functional "glue" to anchor enzymes onto the vesicle surface through non-covalent interaction with exposed Adenine.[2] Unlike covalent systems operating at equilibrium, this transient vesicular glue system mimics far-from-equilibrium biological dynamics, allowing for controllable lifetime and transient regulation via ATP concentration oscillation. Modulating the effective concentration of proteins on the vesicular glue provides us with an efficient mechanism to gain spatiotemporal control over protein activity. Further, the transient upregulation and control of complex cascade reaction networks on the vesicles present an adaptable and dynamic system emulating heterogeneous cellular processes.



Scheme 1. Schematic representation of the transient assembly resulting amplified enzymatic activity.

Acknowledgements

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References

[1] E. Karsenti, *Nat. Rev. Mol. Cell Biol.*, **2008**, *9*, 255–262.

[2] A. Kamra; S. Das; P. Bhatt; M. Solra; T. Maity; S. Rana, *Chem. Sci.*, **2023**, *14*, 9267-9282.

Exercising ligand denticity for the construction of interlocked imine architectures: self-assembly of bis-M_2-stabilised [2]catenane

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The concept of molecular self-assembly plays a pivotal role in supramolecular chemistry. The synthetic methodology allows for the construction of various, often topologically complex supramolecular architectures, including Mechanically Interlocked Molecules (MIMs). The latter constitute a special group of compounds characterized by the existence of a mechanical bond.[2] Prominent instances include catenanes, which consist of two or more interwoven macrocyclic rings,[3] and molecular knots,[4,5] where a single macrocycle is entangled in a manner reflecting non-trivial topologies elucidated by mathematical knot theory. Herein we report on the synthesis and characterization of a bis-M2-stabilised [2]catenane obtained with the use of bipyridine-incorporating diamine and heterocyclic dialdehyde forming a tetradentate coordination motif upon the imine condensation.

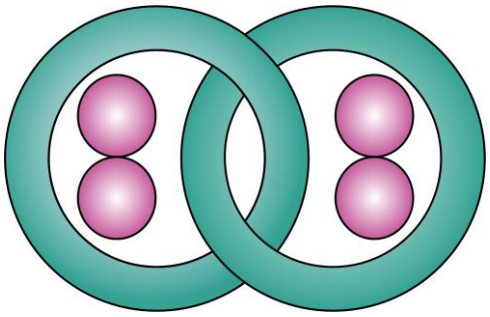

Figure 1. Graphical representation of bis-M2-stabilised [2]catenane.

Acknowledgements

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References

[1] J. R. Nitschke, *Acc. Chem. Res.* **2007**, *40,* 103–112.
[2] C. Bruns, J. F. Stoddart, *The Nature of the Mechanical Bond: From Molecules to Machines*, Wiley, New York, **2016**.
[3] T. Prakasam, M. Lusi, M. Elhabiri, C. Platas-Iglesias, J.-C. Olsen, Z. Asfari, S. Cianférani-Sanglier, F. Debaene, L. J. Charbonnière, A. Trabolsi, *Angew. Chem. Int. Ed.* **2013**, *52*, 9956–9960.
[4] K. S. Chichak, S. J. Cantrill, A. R. Pease, S.-H. Chiu, G. W. V. Cave, J. L. Atwood, J. F. Stoddart, *Science* **2004**, *304*, 1308–1312.
[5] A. Sarwa, A. Białońska, M. Sobieraj, J. P. Martínez, B. Trzaskowski, B. Szyszko, *Angew. Chem. Int. Ed.* **2024**, *63*, e202316489.

Synthesis of hexaphyrin-cyclodextrin receptors for unorthodox (anti)aromatic π-type interactions

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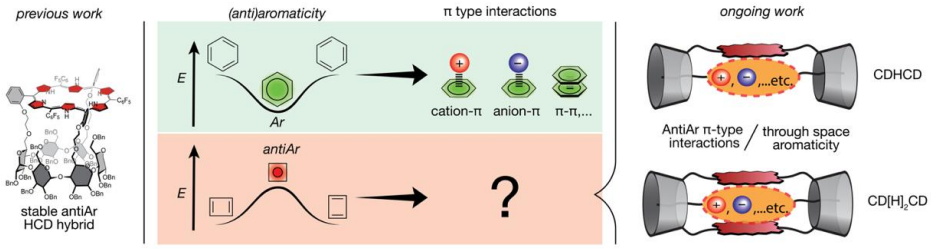
According to Hückel theory, aromaticity is the stabilization of cyclic molecules containing [4n+2] delocalized π electrons.[1] The corresponding gain in stability leads to a ubiquitous representation of this character in the chemical landscape, giving rise to a wide variety of π-type interactions: π•••π stacking,[2] cation•••π,[3] anion•••π,[4] C-H•••π.[5] On the contrary, antiaromaticity containing [4n] delocalized π electrons destabilize cyclic molecules.1 Due to their inherent instability, antiaromatic compounds are difficult to synthesize and handle. Consequently, there is still little known about antiaromatic π-type interactions. However, porphyrinoid macrocycles such as norcorroles[6] or hexaphyrins[7] are known to stabilize antiaromaticity and provided the first evidence of the antiaromaticity within confined nanospace[8] or molecular junction.[9]

Recently, we have developed a family of hybrid molecules composed of cyclodextrin (CD) and hexaphyrin (H) subunits able to stabilize aromatic and antiaromatic states.[10,11] We are now aiming to synthesize hybrid molecules with a sandwich design using two cyclodextrins and two hexaphyrins. The targeted sandwich hybrid will be used as a tool to explore π-type interactions of antiaromaticity (cation-π, anion-π, π-π) and study through-space aromaticity.



References

[1]. Fernández, I. *Aromaticity - Modern Computational Methods and Applications*. Elsevier Inc.; 2021.
[2]. Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525–5534.
[3]. Yamada, S. *Chem. Rev.* **2018**, *118*, 11353–11432.
[4]. Schottel, B. L.; Chifotides, H. T.; Dunbar, K. R. *Chem. Soc. Rev.* **2008**, *37*, 68–83.
[5]. Kiessling, L. L.; Diehl, R. C. *ACS Chem. Biol.* **2021**, *16*, 1884–1893.
[6]. Ito, T.; Hayashi, Y.; Shimizu, S.; Shin, J.; Kobayashi, N.; Shinokubo, H. *Angew. Chem. Int. Ed.* **2012**, *51*, 8542–8545.
[7]. Mori, S.; Osuka, A. *J. Am. Chem. Soc.* **2005**, *127*, 8030-8031.
[8]. Yamashina, M.; Tanaka, Y.; Lavendomme, R.; Ronson, T. K.; Pittelkow, M.; Nitschke, J. R. *Nature* **2019**, *574*, 511–515.
[9]. Fujii, S.; Marqués-González, S.; Shin, J.-Y.; Shinokubo, H.; Masuda, T.; Nishino, T.; Arasu, N. P.; Vázquez, H.; Kiguchi, M. *Nat. Commun.* **2017**, *8*, 15984-15991.
[10]. Ménand, M.; Sollogoub, M.; Boitrel, B.; Le Gac, S. *Chem. Eur. J.* **2018**, *24*, 5804–5812.
[11]. Benchouaia, R.; Cissé, N.; Boitrel, B.; Sollogoub, M.; Le Gac, S.; Ménand, M. *J. Am. Chem. Soc.* **2019**, *141*, 11583–11593.

Chiral Induction of Supramolecular Foldamers

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Chiral π- functional materials are a core research topic across a multitude of diverse fields, spanning materials science, chemistry, medicine, biology and physics.[1] Their photophysical properties have led to their exploitation in a broad spectrum of applications,[2] notably in circularly polarized-light emitting diodes (CP-OLEDs) for their ability to emit circularly polarized light (CPL).[3]

The chirality exhibited by some of the most efficient organic CPL emitters, such as helicenes and helicenoids, originates from their inherent helical nature.[4] This characteristic helical structure can also be exhibited by selected foldamers (discrete oligomers that can fold into a conformationally ordered state in solution), allowing them to emit circularly polarised light if the handedness of the helical structure can be controlled.[5] Moreover, the ability of some foldamers to hybridise[6] generates opportunities to further modulate their emission, facilitated by excimer formation through the strategic use of fluorophores like pyrene.[7]

Here, we present attempts to control the handedness of the supramolecular helical structure of a pyrene appended oligopyridine-dicarboxamide foldamer through the incorporation of a variety of chiral chains to the foldamer backbone, leading to the control of their spectroscopic properties.

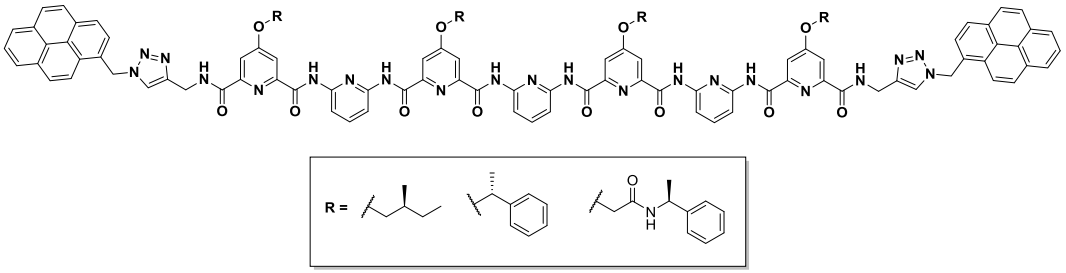

Figure 1. Molecular structure of chiral fluorescent oligopyridine-dicarboxamide foldamers.

Acknowledgements

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References

[1] H. Kuang, C. Xu, Z. Tang, *Adv. Mater.,* **2020**, *32*, 2005110.

[2] J. R. Brandt, F. Salerno, M. J. Fuchter, *Nat. Rev. Chem.,* **2017**, *1*, 0045.

[3 D-W., Zhang, M. Li, C-F. Chen, *Chem. Soc. Rev.,* **2020**, *49*, 1331.

[4] L. Arrico, L. Di Bari, F. Zinna, *Chem. Eur. J.,* **2021**, *27*, 2920; D-W., Zhang, M. Li, C-F. Chen, *Chem. Soc. Rev.,* **2020**, *49*, 1331.

[5] D. Zheng, S. Guo, Lu. Zheng, Q. Xu, Y. Wang, H. Jiang, *Chem. Commun.,* **2021**, *57*, 12016; S. I. Dawson, Á. Mészáros, L. Pethő, C. Colombo, M. Csékei, A. Kotschy, I. Huc, *Eur. J. Org. Chem.,* **2014**, 4265.

[6] L. Faour, C. Adam, C. Gautier, S. Goeb, M. Allain, E. Levillain, D. Canevet, M. Sallé, *Chem. Commun.,* **2019**, *55*, 5743.

[7] F. Aparicio, L. Faour, M. Allain, D. Canevet, M. Sallé, *Chem. Commun.,* **2017**, *88*, 12028.

Solvation-driven unusual structural transition and macroscopic properties in a supramolecular helical polymer

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Benzene 1,3,5-tricarboxamides (BTAs) comprise three amides attached to a benzene core.[1] It generates supramolecular helical rods through a combination of threefold H-bonds and π-π stacking interactions. The dynamic properties of BTA supramolecular polymers make it necessary to use multifarious analytical techniques to get a multi-scale structure of their assemblies.[2] Due to cooperative effects, subtle structural transition in between different types of supramolecular assemblies can be detected for BTA and BTA-related supramolecular polymers.[3] However, a direct relation between the nature of this transition at the molecular level and the related properties at the macromolecular scale is rarely established.

Supramolecular polymers of **BTA^{PPh2}*(S),(S)*** (Figure 1a) were characterized by Variable-Temperature Fourier-Transform Infrared (VT-FTIR, Figure 1b), Circular Dichroism (VT-CD, Figure 1c) analyses as well as SAXS, SANS, calorimetry and electron microscopy analyses. All these data indicate that an intramolecular structural transition occurs in the supramolecular helices in a relatively narrow range of temperature. This structural transition influences both the rheological and catalytic properties of the supramolecular assemblies. This transition is driven by a subtle solvation/desolvation process and can thus be finely tuned by playing on the nature of the solvent.[4]

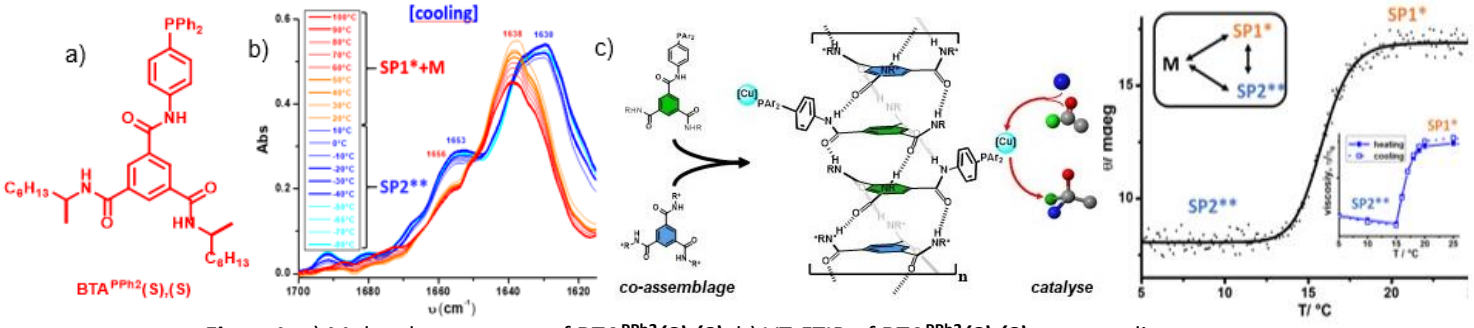

Figure1. a) Molecular structure of **BTA^{PPh2}*(S),(S)***; b) VT-FTIR of **BTA^{PPh2}*(S),(S)*** upon cooling process; c) Self-assembly and VT-CD of **BTA^{PPh2}*(S),(S)***.

Acknowledgements

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References

[1] a) S. Cantekin, T. F. A. de Greef, A. R. A. Palmans, *Chem. Soc. Rev.* **2012**, *41*, 6125; b) Y. Dorca, J. Matern, G. Fernandez, L. Sanchez, *Isr. J. Chem*. **2019**, *59*, 869.

[2] a) Y. Li, X. Caumes, M. Raynal, L. Bouteiller, *Chem. Commun.* **2019**, *55*, 2162; b) Y. Li, L. Dubreucq, B. G. Alvarenga, M. Raynal, L. Bouteiller, *Chem. Eur. J.* **2019**, *25*, 10.

[3] Van Zee, N. J., Mabesoone, M. F. J., Adelizzi, B., Palmans, Meijer, E.W, *Nature* **2018**, *558,* 10.

[4] H. Kong, M. Martínez-Aguirre, Y. Li, L. Bouteiller, M. Raynal, manuscript under preparation.

TUNING TRANSMEMBRANE TRANSPORT OF CHLORIDE BY DYNAMIC COVALENT CHEMISTRY WITH AZINES

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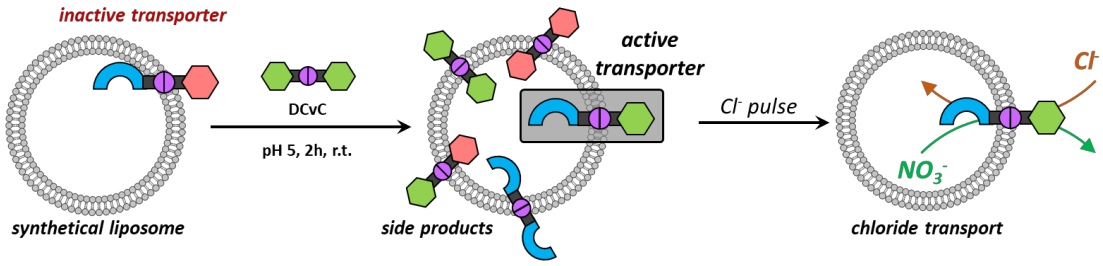
The precise control of transmembrane transport of ions has become a prominent area of research due to its fundamental importance in cellular processes and potential therapeutical applications.[1] Artificial liposomes and fluorescence spectroscopy have emerged as essential tools for observing and analyzing transmembrane transport of ions in an affordable way.[2] The presented system offers an unusual approach to tuning the transmembrane transport of ions in liposomes. Dynamic covalent chemistry (DCvC) is a well-developed synthetic strategy using reversible covalent bonds such as imines, acyl-hydrazones, esters, boronic esters, disulfides or azines to obtain complex molecular and supramolecular systems.[3] DCvC has already found prominent applications in fields like drug delivery and gene therapy.[4-5] This contribution presents the use of DCvC based on azine bonds in modulating the transmembrane transport of chloride in artificial liposomes.[6] Tuning of the transmembrane transport with DCvC requires a reversible bond that can be used in both membranes and aqueous conditions. An active chloride transporter is obtained in-situ inside the lipid bilayer through the dynamic azine metathesis. The external control of transport is achieved through alterations in the structure of the azine building blocks and adjustments of the pH of the liposome solution. In the future, this dynamic method may find application in the development of drug delivery systems.



Acknowledgements

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References

[1]. J. de Jong, J. E. Bos and S. J. Wezenberg, *Chem. Rev.*, **2023**, 123, 8530-8574.
[2]. M. Chvojka, A. Singh, A. Cataldo, A. Torres-Huerta, M. Konopka, V. Šindelář and H. Valkenier, *Anal. Sens.*, **2023**, e202300044.
[3]. J. M. Lehn, *Chem. Soc. Rev.*, **2007**, 36, 151-160.
[4]. S. Ulrich, *Acc. Chem. Res.*, **2019**, 52, 510-519.
[5]. Y. Zhang, Y. Qi, S. Ulrich, M. Barboiu and O. Ramström, *Mater. Chem. Front.*, **2020**, 4, 489-506.

Noncovalent Synthesis of Homo and Hetero-Architectures of Supramolecular Polymers via Secondary Nucleation

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The controlled synthesis of supramolecular polymers (SPs) with diverse architectures is a challenge in supramolecular chemistry. While primary nucleation-driven living supramolecular polymerization (LSP)[1] is well-studied, resulting SPs mostly exhibit one-dimensional (1D) morphology. Here, we introduce a novel approach using secondary nucleation,[2] akin to protein aggregation and small molecule crystallization. We stabilized dormant monomers of **2EH-PDI** and activated them via mechanical stimuli and hetero-seeding with **PE-PDI** seeds. This triggered a secondary nucleation event, forming 3D spherical spherulites and scarf-like SP heterostructures. Our study offers a straightforward molecular design for synthesizing well-defined SP architectures through secondary nucleation.

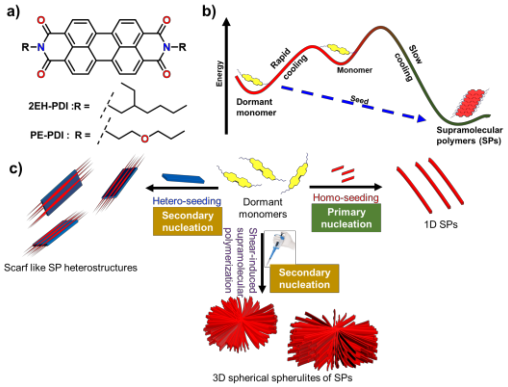

Figure: (a) Chemical structures of **2EH-PDI** and **PE-PDI**. (b) Schematic of dormant monomer formation by 2EH-PDI and their transformation to thermodynamically stable supramolecular polymers (SPs) via seeded living supramolecular polymerization (c) Overview of three noncovalent synthesis approaches: activation of dormant monomers of **2EH-PDI** leads to formation of 1D SPs via homo-seeding, 3D spherical spherulites via shear-induced , and scarf-like SP heterostructures via hetero-seeding.

Acknowledgements

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References

[1] D. Vanderzwaag, T. F. A. DeGreef, E. W. Meijer, *Angew. Chemie - Int. Ed.* **2015**, *54*, 8334–8336.

[2] G. Meisl, J. B. Kirkegaard, P. Arosio, T. C. T. Michaels, M. Vendruscolo, C. M. Dobson, S. Linse, T. P. J. Knowles, *Nat. Protoc.* **2016**, *11*, 252–272.

Unveiling the Liquid-Liquid Phase Separation of Benzene-1,3,5-tricarboxamide in Water

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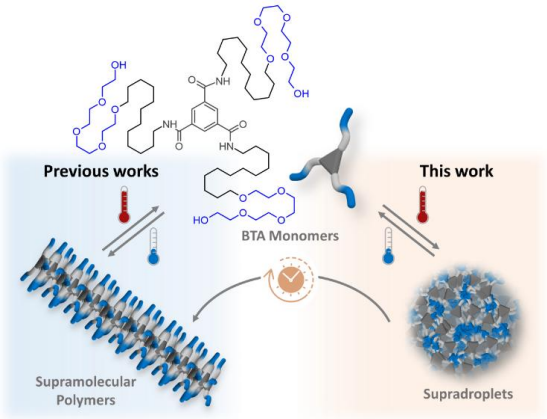
The intricate interplay between self-assembly and phase separation orchestrates biomolecular organization inside cells, thereby dictating the formation of vital structures such as protein assemblies and membraneless organelles (MLOs). However, in the context of supramolecular polymerization, these fundamental processes have traditionally been studied separately. This study reevaluates the supramolecular polymerization process to unveil the presence of phase-separated droplet state. Utilizing the well-studied benzene-1,3,5-tricarboxamide (BTA) supramolecular motif, we explore its thermally driven liquid-liquid phase separation (LLPS). Thermodynamic and kinetic analysis, employing temperature-dependent spectroscopic and microscopic techniques, elucidates the distinct BTA states and their evolution towards the thermodynamic fiber state. This research sheds light on the existence of hidden phases of supramolecular monomers, emphasizing the delicate balance of non-covalent interactions among monomers and with solvents in governing self-assembly vs. phase separation. This is particularly important in comprehending phase separation in the biological realm such as in MLOs, and for applications such as condensate-modifying therapeutics.



Scheme 1. Chemical structure of BTA and schematic illustration of BTA states: monomer, supramolecular polymers, and supra phase separated droplets.

Acknowledgements

We thank Prof. E.W. Meijer for providing BTA and for the valuable discussions. Special thanks to Prof. A. Walther, Prof. P. Besenius, and Prof. S. Seiffert for the spectroscopy and microscopy facilities. Funding from the DFG (Deutsche Forschungsgemeinschaft) is acknowledged: S.D. is member of the GRK 2516 and M.K. is the recipient of a doctoral position within the GRK 2516 program. Elyra7 (SIM microscope) was funded by the Gutenberg Research College and Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) - 497845157.

References

[1] L. Su, J. Mosquera, M. F. J. Mabesoone, S. M. C. Schoenmakers, C. Muller, M. E. J. Vleugels, S. Dhiman, S. Wijker, A. R. A. Palmans, E. W. Meijer, *Science*, **2022**, *377*, 213–218.

[2] C. Yuan, A. Levin, W. Chen, R. Xing, Q. Zou, T. W. Herling, P. K. Challa, T. P. J. Knowles, X. Yan, *Angew. Chem. Int. Ed*., **2019**, *58*, 18116–18123

In Vitro Fate of Self-Assembled DNA Amphiphiles: Controlling Disassembly

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Hijacking the chemistry of automated DNA synthesizers, our group has pioneered the creation of sequence-defined DNA amphiphiles. These precise block copolymers bear a hydrophobic portion conferring them interesting self-assembly properties: controllable morphologies, sequence-dependent assembly, … These molecules have found multiple applications in biology, especially in gene silencing where they show activity without the need for external transfection agents, acting as self-delivering therapeutics. However, because they are held together by weak non-covalent interactions, dilution below their critical micellar concentration and interaction with serum proteins *in vitro* can result in their disassembly (Figure 1). Here, we describe several approaches to strengthen these self-assembled structures by borrowing tools from dynamic covalent chemistry and photochemistry, adding stability via the hydrophobic core or the DNA corona, respectively.[1] We show that high therapeutic efficiency lies in a balance between extracellular stability of self-assembled nanostructures and their intracellular dissociation.[2] This research brings forward a new generation of gene-silencing drugs paving the way for more straightforward translation to *in vivo* and preclinical applications.

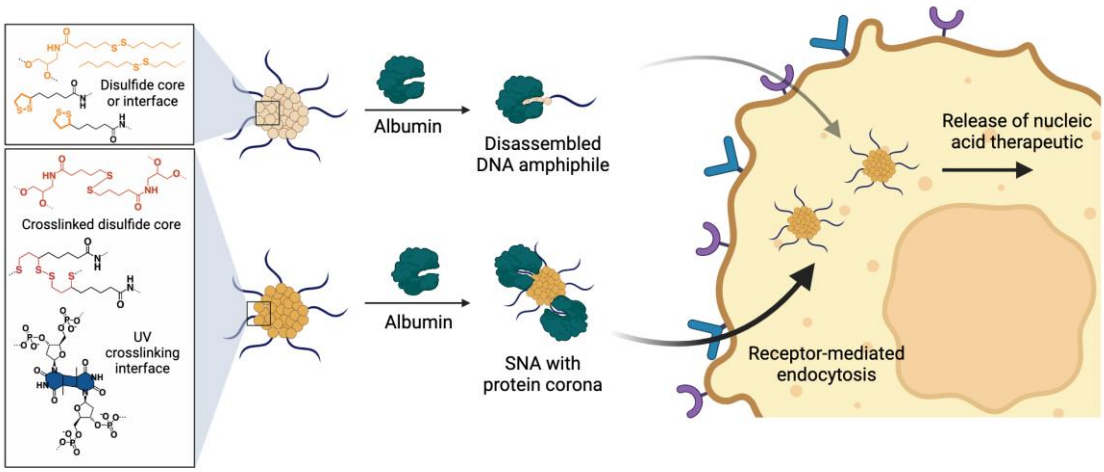

Figure 1. Self-assembled DNA amphiphiles made from different hydrophobic units for post-assembly covalent crosslinking. Crosslinked micelles are more resistant to disassembly by interaction with serum protein, resulting in higher cellular uptake but can hamper intracellular therapeutic release.

Acknowledgements

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References

[1] S. Faiad,+ Q. Laurent,+ A. L. Prinzen, J. Asohan, D. Saliba, V. Toader, H. F. Sleiman, *Angew. Chem. Int. Ed.* **2023**, *62*, e202315768.

[2] J. Asohan, H. H. Fakih, T. Das, H. F. Sleiman, *ACS Nano* **2024**, *18*, 3996–4007.

DESIGNING MAGNETIC COORDINATION DENDRIMERS USING A SUPRAMOLECULAR 'COMPLEX AS LIGAND' APPROACH

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Developed in the 1980s, dendrimer chemistry has opened up new perspectives in fields as diverse as catalysis, molecular electronics and artificial photosynthesis.[1] Surprisingly, however, magnetic dendrimers are not common in the literature due to puzzling difficulties in their synthesis and characterization.[2] In this context, the design of such polymetallic and monodisperse starburst architectures, endowed with magnetic properties, is therefore a real challenge. [3]

Following a supramolecular "complex as ligand" approach, we succeeded in this challenge by carrying out the synthesis, characterization (including X-Ray diffraction) and study of magnetic dendrimers. Our synthetic strategy essentially relies on (i) oxalate-based coordination chemistry as the core of the architecture and (ii) trinuclear complexes, $LnCo_2$ for the branches (with Ln a lanthanide and Co, the Klaui ligand) that feature single-molecule magnet properties. The combination of these two building blocks allows us to obtain supramolecular and dendritic assemblies.

The versatility of this approach makes it possible to anticipate the properties according to the choice of metal cations involved in the structure (single molecule magnets or giant spin values, etc.). Thus, we obtained hetero-tri-metallic magnetic dendrimers, MLn_3Co_6 and $ZrLn_4Co_8$ (with M=Co or Cr, and Ln=La, Tb, Dy, Er, …, Figure 1) fully characterized by X-ray diffraction.[4],[5] The magnetic properties are in good agreement with the expected theoretical models. This type of compound could be of great interest for applications in information storage or magnetic refrigeration.

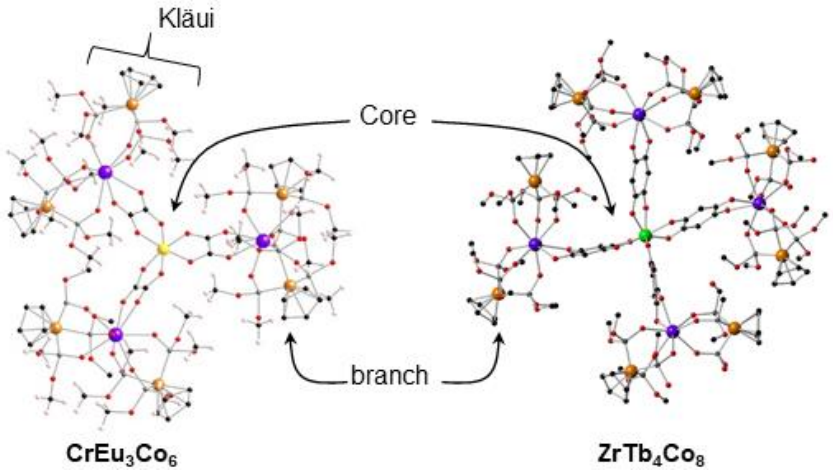

Figure 1. X-ray structures of magnetic dendrimers: $CrEu_3Co_6$ and $ZrTb_4Co_8$

References

[1] Astruc, D; Boisselier, E; Ornelas, C; *Chem. Rev.* **2010**, *110* (4), 1857-1959.

[2] Racja, A; Wongsriratanakul, J ; Racja, S; Cerny, R; *Angew. Chem.* Int. Ed. **1998**, *37* (9), 1229-1232.

[3] Suzana, I; Forté, J; Von Barbeleden, J; Pillet, S; Marvaud, V; Malischewski, M, *manuscript in preparation*

[4] Suzana, I; Rupf, S; Rousset, E; Rahman, A. K. F.; Klemke, B; Marvaud, V; Malischewski, M, *manuscript in preparation*

[5] Pécou, C; Suzana, I; Forté, J; Malischewski, M, *manuscript in preparation*

Synthesis and study of new calix[6]arene-based complexes and their application for molecular recognition

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Calixarenes are macrocyclic polyphenolic compounds that have been extensively studied for several decades and have found numerous applications in various fields of chemistry.[1] Their success can be attributed, in large part, to the numerous synthetic methods developed for their itero[2] - and regioselective modification, both at the small rim and the large rim.[3]

Few synthetic methodologies yielding tris-functionalized C_{3v}-symmetrical calix[6]arenes are reported. In this work, three allyl protecting groups are selectively placed in 1,3,5 alternate positions of calix[6]arenes Removal of the protecting allylic groups gives access to sophisticated calix[6]arenes that can be further modified. The potential of these new C_{3v}-symmetrical molecular platforms is notably exemplified through the development of a new family of calix[6]arene-based N-ligands (Figure 1).

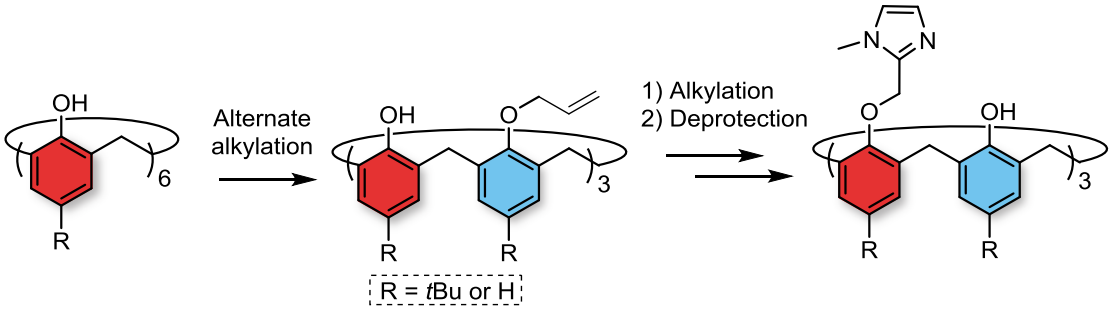

Figure 1. Synthesis of calix[6]arene-based ligands via "alternate alkylation" strategy.

The derived zinc complexes were investigated in host-guest chemistry, and the results were compared with those of previous calixarene-based zinc complexes.[4] Interestingly, the presence of the phenol units makes them suitable to recognize anions, which was rarely observed in previous complexes.[5] Moreover, the presence of hindered tert-butyl groups has a strong influence on the recognition outcome.

Acknowledgements

This research was supported by the Fonds pour la formation à la Recherche dans l'Industrie et dans l'Agriculture (FRIA-FRS, Belgium).

References

[1] Gutsche, C. D. Calixarenes: An Introduction, 2nd ed., Monographs in Supramolecular Chemistry (Ed.: J. F. Stoddart); The Royal Society of Chemistry, Cambridge, **2008**.
[2] Lavendomme, R.; Jabin, I. Iteroselectivity, the Missing Sibling of Chemo-, Regio-, and Stereoselectivities. *Cell Reports Phys*. Sci. **2022**, *3*, 101121.
[3] Lavendomme, R.; Zahim, S.; De Leener, G.; Inthasot, A.; Mattiuzzi, A.; Luhmer, M.; Reinaud, O.; Jabin, I. Rational Strategies for the Selective Functionalization of Calixarenes. *Asian J. Chem.* **2015**, *4,* 710–722.
[4] Le Poul, N.; Y, Le Mest.; Jabin, I.; Reinaud, O. *Acc. Chem. Res*. **2015**, *48*, 2097–2106.
[5] De Leener, G.; Over, D.; Reinaud, O.; Jabin, I. *Org. Biomol. Chem*. **2023**, *21*, 1172–1180

STIMULI-SENSITIVE LUMINESCENT MULTIMETALLIC Cu(I) SUPRAMOLECULAR ASSEMBLIES

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An increasing interest is devoted to Cu(I) assemblies as attractive photoluminescent materials for lighting and stimuli-sensitive sensor applications, taking advantage of both the various photophysical properties and the large flexibility of the coordination sphere exhibited by derivatives based on this ion.[1] Using different pre-assembled photoactive {Cu(I)}n precursors (n = 3,4) bearing significant conformation flexibility,[2] new polymeric Cu(I) luminescent assemblies such as **A_{1-6}** will be presented, bearing an original irreversible non-destructive solid-state thermal transition of their luminescence properties that opens appealing perspectives for innovative solid-state temperature sensors' design.[3] In addition, luminescent Cu(I) multimetallic assemblies bearing Cu(I) bimetallic subunits such as **B** in which very unusual bridging aqua ligands are observed will be described.[4] Detailed photophysical properties of these derivatives will be discussed together with their stimuli-sensitive behaviors that are assigned to the great supramolecular flexibilities of these assemblies.

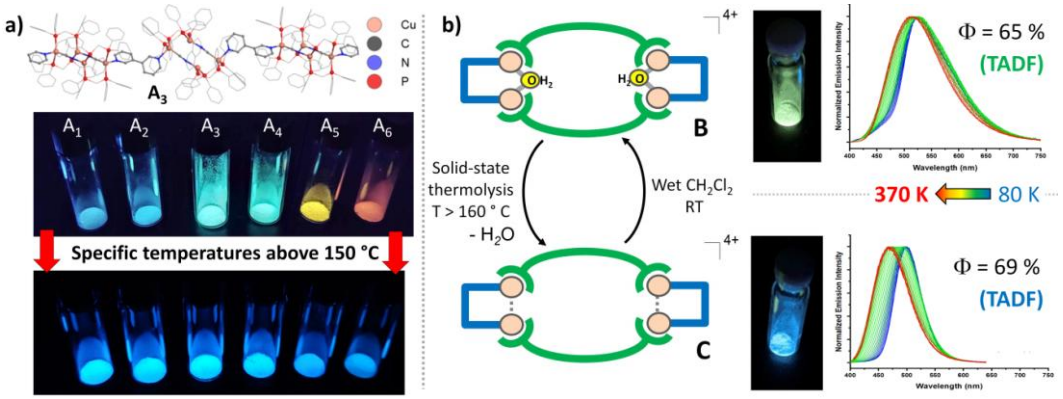

Figure 1. a) examples of the solid-state thermal transitions of the luminescence of the 1D-coordination polymers **A_n**, b) luminescent metallacycle **B** bearing a bridging aqua ligand and solid-state thermal transition towards the metallacycle **C** impacting the luminescence properties of these derivatives.

References

[1] Yam, V. W.-W.; Au, V. K.-M.; Leung, S. Y.-L. *Chem. Rev.* **2015**, *115*, 7589; b) Czerwieniec, R.; Leitl, M. J.; Homeier, H.H.H.; Yersin, H. *Coord. Chem. Rev.* **2016**, *325*, 2; c) Kobayashi, A.; Kato, M. *Chemistry Letters* **2017**, *46*, 154; d) Perruchas, S. *Dalton Trans*. **2021**, *50*, 12031; e) Lescop, C. *Acc. Chem. Res.*, **2017**, 50, 885.

[2] a) Lescop, C. *Chem. Rec.* **2021**, *21*, 544; b) Evariste, S.; Khalil, A.M.; El Sayed Moussa, M.; Chan, A. K.-W.; Hong, E. Y.-H.; Wong, H.-L.; Le Guennic, B.; Calvez, G.; Costuas, K.; Yam, V. W.-W.; Lescop, C. *J. Am. Chem. Soc.*, **2018**, *140*, 12521. c) El Sayed Moussa, M.; Khalil, A. M.; Evariste, S.; Wong, H.-L.; Delmas, V.; Le Guennic, B.; Calvez, G.; Costuas, K.; Yam, V. W.-W.; Lescop, C. *Inorg. Chem. Front*. **2020**, *7*, 1334; d) Moutier, F.; Schiller, J.; Lecourt, C.; Khalil, A. M.; Delmas, V.; Calvez, G.; Costuas, K.; Lescop, C. *Chem. Eur. J.* **2022**, 28, e202104497; f) C. Lecourt, R. Utrera Melero, J. Schiller, F. Moutier, V. Dorcet, G. Calvez, C. Poidevin, K. Costuas, M. Scheer, C Lescop, *Inorg. Chem. Front.*, **2023**, doi.org/10.1039/D3QI01544K.

[3] Lescop,C., EP3820929, 2020.

[4] Evariste, S., Khalil, A. M., Kerneis, S., Xu, C., Calvez, G., Costuas, K., Lescop, C. *Inorg. Chem. Front.*, **2020**, *7*, 3402.

Transient Supramolecular Polymers by pH-Gated Conformational Control of a Self-Assembling Cyclodextrin

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β-Cyclodextrins possess a hydrophobic cavity which exhibits a high affinity for adamantane moieties.[1] Functionalization of β-CD with this moiety generally leads to self-inclusion of the adamantyl group notably via a tumbling process of one of the sugar units resulting in a non-interacting monomeric object.[2] Bridging the primary rim of the cyclodextrin avoids this process and keeps the adamantyl group out its own cavity. As a result, supramolecular polymerization can occur.[3]

Here we show that by loosening the bridge both processes can be brought into competition leading to a dynamic system, between a self-included "inert" state being thermodynamically stable and an outwardly-oriented "active" state able to polymerize but thermodynamically unstable. We further show that tuning the pH conditions of this equilibrium allows to control interconversion of the species up to a "frozen" state.

The thermodynamics and kinetics behind this pH-gated phenomenon were deciphered allowing programmed depolymerization of the supramolecular polymer but also the release of the hydrophobic guest from the self-included form thus reenabling the formation of the supramolecular polymer. This allows a selective access to each state of this system.

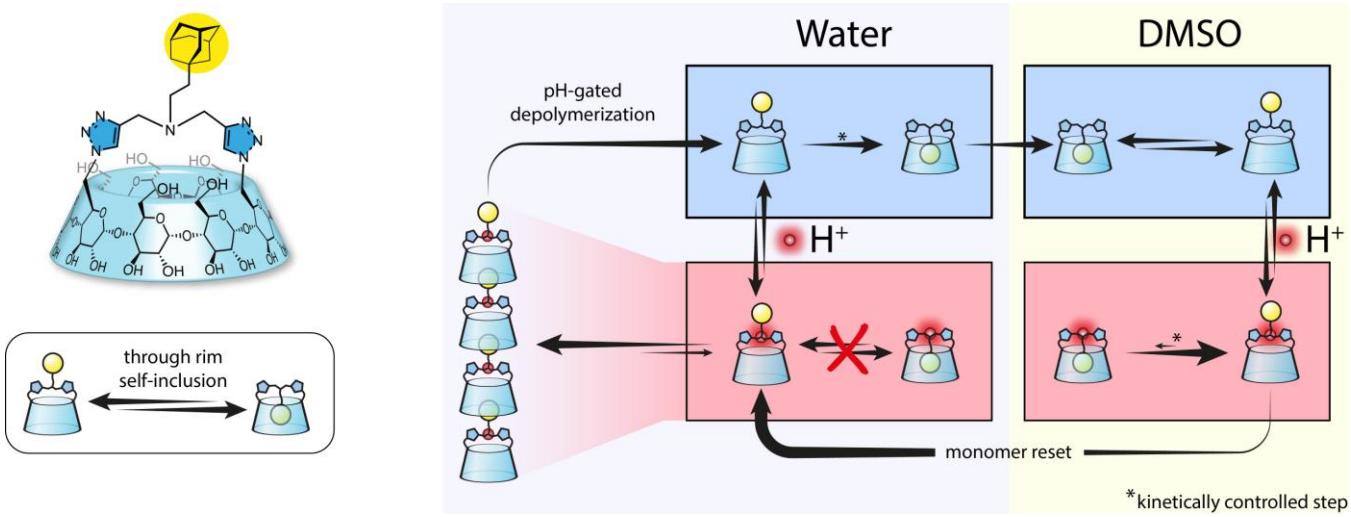

Figure 1. System behaviour depending of pH and solvent.

References :

1. Rekharsky, M. V.; Inoue, Y. Complexation Thermodynamics of Cyclodextrins. *Chem. Rev*., **1998**. *98*, 1875-1917. DOI : 10.1021/cr970015o
2. Tran, D. N.; Colesnic, D.; Adam de Beaumais, S.; Pembouong, G.; Portier, F.; Queijo, A. A.; Tato, J. V.; Zhang, Y.; Ménand, M.; Bouteillier, L.; Sollogoub, M. Cyclodextrin-adamantane conjugates, self-inclusion and aggregation versus supramolecular polymer formation. *Org. Chem. Front.*, **2014**, *1*, 703-706. DOI: 10.1039/C4QO00104D
3. Evenou, P.; Rossignol, J.; Pembouong, G.; Gothland, A.; Colesnic, D.; Barbeyron, R.; Rudiuk, S.; Marcelin, A-G.; Ménand, M.; Baigl, D.; Sollogoub, M. Bridging β-cyclodextrin prevents self-inclusion, promotes supramolecular polymerization, and promotes cooperative interaction with nucleic acids. *Angew. Chem. Int. Ed.*, **2018**, *57*(26), 7753-7758. DOI: 10.1002/anie.201802550

Electrochemically Activated Halogen Bonding On Gold Surfaces For Organocatalysis

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Non-covalent interactions play a key role in supramolecular chemistry, such as chemical reactivity in catalysis and molecular detection. Halogen bonding (XB) is an attractive non-covalent interaction between a halogen donor and a Lewis base, its application in organo-catalysis is still at an early stage but has already proven relevant.[1] The use of electrochemical methods to assist or to drive catalytic reactions can be a "green" alternative for the development of novel analytic and synthetic applications. In our lab previous works have demonstrated electrochemical monitoring, activation, and tuning the strength of halogen bonding in solution,[2] as well as at the solid/liquid interface.[3] The most recent of these uses electrochemistry as a trigger for catalytic activation in homogeneous solutions, under electrolytic conditions resulting in the activation and strengthening of the XB interaction between catalyst and substrate.[4]

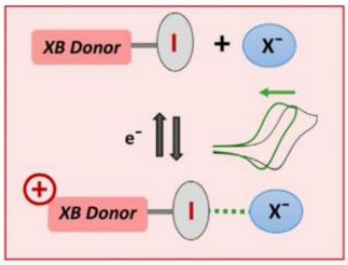

Figure 1. Electrochemically activated halogen bonding

In this field there is a push to move towards heterogeneous catalysis to improve applicability of halogen bonding catalytic systems. Building on previous work done on electrochemically deposited monolayers[3] a series of catalysts featuring 5-iodo 1,2,3-triazoles[5] were prepared for catalytic reactions: including Ritter[6] and Friedel-Crafts alkylation[7]. The catalysts shown in Figure 2 are being synthesized. The segments of catalyst are currently connected via click chemistry[8,9], where the iodinated 1,2,3-triazole acts as the catalytic site[5]. The interest in investigating the 1,5 regioisomer derives from possible effects of the spatial disposition of ferrocene and iodo substituents on the monolayer. All molecules are subject to preliminary electrochemical studies.

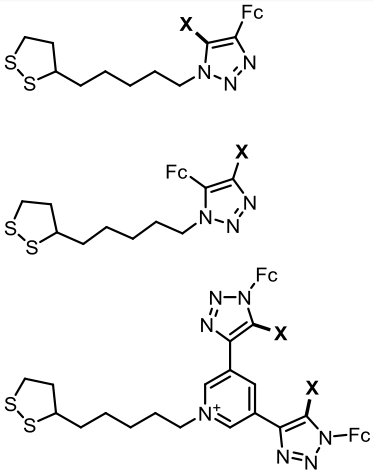

Figure 2. monodentate and bidentate catalysts with 1,2-dithiolane graft Fc
Fc = *ferrocene*; X = H, I

References

[1] Sutar, R. L., & Huber, S. M., *ACS Catalysis* **2019**, *9*(10), 9622-9639.

[2] Groni, S.; Maby-Raud, T.; Fave, C.; Branca, M.; Schöllhorn, B. *Chem. Commun*. **2014**, *50* (93), 14616-14619.

[3] Hijazi, H., Levillain, E., Schöllhorn, B., & Fave, C., *ChemElectroChem* **2022**, *9(11)*, e202200192.

[4] Engelage, E., Hijazi, H., Gartmann, M., Chamoreau, L. M., Schöllhorn, B., Huber, S. M., & Fave, C., *Physical Chemistry Chemical Physics* **2021**, *23(7)*, 4344-4352.

[5] Melnyk, N., Garcia, M. R., & Trujillo, C., ACS *Catalysis* **2023**, *13(23)*, 15505-15515.

[6] Perera, M. D., & Aakeröy, C. B., *New Journal of Chemistry* **2019**, *43*(21), 8311-8314.

[7] Dreger, A., Engelage, E., Mallick, B., Beer, P. D., & Huber, S. M., *Chemical Communications* **2018**, *54*(32), 4013-4016.

Fabrication of novel porphyrin-based nanomaterials for self-assembly application

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The fabrication of well-defined nanostructures of chromophores via self-assembly is an active area of research with diverse applications in materials science. In particular, porphyrin derivatives, due to their rigid planar macrocyclic structure and intrinsic optical properties, have the necessary features to act as building blocks for functional materials that take advantage of these characteristics. It is these desirable optical and electronic properties that have allowed application in optical devices, solar cells, and also biochemical systems such as artificial photosystems and photocatalysis. Herein in this poster, we revealed three different porphyrin molecules have been involved in various applications. The self-assembly of Porphyrin 1 has been controlled successfully by cytosine into a light-harvesting antenna-like ring system at the ratio of 8 molar as shown in figure 1. Secondly, a new design and synthesis of fluorinated porphyrin was revealed and being assembled into a micro-rods like structure and revealed a higher photocatalytic performance Finally, arginine-induced the assembly of protoporphyrin at aqueous solution was reported and show a higher photocatalytic performance under visible light.

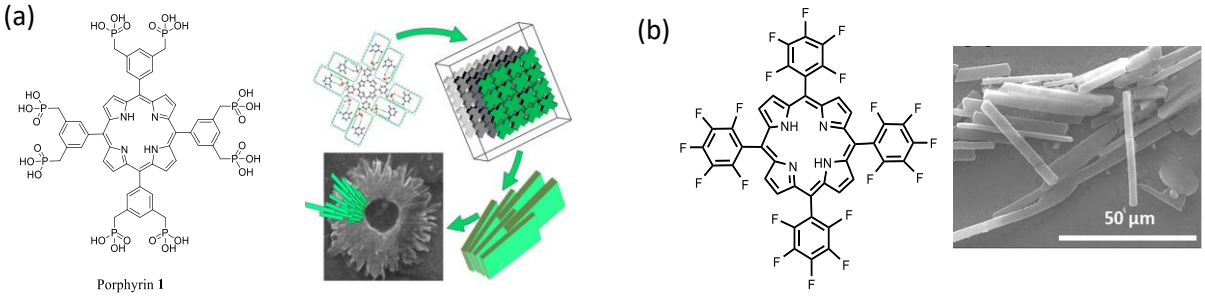

Figure 1. (a)The structure of porphyrin 1 along with the self-assembly with cytosine at 1:8 molar ratio in ring-like, (b) fluorinated porphyrin and a Micro-rod self-assembled of fluorinated porphyrin.

Acknowledgements

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References

[1] M. D. Aljabri, R. W. Jadhav, M. Al Kobaisi, L. A. Jones, S. V. Bhosale and S. V. Bhosale, *ACS Omega*, **2019**, *4*, 11408-11413.

[2] M. D. Aljabri, D. D. La, R. W. Jadhav, L. A. Jones, D. D. Nguyen, S. W. Chang, L. D. Tran and S. V. Bhosale, *Fuel*, **2019**, *254*, 115639-115645.

[3] M. D. Aljabri, N. M. Gosavi, L. A. Jones, P. P. Morajkar, D. D. La, and S. V. Bhosale, *Molecules* **2019**, *24*, 4172-4185.

Cyanide cages as receptors and supramolecular building units

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Coordination-based cages attire a lot of attention of modern chemistry due to the possibility of constructing molecular structures of very various nature, geometry and internal space size. Typically these are made using late transition metals assuring strong coordination bonding with an organic bridging ligand. However, the construction of similar 3d-metal-based assemblies is more challenging as their ability to stabilize backbonding is significantly lower.
Guided by research in the field of novel magnetic switching compounds, our research group interested in cyanide-bridged complexes, more particularly, on octametallic assemblies of cubic geometry. Those are made with 3d-metal cations in each corner interlinked by cyanide anions at the edges. (Fig.°1a) The remaining coordination vacancies at each metal cation are blocked by organic ligands. Due to the three-dimensional coordination bonding, such cubes are significantly more stable than other examples of cyanide polymetallic structures permitting their study in solution.
The π-electron rich cyanide anions at edges of a cube form an internal cavity that can bind cations of appropriate size. In this communication, firstly, we aim to show our findings in host-guest chemistry of such cubic octametallic cages[1] and influence of such interactions on the physical and electrochemical properties of the complexes.[2] Secondly, we will demonstrate that design of organic ligands on each metal can be used to promote supramolecular interactions between distinct complexes. We have recently focused our attention on the development of organized networks of cubes.[3] (Fig.°1b) Such networks feature switching magnetic properties, tunable porosity, negatively charged framework and are therefore interesting in sensing and ion-conductivity applications.

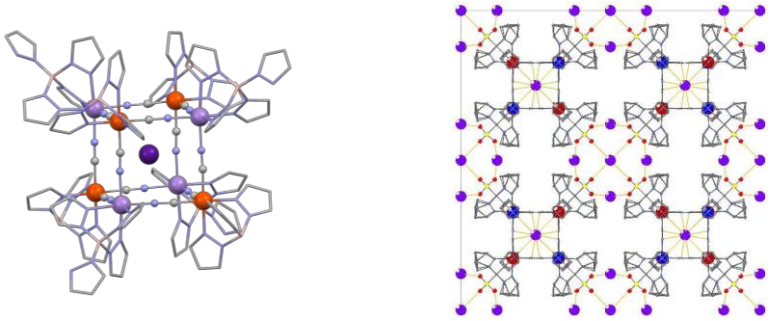

Figure 1. a) an example of a $Cs^{+}\subset\{[Fe^{II}(Tp)(CN)_3]_4\ [Co^{II/III}(pzTp)]_4\}^{-}$ complex and b) XRD structure of an assembly of cubic complexes carrying peripheral sulfate group.

References

[1] J.-R. Jiménez, M. Tricoire, D. Garnier, L.-M. Chamoreau, J. von Bardeleben, Y. Journaux, Y. Li, R. Lescouëzec, *Dalton Trans.* **2017**, *46*, 15549–15557. DOI: 10.1039/C7DT02989F
[2] J. Glatz, J.-R. Jiménez, L. Godeffroy, H. J. von Bardeleben, L. Fillaud, E. Maisonhaute, Y. Li, L.-M. Chamoreau, R. Lescouëzec, *JACS* **2022**, *144* (24), 10888-10901. DOI: 10.1021/jacs.2c03421
[3] Q. P. Xuan, J. Glatz, A. Benchohra, J.-R. Jiménez, R. Plamont, L.-M. Chamoreau, A. Flambard, Y. Li, L. Lisnard, D. Dambournet, O. J. Borkiewicz, M.-L. Boillot, L. Catala, A. Tissot, R. Lescouëzec, *J. Mater. Chem. C*, **2021**, *9*, 8882-8890. DOI: 10.1039/D1TC01825F

SUPRAMOLECULAR ASSEMBLIES OF DNA/OLIGOTHIOPHENE: BINDING, CHIROPTICAL PROPERTIES AND MORPHOLOGY

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DNA is considered as a key target for medical diagnosis, food safety, and many other fields.[1] Providing novel molecular materials for optical detection and imaging of DNA is of great interest. In this regard, cationic π-conjugated oligothiophenes have emerged as appealing candidates as they combine solubility in aqueous media and tunable design to achieve targeted supramolecular recognition.[2,3] Additionally, one of the particularities of conjugated oligothiophenes is the sensitivity of their chiroptical properties to minor perturbations that can influence their conformation, such as the interactions with a biomacromolecule.[3]

In order to evaluate their potential as molecular probes for DNA optical sensing and imaging, we have studied complexes formed by supramolecular self-assembly between a series of newly designed cationic π-conjugated oligothiophenes (**Figure 1**) and various DNA (different sequences and lengths) through chiroptical spectroscopy (absorption UV-Vis, circular dichroism and fluorescence) and microscopy techniques (atomic force microscopy and cryogenic transmission electron microscopy).

Our results reveal that the nature, position, and number of cationic substituents strongly influence the interactions with DNA and the binding affinities. Remarkably, the binding of T3Im **(Figure 1)** to DNA shows promising fluorescence properties as a result of a preferential adsorption along DNA minor grooves.

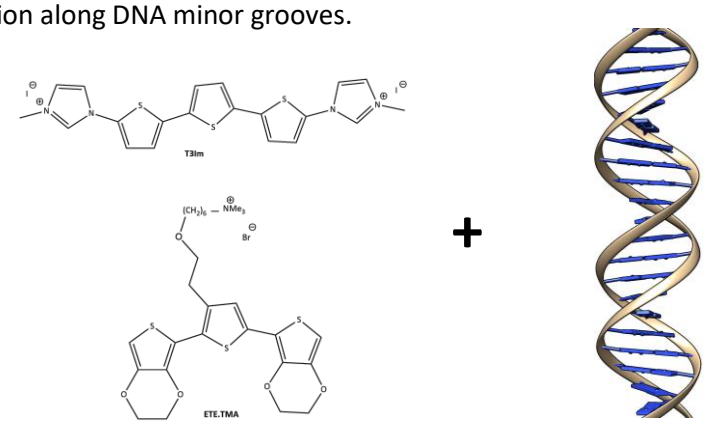

Figure 1. Left: Chemical structures of the cationic π-conjugated oligothiophenes under study. For each compound, supramolecular assembly with DNA is studied in aqueous solution and in solid state.

Acknowledgments

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References

[1] C. Chen, J. Wang, *Analyst*, **2020**, 145,1605-1628.
[2] G. Barbarella, M. Melucci, G. Sotgiu, *Adv. Mater*, **2005**, 17, 1581-1593.
[3] Conjugated Polyelectrolytes: Fundamentals and Applications, edited by Liu, B. & Bazan, G. C., Wiley-VCH, **2013**.

Crownphyrins: Metal-Mediated Transformations of the Porphyrin-Crown Ether Hybrids

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Crownphyrins represent a distinct category of macrocyclic compounds resulting from the fusion of porphyrins and crown ethers (Figure 1)[1,2]. Their structural features render them as versatile hosts with the ability to efficiently bind neutral and ionic guests. The unique coordination behavior arises from dynamic covalent imine linkages connecting the dipyrrin segment with the ether chain, a feature not commonly observed for other porphyrinoids. Our investigations have unveiled the potential applications of crownphyrins in supramolecular chemistry, where they function as intriguing ligands, forming coordination compounds with various metal cations, including but not limited to zinc(II), cadmium(II), mercury(II), and lead(II). These metal-crownphyrin complexes exhibit diverse properties, such as the reversible expansion and contraction of the macrocycle in response to external stimuli. A notable illustration is the figure-eight mercury(II) assembly, transformable into a metal-free crownphyrin macrocycle through a selective ring contraction induced by [2.2.2]cryptand. This transformation provides a unique avenue to understand the dynamic properties of crownphyrins. Beyond their role in supramolecular chemistry as dynamically self-assembled architectures, the captivating attributes of crownphyrins position them as promising subjects for future exploration in the construction of stimuli-responsive materials, catalysis, artificial receptors, molecular machines, and optical sensors.

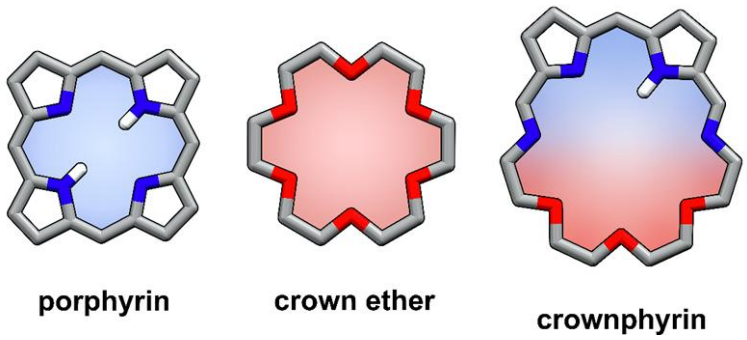

Figure 1. Crownphyrin – a hybrid of porphyrin and crown ether.

References

[1] M. Matviyishyn, A. Białońska, B. Szyszko; *Angew. Chem. Int. Ed.* **2022**, 61, e202211671/1-e202211671/10.

[2] M. Matviyishyn, B. Szyszko, *Beilstein J. Org. Chem.* **2023,** *19,* 1630–1650.

β-sheet mimic foldamers

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Functions and properties of molecules are intimately related to their shape. This is particularly true in Nature where biomolecules functions only arise from the folding of linear oligomeric peptides or nucleotides into 3-D architectures. With the objective of mimicking functional natural biomolecules, chemists have developed synthetic oligomeric molecules named as "foldamers" that are designed to fold into compact architectures. From the beginning of this research field, most of research have focus on the development and use of helical shape foldamers mimic of α-helices of proteins.[1] These predominant folding pattern mostly rely in its ability in maximizing intramolecular interactions and reducing their potential for nonspecific intermolecular interactions, producing discrete and soluble objects. At the opposite, β-sheets mimics have much less frequently been observed probably due to their tendency to form aggregates and to precipitate which makes them difficult to isolate and characterize. For the last decade we have developped new multistranded sheets structure based on aromatic oligoamide β-sheet foldamers stabilized by π–π interactions between short linear segments and rigid turn units. This design has allowed the preparation of linear,[2] curved, [3] multistranded, macrocyclic, and self-assembled sheet structures[4] that will be described in this presentation.

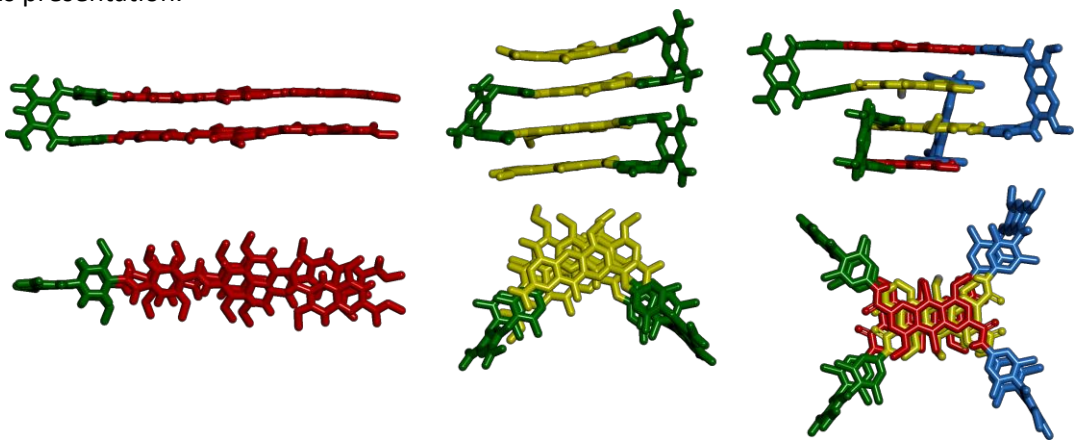

Figure 1. X-ray structures of β-sheet mimic foldamers developed in the group.

Acknowledgements

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References

[1] P. Sang, J. Cai, *Chem. Soc. Rev.*, **2023**,52, 4843; S. Rinaldi, *Molecules,* **2020**, 25(14), 3276.

[2] L. Sebaoun, V. Maurizot, T. Granier, B. Kauffmann, I. Huc*, J. Am. Chem. Soc*., **2014**, 136, 2168; L. Sebaoun, B. Kauffmann, T. Delclos, V. Maurizot, I. Huc *Org.Lett*., **2014**, 16, 2326.

[3] A. Lamouroux, L. Sebaoun, B. Wicher, B. Kauffmann, Y. Ferrand, V. Maurizot, I. Huc, J. Am. Chem. Soc. 2017, 139, 14668; V. Maurizot, S. Massip, J.-M. Leger, G. Deleris, *Chem. Comm*., **2009**, 38, 5698.

[4] J. Atcher, P. Mateus, B. Kauffmann, F. Rosu, V. Maurizot, I. Huc . *Angew. Chem. Int. Ed.,* **2021**, 60, 2574.

Synthesis and assembly of stimuli-responsive amphiphiles for targeted diagnostics and drug delivery

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The current project aims to develop nanocarriers that possess crucial stealth properties but which can activate their cell-targeting properties in the presence of specific stimuli. In recent decades, functional supramolecular systems have played an important role in the development of innovative materials, e.g. for drug delivery. However, such systems encounter various obstacles in terms of circulation, targeting efficiency and specificity of drug release. In biomedical applications, polyethylene glycol (PEG) functionalization has been an important approach to modify nanocarriers such as liposomes, prevent phagocyte-mediated uptake and prolong their circulation time in the blood. However, this approach faces its limitations as the high stability of stealth liposomes prevents specific uptake by the desired cellular target [1].
To overcome this dilemma, this study investigates the assembly of light-cleavable PEGylated lipids, conventional phospholipids (e.g. POPC) and targeting ligands to develop stimuli-responsive stealth liposomes. Coumarin derivatives are used as a light-responsive linker connected to the hydrophobic lipid via a carbonate bond that can be irreversibly cleaved, leading to elimination of a PEG-coumarin fragment and exposure of tumour-targeting ligands on the liposome (Figure 1). Previously our group has investigated the self-assembly of stimuli-responsive amphiphiles to form nanovesicles and giant unilamellar vesicles [2]. Our current aims are to explore an irreversible light-responsive approach to overcome the PEG dilemma and develop nanocarriers for applications in diagnostics, targeted delivery of therapeutics, as well as applications in systems chemistry such as vesicle-vesicle communication.

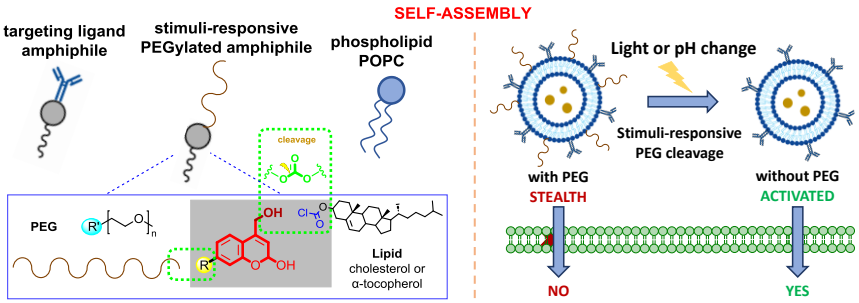

Figure 1. Self-assembly of amphiphiles for the formation of stimuli-responsive stealth liposomes.

Acknowledgements

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References

[1] He, Q.; Chen, J.; Yan, J.; Cai, S.; Xiong, H.; Liu, Y.; Peng, D.; Mo, M.; Liu, Z. *AJPS*, **2020**, *15*, 416–448.
[2] Albanese, P.; Cataldini, S.; Ren, C. Z. J.; Valletti, N.; Brunetti, J.; Chen, J. L. Y.; Rossi, F. *Pharmaceutics*, **2022**, *14*, 2777.

Synthetic Supramolecular Receptors in Perfluorinated Liquids: Unlocking Enhanced Recognition.

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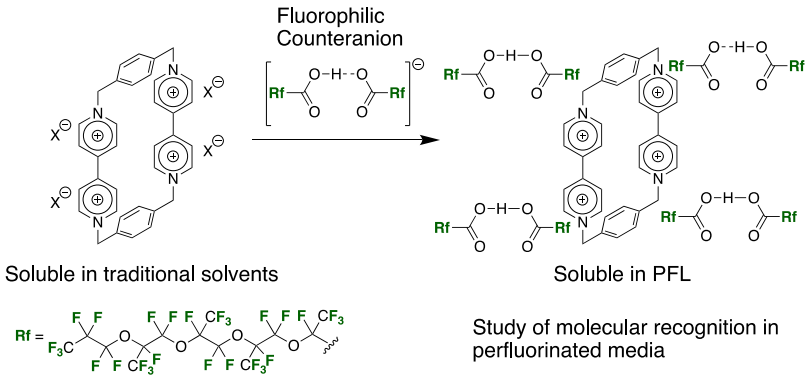
Synthetic supramolecular receptors have emerged as powerful tools for molecular recognition thanks to the tunability in order to selectivity towards specific molecules.[1] Their ability to mimic natural binding mechanisms makes them valuable in fields from molecular recognition,[2] separation[2] or catalysis.[3] However, their traditional use in organic solvents often presents limitations due to solvent interference.[2]

This work explores the potential of perfluorinated liquids (PFLs) as alternative medium for synthetic supramolecular receptors.[4] PFLs exhibit exceptional properties, including inertness, immiscibility with most common solvents, and minimal interactions with other molecules of solvent and solutes. These features unlock exciting possibilities for receptor applications where traditional solvents fall short.[5]

This research aims to use previously developed fluorophilic counteranions[6] to solubilise cationic receptors to perform molecular recognition in PFLs and uncover how this shift enhances their association constants. This enhanced binding holds significant promise for various applications, including selective purification of polyaromatic hydrocarbons and cleaning of pollutants.



Scheme 1: Solubilization of cationic receptor in PFL by fluorophilic counteranion strategy.

References

[1] D. Zhang, A. Martinez, J.-P. Dutasta, *Chem. Rev.*, **2017**, *117*, 4900-4942.
[2] A. P. Davis, *Chem. Soc. Rev.*, **2020**, *49*, 2531-2545
[3] P. Zhang, C. Tugny, J. Meijide Suárez, M. Guitet, E. Deratm N. Vanthuyne, Y. Zhang, V. Mouriès-Mansuy, M. Méenand, S. Roland, L. Fensterbank, M. Sollogoub, *Chem*, **2017**, *3*, 174-191
[4] J. Hu, J. S. Ward, A. Chaumont, K. Rissanen, J.-M. Vincent, V. Heitz, H.-P. J. de Rouville, *Angew. Chem. Int. Ed.* **2020**, *59,* 23206–23212
[5] L. P. Barthel-Rosa, J.A. Gladysz, *Coord. Chem. Rev.* **1999**, *190*, 587-605
[6] R.C. da Costa, T. Buffeteau, A. Del Guerzo, N. D. McClenaghan, J.-M. Vincent, Chem. Commun., **2011**, *47*, 8250-8252

Comparative Study of New Halogen and Hydrogen Chiral Supramolecular Polymers Driven By Anions

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The detection and quantification of anionic species is a relevant area of interest among the scientific community, due to the important role of the anions in biological systems and contamination of some environmental spaces. A number of new chemosensors have been developed in order to detect and quantify those anionic species [1].

In the last years, new noncovalent interactions have emerged as strong alternatives to the widely known hydrogen bonding, such as the anion–π (or cation), halogen or chalcogen bonding interactions [2]. The term halogen [3] or chalcogen bonding is used in analogy with the well-known hydrogen bonding (HB) and is the noncovalent bonding interaction between halogen atoms that function as electrophilic centers (Lewis acids) and neutral or anionic Lewis bases.

We present here two new receptors based on the hydrogen and halogen bonding interaction, with the triazolium (hydrogen or iodine) moiety as the anion binding site and the hydrobenzoin as spacer. These receptors have been synthesized by easy and quick reactions and a final 1,3–dipolar cycloaddition (Huigsen's reaction). ^{1}H-NMR, UV–Vis and Fluorescence spectroscopies studies have been performed in order to do a comparative study in the anion recognition abilities of the different receptors. The formation of supramolecular polymers has also been studied.

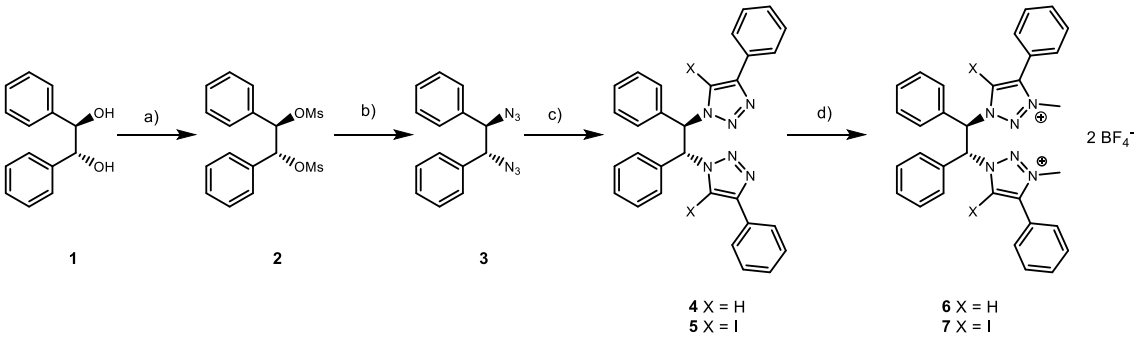

Fig1. Synthetic route of the new receptors

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References

[1] Molina, P.; Caballero, P.; Zapata, P. *Chem. Rev.* **2017**, *117*, 9907–9972

[2] Pascoe, D; Ling, K.B; Cockroft, S.L. *J. Am. Chem. Soc.,* **2017** *139,* 15160–15167

[3] Clark, T; Hennemann, M.; Murray, J.S. . *J. Mol. Model.,* **2007** *13,* 291-296

Macrocyclic 'Chemical Nose Sensor Array' for identification and prediction of preeclampsia outcomes in patient serum samples

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The biomolecular compositions of body fluids are a direct reflection of severity and progression of diseased states[1]. We aim to investigate a non-specific serum-based, 'chemical nose' diagnostic approach that mimics the differential sensing of the human olfactory system[2-6], thereby generating a unique fingerprint that can be tied back to the serum composition.

We have developed such a sensor array with cross-reactive synthetic receptors based on the host- guest interaction of triphenylamine derivatives(TPA) with the macrocycle Cucurbit[7]uril(CB[7]). The host-guest inclusion complex of TPA-CB[7] imposes a structural confinement on the TPA's and enhances their fluorescence intensity, while CB[7] provides diverse binding modes for generation of distinct fluorescent fingerprints upon interaction with biomolecules. This sensing strategy has been extended to a droplet-based microfluidic device to evaluate the array with reduction in sample volumes in the nanolitre range. Pre-existing cohorts of preeclamptic serum samples have been assessed and the generated fluorescence signatures have been processed by suitable statistical approaches such as Linear Discriminant Analysis to obtain efficient discrimination of healthy and PE samples.

We have thus far been able to generate fluorescence fingerprints to discriminate a range of 14 protein analytes in simple (PBS) and complex media (human serum). The capacity of the chemical nose to discriminate between preeclamptic and non-preeclamptic patient samples has been evaluated with 17 serum samples to establish a proof of concept with 96% accuracy. The system has further been optimized on a dedicated droplet-based microfluidic platform, where the detected fluorescence output signal has been correlated with the initial droplet composition to provide discrimination of selected proteins analytes.

Herein, we have developed a 'chemical nose' sensor for fingerprinting and pattern recognition of biomolecules. This system could provide a new diagnostic methodology for complex diseases like preeclampsia[7-8] and will enable us to propose a strategy for big data analysis based on chemical sensing and machine learning.

References

[1] L. M. Killingsworth, J. C. Daniels, *CRC Crit. Rev. Clin. Lab. Sci.,* **1979**, 11, 1–30.
[2] Y. Geng, W.J. Peveler, V. Rotello, *Angew. Chem. Int. Ed.,* **2019**, 58, 5190-5200.
[3] Q. Xu, Y. Zhang, B. Tang, C. Zhang, *Anal. Chem*., **2016**, 88, 2051–2058.
[4] Z. Li, J. R. Askim, K. S. Suslick, *Chem. Rev.,* **2019**, 119, 231–292.
[6] J. J. Lavigne, E. V. Anslyn, *Angew. Chem. Int. Ed.,* **2001**, 40, 3118–3130.
[7] A. L. Tranquilli, *Int. J. Womens Cardiovasc. Health,* **2014**, 4, 97–104.
[8] K. A. Pennington, J. M. Schlitt, D. L. Jackson, L. C. Schulz, D. J. Schust, *Dis. Model. Mech.* **2012**, 5, 9-18.

RedBox: A New G4 DNA Binding Agent

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G-quadruplexes (G4s) are DNA sequences rich in guanine that form a four-stranded structure composed of stacked guanine tetrads. These structures are present in various parts of the genome and many of them play an important role in controlling the activity of specific oncogenes like *c-MYC*. As a result, this kind of DNA has become a novel target in the quest for anti-cancer treatments.[1]

Our group has developed a hydrazone-based polycationic cyclophane, known as *RedBox,*[2] which contains multiple flat aromatic rings, making it well suited for non-covalent interaction with this type of DNA structure. In addition, under physiological conditions, it presents charged groups that promote electrostatic interactions with the phosphate groups of the biomolecule, thereby enhancing the stability of the DNA-ligand complex.

We have characterized the interaction between the *RedBox* and G4 DNA sequences of several oncogenes such as *c-MYC*, *c-KIT*, and *h-TERT*, as well as with standard double-stranded DNA models using a variety of methods. These include variable temperature circular dichroism, isothermal titration calorimetry, and also computational modeling through *in silico* molecular docking, in which we observed selectivity of *RedBox* binding to the *c-MYC* quadruplex. Interestingly, when we evaluated its toxicity on HEK293T cells and examined its impact on gene expression regulation through PCR analysis, the results showed a low toxicity to non-cancer cells as well as selectivity for the regulation of the *c-MYC* quadruplex *in vitro*.

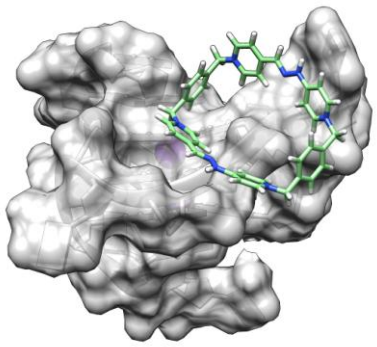

Figure 1. Docking structure proposed for the *c-MYC-RedBox* complex.

References

[1] Domarco, O; Lötsch, D; Schreiber, J; Dinhof, C; Van Schoonhoven, S; García, M. D.; Peinador, C.; Keppler, B. K.; Berger, W.; Terenzi, A. Self-Assembled Pt2L2 Boxes Strongly Bind G-Quadruplex DNA and Influence Gene Expression in Cancer Cells. *Dalt. Trans.* **2017**, 46 (2), 329-332.

[2] Blanco-Gómez, A.; Neira, I.; Barriada, J. L.; Melle-Franco, M.; Peinador, C.; García, M. D. Outside the "Blue Box": From Molec ular to Supramolecular pH-Responsiveness. *Chem. Sci.* **2019**, 10 (46), 10680-10686.

Molecular tweezers with commutable redox and luminescent properties

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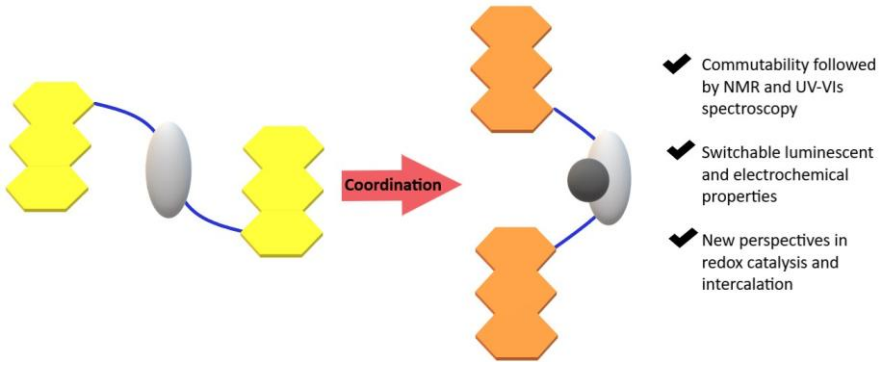
Many studies in supramolecular catalysis have been dedicated to the allosteric effect since a few decades. The capacity to control the activity of a synthetic catalyst shows great promise to understand and mimic the regulation of enzymes activity. To achieve this, a variety of systems commutable with different physical (light, electrical potential) or chemical (protonation, coordination, etc.) stimuli have been synthesized. However, synthetic allosteric systems are still underexplored.

Flavins are common redox cofactors in biological systems that play a pivotal role in electron transport and redox catalysis in enzymes. Flavin-dependent enzymes experience a growing interest in biocatalysis.[1] Using a molecular design based on tweezers featuring a terpyridine commutable unit that can switch from an open to a closed form and vice-versa, we have introduced alloxazine redox subunits, of which our team has experience, as easily accessed flavin isomers, on the tweezer.

We will describe the synthetic access, redox and luminescence properties of these redox-active tweezers as well as commutation studies with different zinc salts.



Scheme 1. Effects of commutability on alloxazine-based tweezers

References

[1] Liu, Y.; Bender, S. G.; Sorigue, D.; Diaz, D. J.; Ellington, A. D.; Mann, G.; Allmendinger, S.; Hyster, T. K. *J. Am. Chem. Soc.* **2024**, jacs.4c00927.

[2] Das, A.; Schleinitz, J.; Karmazin, L.; Vincent, B.; Le Breton, N.; Rogez, G.; Guenet, A.; Choua, S.; Grimaud, L.; Desage-El Murr, M. *Chem. Eur. J.,* **2022**, *28*, e202200596.

[3] Benda, L.; Doistau, B.; Rossi-Gendron, C.; Chamoreau, L.-M.; Hasenknopf, B.; Vives, G. *Commun Chem* **2019**, *2*, 144.

Modular approach for the synthesis of novel forms of nanocarbon from calixarene: Calixcones

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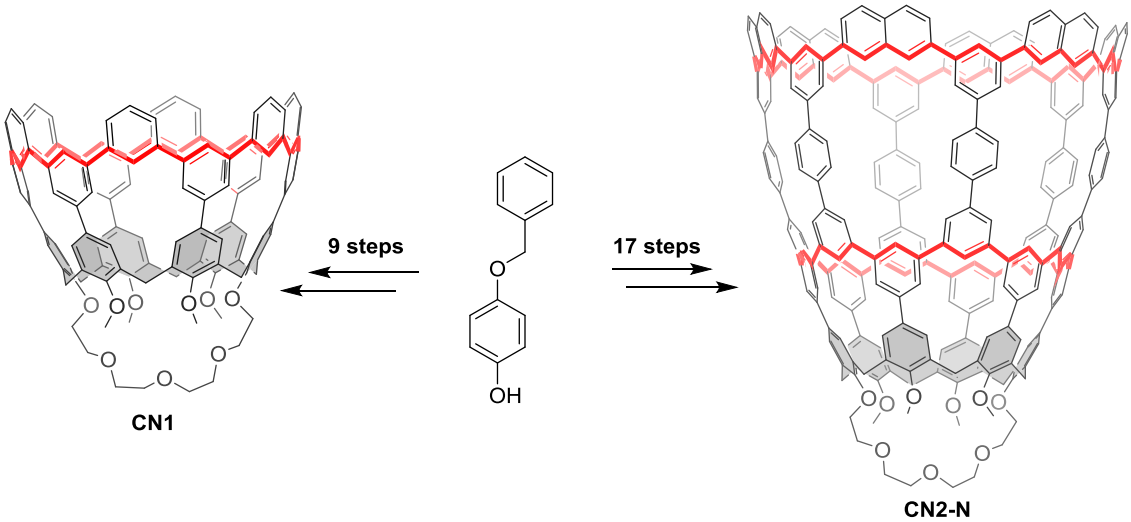
With recent developments in the field of nanomaterials, research on bottom-up synthesis of carbon nanostructures such as carbon nanotubes and graphene nanoribbons has been a subject of great scientific interest worldwide.[1] In this context, based on our previous work,[2] we designed and successfully synthesized a new family of nanocarbons termed calixcones exhibiting exotic structures (Scheme). The synthetic approach involves the use of preassembled aromatic units organized on a calixarene scaffold via an iterative cascade Suzuki-Miyaura cross-coupling. Using calixarenes offers a powerful template for building arbitrarily lengthened and diameter-controlled structures in contrast to current methods. Additionally, the calixarene rings are directly involved in the conjugated system, significantly increasing the rigidity and reinforcing the electronic potential of the resulting calixcones. Photophysical studies and DFT calculations of the calixcones CN1 and CN2-N have revealed promising electronic and optical behaviors. Moreover, these calixcones architectures open up new landscape applications in the area of supramolecular chemistry due to their large cavity.



Scheme: Synthetic pathway of the synthesis of CN1 and CN2-N starting from p-(benzyloxy)phenol.

Acknowledgements

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References

[1] Y. Segawa, H. Ito, K. Itami, Nat. Rev. Mater., 2016, 1, 15002.

[2] E. André, B. Boutonnet, P. Charles, C. Martini, J-M. Aguiar-Hualde, S. Latil, V. Guérineau, K. Hammad, P. Ray, R. Guillot, V. Huc. Chemistry-a European Journal., 2016, 22, 3105-3114.

Multifunctional Dissymmetric Molecular Tweezers

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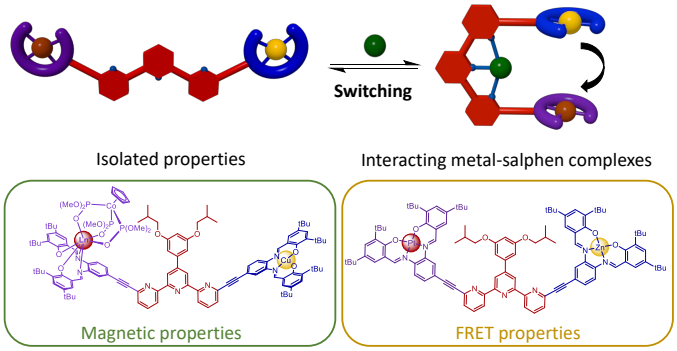
Greatly inspired by biological molecular machines, artificial molecular devices such as motors or switches have been developed over the years.[1] These machines produce mechanical movements in response to specific stimuli. Among them, molecular tweezers are a unique class of switches that can reversibly shift from an open to a closed state upon application of a chemical, electro- or photo-chemical stimulus.[2] Over the past decade, our group has successfully developed a family of switchable molecular tweezers based on a terpy(M-salen)$_2$ architecture. A coordination stimulus has been used to modulate luminescent,[3] magnetic[4] and catalytic properties[5] depending on the nature of the M-salen moities. As a proof of concept, we have shown that a six-level system can be achieved with the combination of three orthogonal stimuli for homonuclear tweezers.[6]

We aim to reach advanced multifunctional systems by developing dissymmetric molecular tweezers. Our objective is to modulate the luminescence properties of heteronuclear tweezers by controlling Förster Resonance Energy Transfer between the two metal-salphen units. Zn-salphen and Pt-salphen were selected due to the overlap between the emission of Zn and the absorption of the Pt moiety. Due to the large intramolecular distance in the open form, we expect independent luminescence properties. However, the spatial proximity of the closed state should allow for efficient transfer energy from the Zn to the Pt-salphen. More sophisticated systems incorporating 4f lanthanide ions are investigated to combine luminescence and magnetic properties. The synthesis and studies of the heterometallic tweezers will be presented.



Acknowledgements

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References

[1] Erbas-Cakmak, C. T. McTernan, A. L. Nussbaumer, D. A. Leigh, *Chem. Rev.*, **2015**, *115*, 10081-10206.

[2] P. Msellem, M. Dekthiarenko, N. Hadj Seyd, G. Vives. *Beilstein J. Org. Chem.*, **2024**, *20*, 504–539.

[3] B. Doistau, A. Tron, S. A. Denisov, G. Jonusauskas, N. D. McClenaghan, G. Gontard, V. Marvaud, B. Hasenknopf, G. Vives, *Chem. Eur. J.,* **2014**, *20*, 15799-15807.

[4] B. Doistau, L. Benda, J.-L. Cantin, O. Cador, F. Pointillart, W. Wernsdorfer, L.-M. Chamoreau, V. Marvaud, B. Hasenknopf, G. Vives, *Dalton Trans.*, **2020**, *49*, 8872-8882.

[5] L. Benda, B. Doistau, C. Rossi-Gendron, L.-M. Chamoreau, V. Marvaud, B. Hasenknopf, G. Vives, *Commun Chem.*, **2019**, *2*, 144.

[6] B. Doistau, L. Benda, J.-L. Cantin, L.-M. Chamoreau, E. Ruiz, V. Marvaud, B. Hasenknopf, G. Vives, *J. Am. Chem. Soc.*, **2017**, *139*, 9213-9220.

DESIGN AND SYNTHESIS OF TRANSMEMBRANE TRANSPORTERS FOR PHOSPHATE

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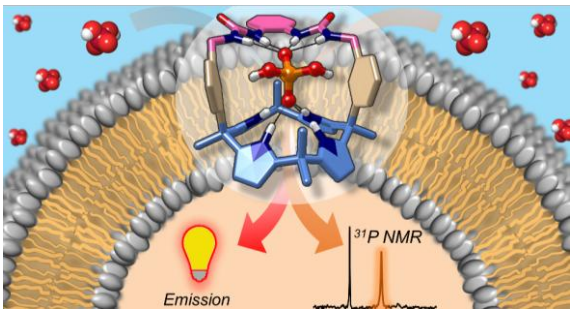
Inorganic phosphate homeostasis is regulated by the concerted work of different phosphate transport proteins, whose malfunction can lead to a variety of diseases.[1] A potential treatment for such diseases could be the use of small synthetic molecules that mimic the behaviour of transport proteins.[2]

Achieving selectivity for oxyanions over more simple spherical anions (e.g. chlorides, fluorides) is yet a challenging task. Because of the strong hydration energies (which makes extraction from the aqueous phase into the apolar interior of the lipid bilayer more difficult) and the speciation of inorganic phosphates with multiple negative charges ($H_2PO_4^-$ and HPO_4^{2-}), extraction and transport of phosphorylated compounds are particularly difficult. The key to transporting and extracting such highly hydrated anions is the formation of multiple H-bonds to the anion.[3]

Here we report the first examples of inorganic phosphate transport based on strapped calix[4]pyrrole supramolecular structure.[4] Volume-specific sites with multivalent interactions allowed the extraction of strongly hydrated $H_2PO_4^-$ into the lipid bilayer while shielding its charges from the lipophilic bilayer interior and transferring them through the membrane. Phosphate transport was monitored by emission spectroscopy using an encapsulated phosphate sensitive europium(III) probe.[5] Furthermore, the ^{31}P-NMR spectroscopy assay was used to confirm and identify the transported phosphate species.



Acknowledgements

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References

[1] N. Hernando, L. Gagnon, E. Lederer, *Physiol. Rev.*, **2021**, *101*, 1–35.
[2] H. Li, H. Valkenier, A. G. Thorne, C. M. Dias, J. A. Cooper, M. Kieffer, N. Busschaert, P.A. Gale, D. N. Sheppard, A. P. Davis, *Chem. Sci.*, **2019**, *10*, 9663–9672.
[3] L. Martínez-Crespo, H. Valkenier, *ChemPlusChem* **2022**, e202200266.
[4] A. Cataldo, K. Norvaisa, L, Halgreen, S. E. Bodman, K. Bartik, S. J. Butler, H. Valkenier, *J. Am. Chem. Soc.* **2023**, *145*, 16310–16314.
[5] S. E. Bodman, C. Breen, F. Plasser, S. J. Butler, *Org. Chem. Front.*, **2022**, *9*, 5494–5504.

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]

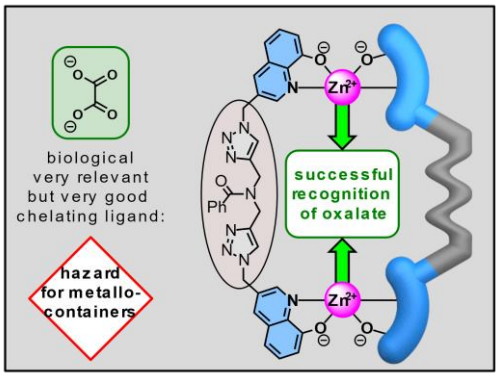

Figure 1: Schematic representation of the new, more flexible system capable of binding oxalate.

[1] D. M. Greenberg, *Chemical Pathways of Metabolism*. Elsevier Science & Technology: Saint Louis, USA, **1954**.

[2] D. A. Bender, *Amino Acid Metabolism*. Wiley-Blackwell: Hoboken, USA, **2012**.

[3] B. Hoppe, *Nat. Rev. Nephrol.*, **2012**, *8*, 467-475.

[4] S. Butler, K. Jolliffe, Org. *Biomol. Chem.*, **2020**, *18*, 8236-8254.

[5] D. Van Craen, M. G. Kalarikkal, J. J. Holstein, *J. Am. Chem. Soc.*, **2022**, *144*, 18135-18143.

[6] manuscript submitted

FUNTIONALIZED ORGANIC CAGES FOR THE ENCAPTULATION OF ANTICANCER DRUGS.

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Molecular cages interest has increase in recent years, due to their internal cavity with high potential application, mimicking the catalytic site of the proteins. Molecular cages have been used in small molecule adsorption, storage, sensing, catalysis, and transport; there is a limited number of reports describing the use of purely organic cages in biological applications, such as intelligent drug delivery.[1.]

In this communication, we will show the synthesis of molecular cages to address a key issue in anticancer drug therapy: mitigating the side effects of high-toxic anticancer drugs by encapsulation within an appropriate molecular cage. Encapsulation in the cavity confined space will diminish drug toxicity. The functionalization of organic building blocks to achieve water solubility for drug delivery presents a synthetic challenge. Our research will show progress in this regard.

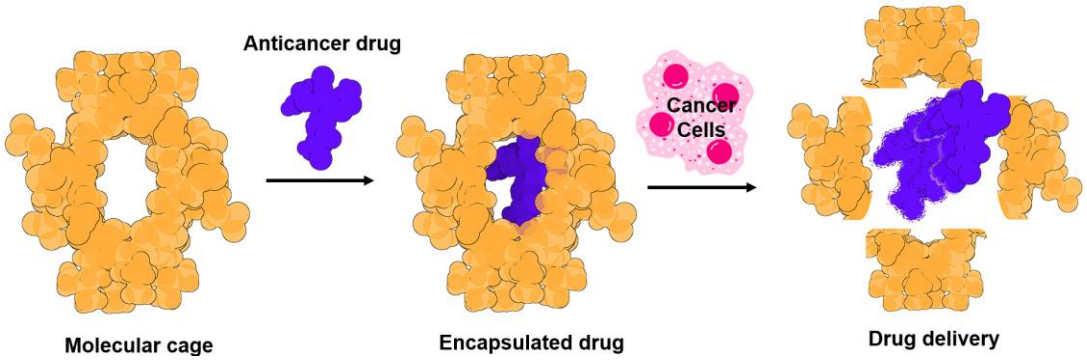

Figure 1. Functionalized molecular cage with water solubilizing groups for the encapsulation of anticancer drugs.

Acknowledgements

V.M.C thanks the financial support from project CIDEGENT/2020/031 funded by the Generalitat Valenciana. E.O.G. is grateful to the Generalitat Valenciana for the Grisolia grant (CIGRIS/2021/128). This research was supported by project PID2020-113256RA-I00 funded by MCIN/ AEI /10.13039/501100011033, by projects PID2021-128141OB-C22 and PID2021-126304OB-C41 funded by MCIN/ AEI /10.13039/501100011033/ and by European Regional Development Fund - A way of doing Europe, and by Generalitat Valenciana (CIPROM/2021/007). This research was also supported by CIBER -Consorcio Centro de Investigación Biomédica en Red- (CB06/01/2012), Instituto de Salud Carlos III, Ministerio de Ciencia e Innovación.

References

[1] Montà-González, G. Sancenón, F.; Martínez-Máñez, R.; Martí-Centelles, V. *Chem. Rev.* **2022**, *122*, 13636-13708.

The Intracavity Extension of Hetero-2,7-naphthiporphyrins in Reactions with Alkylamines

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Abstract

Carbaporphyrinoids are porphyrin analogs incorporating carbon atoms within their cavities.[1] Representative exampes of this group are naphthiporphyrins.[2] The reaction of 28-selena- and 28-thia-2,7-naphthiporphyrins with diethylamine (DEA) and triethylamine (TEA) lead to the formation of three alkylamine-bridged intracavity-extended macrocycles incorporating naphthotetrahydropyridine, naphthopyrrolotetrahydro-1*H*-azepine, and naphthodihydro-2*H*-pyran moieties, respectively.[3] This peculiar reactivity of carbaporphyrins signifies the need for careful assesment of the choice of a base in the various reactions carried out with porphyrinoids.

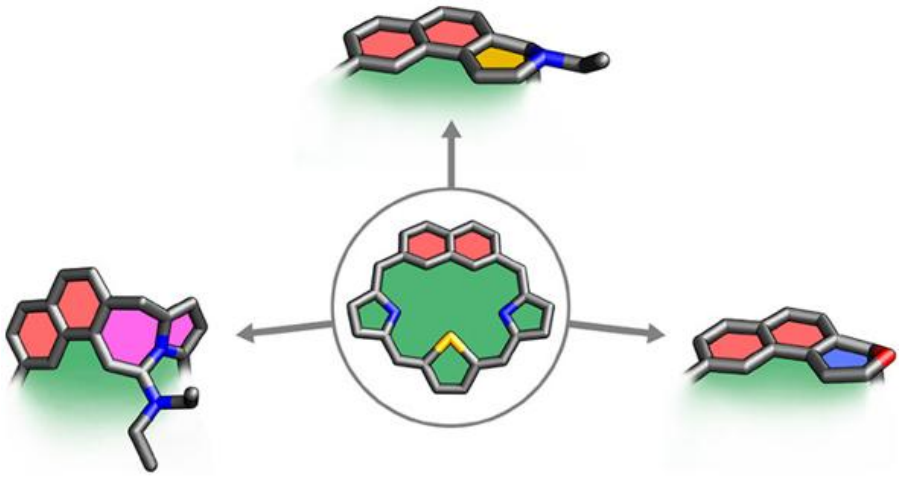

Figure 1. The new heterocyclic moieties incorporated in the intracavity-extended porphyrinoids.

Acknowledgements

This work was supported by the National Science Centre of Poland upon Grant 2020/38/E/ST4/00024.

References

[1] B. Szyszko, L. Latos-Grażyński. *Angew. Chem. Int. Ed.* **2019**, 59, 16874-16901.

[2] T. D. Lash, A. M. Young, J. M. Rasmussen, G. M. Ferrence. *J. Org. Chem.* **2011**, 76, 5636-5651. B. Szyszko, M. Matviyishyn, S. Hirka, E. Pacholska-Dudziak, A. Białońska, L. Latos-Grażyński. *Org. Lett.* **2019**, 21, 7009-7014.

[3] K. Ślusarek[‡], J. P. Perdek[‡], A. Białońska, R. A. Grzelczak, B. Szyszko. *Org. Lett.* **2023**, *25*, 4735-4739

Chiral induction to supramolecular helical polymers and catalysts with chiral anions

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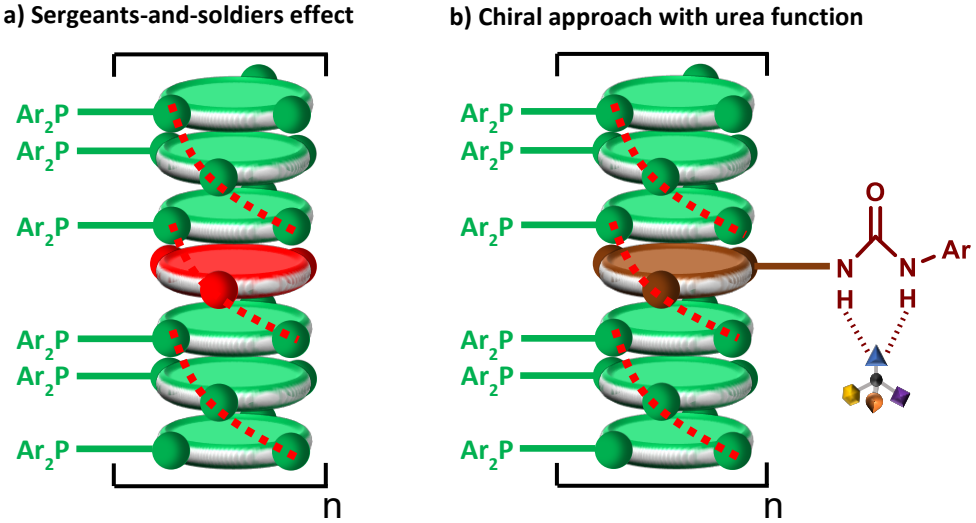
Supramolecular polymers constituted of non-covalent monomeric units has emerged in the last decades in the field of science materials engineering for various applications.[1] Introducing stereochemical information in these systems is leading to the formation of homochiral helices, mostly through the use of enantiopure monomers embedding a stereochemical center in their side chain, also called the sergeants-and-soldier effect (***Scheme 1a***).[2] Hydrogen-bonded supramolecular polymers are inherently sensitive to competitive anions that can be used to modulate the length and thus the selectivity of supramolecular helical catalysts based on benzene-1,3,5-tricarboxamide (BTA) monomers.[3] We are now interesting in probing chiral ions as triggers for the formation of homochiral supramolecular helices. The strategy consists in interacting achiral BTA or triarylamine trisamide (TATA) monomers appended with a urea function with enantiopure anions (***Scheme 1b***). Our results reveal that induction of chirality is indeed efficient when substituted bi-naphthyl-phosphoric acids, 3,3'-bis(2,4,6-triisopropyl-phenyl)-1,1'-binaphthyl-2,2'-diyl hydrogenphosphate (TRIP) is used as chiral anion, exclusively with the TATA platform.



Scheme 1 : a) Chirality transfer by the use of enantiopure monomers b) Chiral induction by interaction of chiral triggers with urea-containing monomers

References

[1] T. De Greef, E.W. Meijer, *Nature*, **2008**, *453*, 171-173.
[2] M. Liu, L. Zhang, T. Wang, *Chem. Rev.*, **2015**, *115*, 7304−7397.
[3] Y. Li, X. Caumes, M. Raynal, L. Bouteiller, *Chem. Commun.*, **2019**, *55*, 2162–2165.

SELF-ASSEMBLING NARROW-BANDGAP RYLENES FOR PHOTOVOLTAIC APPLICATIONS

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Rylenes derivatives are a family of aromatic molecules that are widely used in organic photovoltaic applications. They have excellent chemical and thermal stability, and are recognized for their electron-transport abilities[1–3]. They are easier to modify, and to handle than fullerenes, making them a good candidate to replace them, as non-fullerenes acceptors. To this end, we prepared seven molecules with a rylene core (naphthalene diimide or perylene diimide), as electron acceptors. Then we attached lateral chains composed by electron donor groups and weaker electron acceptor groups.

Moreover, rylene derivatives are known to strongly aggregate via π-π stacking[4,5], which can induce intermolecular recombination, that can quench the energy conversion mechanism. To overcome this, the design of those molecules was made to give liquid-crystal properties. It enables us to control the spontaneous organization of the molecular units, into columnar stacks. Thus, defects can be “repaired” via thermal annealing, and columnar structures can be aligned parallel to the electrode surface.

These molecules have a very wide area of absorption (up to 50% of natural light).

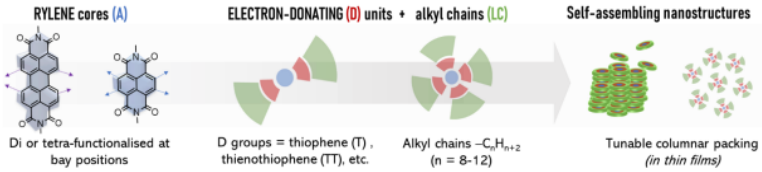

Figure 1: overview of design strategy for the rylene-based self-assembling nanostructures.

Key words : Organic photovoltaic, self-assembly, liquid crystal, rylenes, non-fullerene acceptors

Acknowledgements

ED397 Chimie et Physique des Matériaux, Sorbonne Université, CNRS (funding)

References

[1] X. Zhan, A. Facchetti, S. Barlow, T. J. Marks, M. A. Ratner, M. R. Wasielewski, S. R. Marder, *Adv. Mater.* **2011**, *23*, 268–284.
[2] F. Würthner, C. R. Saha-Möller, B. Fimmel, S. Ogi, P. Leowanawat, D. Schmidt, *Chem. Rev.* **2016**, *116*, 962–1052.
[3] L. Dou, Y. Liu, Z. Hong, G. Li, Y. Yang, *Chem. Rev.* **2015**, *115*, 12633–12665.
[4] C. Li, H. Wonneberger, *Adv. Mater.* **2012**, *24*, 613–636.
[5] A. Nowak-Król, F. Würthner, *Org. Chem. Front.* **2019**, *6*, 1272–1318.

Triarylamine based supramolecular gels

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Supramolecular polymers based on triarylamine units represent a new and attractive class of organic functional materials with innovative conducting and waveguiding properties.[1,2] These molecules, when decorated by lateral amide groups, undergo supramolecular polymerization by π-π stacking and hydrogen bonding interactions leading to the formation of columnar primary stacks. These self-assembled structures can be further involved into higher order aggregation processes leading to bundles of fibers and gels.[3] In this poster, we describe the design and synthesis of a new triarylamine trisamide able to form thermoreversible physical gel in toluene. Microscopic investigation including TEM, SEM and AFM experiments demonstrate the formation of rigid ribbons made of nanometer-height sheets. We also explore the optical and light emission properties of these structures to get insights into possible conducting properties.

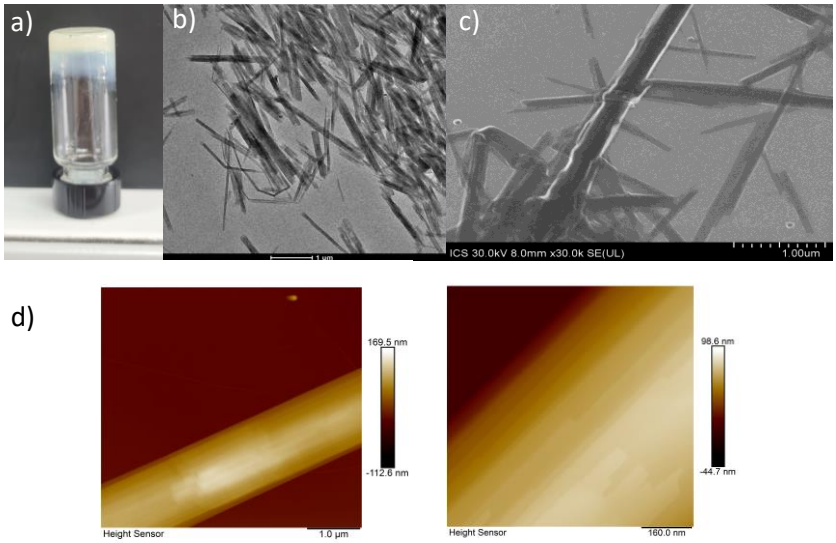

Figure 1. a) Tube inversion experiment in toluene; b-c) TEM (b) and SEM (c) image of the gel in toluene; d) AFM images of a solution in toluene

Acknowledgements

This work was granted by the Agence Nationale de la Recherche as part of the ANR JCJC TemplaSup project (ANR-20-CE06-0015).

References

1. Moulin, E., Armao, J. J. & Giuseppone, N. Triarylamine-Based Supramolecular Polymers: Structures, Dynamics, and Functions. *Acc. Chem. Res.* **52**, 975–983 (2019).
2. Armao, J. J. *et al.* Healable supramolecular polymers as organic metals. *J. Am. Chem. Soc.* **136**, 11382–11388 (2014).
3. Liang, T. *et al.* Covalently Trapped Triarylamine-Based Supramolecular Polymers. *Chem. - A Eur. J.* **25**, 14341–14348 (2019).

Investigating Glycopolymer-Lectin Interactions: Towards Enhanced Biomedical Applications through Dynamic Combinatorial Chemistry

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Polymers used as coatings and wrapping agents are ubiquitous in everyday life, providing protection from conditions and external stimuli as well as increasing shelf-life and stability. This work aims to transpose these desirable benefits to biological objects on the micro- and nanoscale, such as bacterial cells and virus-like particles (SV40 viral capsid), for potential applications in fields such as targeted drug delivery and vaccine technology. One method to achieve this relies on specific molecular recognition events between carbohydrate-decorated polymer chains and lectins on the object's surface. Highly water-soluble synthetic polymers were prepared bearing aromatic aldehyde appendages allowing for further functionalization with carbohydrate residues via dynamic acylhydrazone bond formation. This dynamic combinatorial chemistry (DCC) approach allows the selectivity of lectins for different carbohydrates on the polymer to be studied through acylhydrazone exchange followed by ^{1}H NMR spectroscopy.[1] Glycopolymer-lectin interactions have also been quantified as binding constants via fluorescence titrations. The multivalent effect of polymer chains decorated with multiple carbohydrate moieties results in greatly improved binding affinities, which is essential for the polymer chains to concentrate on the object's surface. To fully encapsulate the object the polymer chains must be cross-linked. Dynamic cross-linkers placed within single polymer chains undergo intra- to intermolecular exchange once concentrated, resulting in the formation of a continuous polymer film around the object.[2]

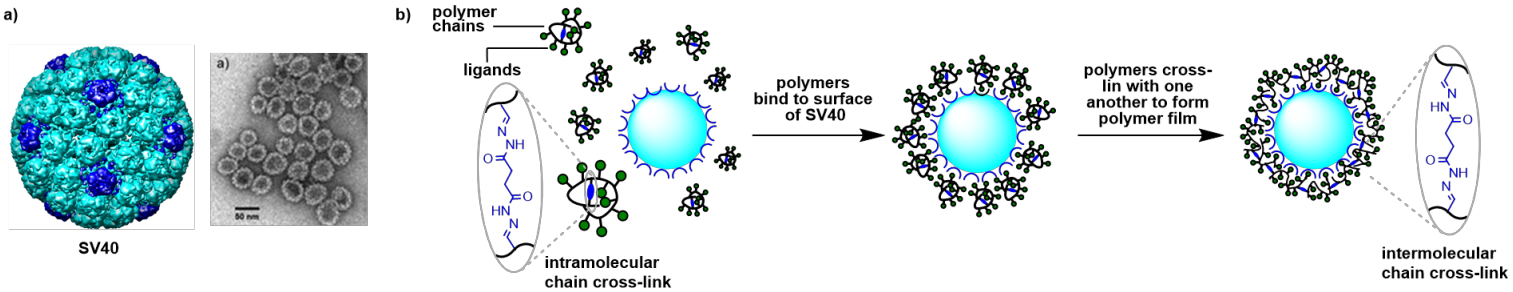

Figure: a) Structure and TEM image of SV40 viral capsid; b) Wrapping of SV40 in a intermolecularly cross-linked polymer film.

Acknowledgements

We thank the Leverhulme Trust for their generous support (RPG-2021-135).

References

[1] C. S. Mahon, M. A. Fascione, C. Sakonsinsiri, T. E. McAllister, W. B. Turnbull, D. A. Fulton, *Org. Biomol. Chem.*, **2015**, *13*, 2756-2761.

[2] P. L. Higgs, J. L. Appleton, W. B. Turnbull, D. A. Fulton, *Chem. Eur. J.*, **2021**, *27*, 17647-17654.

TITLE: NEW INSIGHTS ABOUT STRUCTURE/OPTICAL WAVEGUIDE BEHAVIOR RELATIONSHIPS IN LINEAR BISETHYNYLBENZENES

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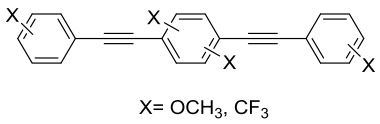
1D organic micro/nanostructures (OMNSs) based on π-conjugated molecules are considered ideal and attractive building units for the development of supramolecular structures with optical waveguiding behavior.[1] These components play a pivotal role in the next generation of high-performance electronic and photonic devices. In this work, we report the synthesis, aggregate formation and the study of the crystal structure and waveguide properties of a series of 1,4-bis(phenylethynyl)benzene derivatives (Figure 1a). In order to obtain broad structure/property relationships. These simple molecules constitute a good choice, which is important for their real implementation in photonic devices. In addition, they can be easily modified to determine the influence of small structural modifications into the supramolecular structure and in its optical properties.

The excellent morphologies of some of the obtained aggregates have made their study feasible by X-ray diffraction. An in-depth analysis of crystal structures concluded that the presence of internal channels inside the crystal is beneficial for optical waveguiding (Figure 1b).[2] This important conclusion has been supported by previous X-Ray in structures reported by our group.

a)



b)

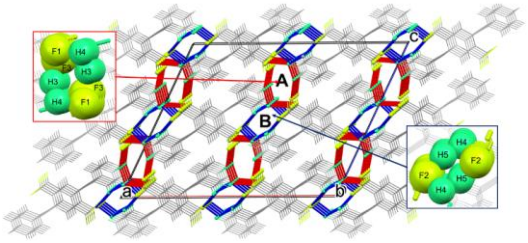


Figure 1. a) Chemical structure of 1,4-bis(phenylethynyl)benzene derivatives. b) Crystal structure with internal channels.

Acknowledgements

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References

[1] S. Wu, B Zhou, D. Yan. *Adv. Opt. Mater.* **2021**, 2001768

Zn(II)- Metallosurfactant Mediated Biosupramolecular Coassembly: Oligonucleotide digestion and Phoresis

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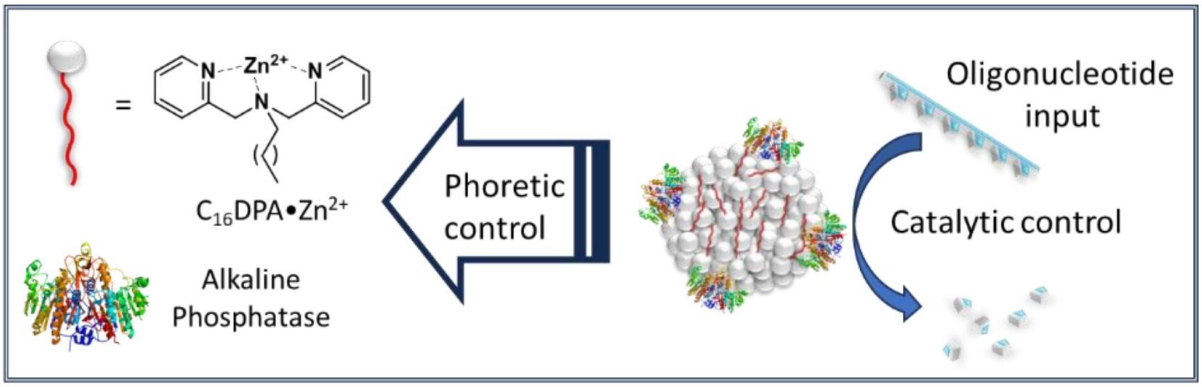
The coordination of biomolecules interacting in intricate networks of biological circuitry is one of the fascinating aspects of life. These networks are capable of processing enormous numbers of parallel signals into particular downstream outputs, incorporating functions like dynamic specificity, stimuli responsiveness, and adaptability for precise spatiotemporal control over catalysis.[1] Biosensing and catalysis can both benefit from the unique biomolecular recognition capability that biosupramolecular networks can tap into to simulate such processing capacity in artificial systems.[1,2] Herein, a biosupramolecular catalytic system based on the co-assembly of phosphoesters or sequence-specific oligonucleotide substrates by Zn(II)-metallosurfactant and alkaline phosphatase enzyme will be introduced.[3] First, it will be demonstrated that Zn(II) in the hydrophobic chain and headgroup of a surfactant is required for the interaction of phosphoesters and proteins/enzymes. Sequence-specific oligonucleotide perception and digestion is the most fascinating feature of this biosupramolecular technique. Extensive isothermal titration calorimetry studies for both oligonucleotide-specific binding and catalytic activation/inhibition events will be used to demonstrate the enthalpy-entropy imbalance. Due to its ability to quantify energy in intricate substrate-mediated supramolecular catalytic systems, this data will be extremely valuable. At last findings about supramolecular binding and catalysis-driven phoretic drift in a substrate and receptor gradient will be shown. These findings may have future implications for the construction of synthetic, spatiotemporally controlled catalytic systems, ranging from microsized precision transport vehicles.



References

[1]. Watson, E. E.; Angerani, S.; Sabale, P. M.; Winssinger, N. Biosupramolecular Systems: Integrating Cues into Responses. *J. Am. Chem. Soc.* **2021**, *143* (12), 4467–4482.

[2]. Aastha; Priyanka; Maiti, S. Simultaneous Quantification of Serum Albumin and Gamma Globulin Using Zn(Ii)-Metallosurfactant *via* a Coffee Ring Pattern. *Chem. Commun.* **2023**, *59* (43), 6536–6539.

Heteroleptic copper(I) complexes prepared from a tetra-phenylbenzene-substituted phenanthroline ligand

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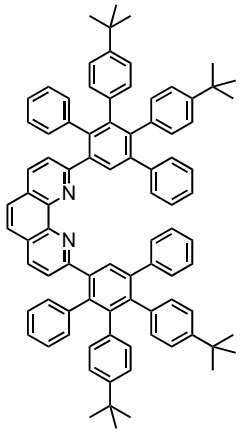
The coordination of diimine aromatic ligands with copper(I) has been widely used for the construction of fascinating metallo-supramolecular nanostructures. Classical examples include helicates, cages and molecular grids. In these particular cases, the kinetic instability of the copper(I) complexes leading to ligand dissociation in solution is a clear advantage. The dynamic character allows actually for correction of possible errors during the self-assembly process and the equilibrium is therefore totally driven towards the most stable product.[1] On the other hand, this kinetic instability means also that the coordination of different ligands around the same copper(I) cation is particularly difficult to control.[2] The pioneering work of Sauvage has shown that the heteroleptic coordination of copper(I) can be favored by combining a macrocyclic chelating ligand with an acyclic one.[3] Another very efficient strategy to control the coordination of two different ligands around a copper(I) cation has been developed by Schmittel and co-workers.[4] In this case, one of the two chelating ligands is decorated with large substituents preventing the formation of a stable homoleptic copper(I) complex. As part of this research, we became interested in evaluating the potential of a new diaryl-1,10-phenanthroline ligand for the formation of stable heteroleptic copper(I) complexes.[5] In the design of the ligand, the two aryl subunits have been only substituted in one *ortho* position. As a result, their relative orientation is either *Syn* or *Anti* thus leading to an unprecedented isomerism in the resulting copper(I) complexes. The latest developments on the preparation of heteroleptic copper(I) complexes from this particular ligand will be presented.



Acknowledgements

Financial support from the *Fondation Jean-Marie Lehn* is gratefully acknowledged.

References

[1] J.-M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH, Weinheim, 1995.

[2] a) M. Holler, B. Delavaux-Nicot, J.-F. Nierengarten, *Chem. Eur. J*. **2019**, *25*, 4543-4550. b) T.-A. Phan, N. Armaroli, A. Saavedra Moncada, E. Bandini, B. Delavaux-Nicot, J.-F. Nierengarten, D. Armspach, *Angew. Chem. Int. Ed*. **2023**, *62*, e202214638.

[3] a) C. O. Dietrich-Buchecker, J.-P. Sauvage, J.-P. Kintzinger, *Tetrahedron Lett.* **1983**, *24*, 5095-5098. b) C. O. Dietrich-Buchecker, J.-P. Sauvage, *Tetrahedron* **1990**, *46*, 503-512.

[4] a) M. Schmittel, A. Ganz, *Chem. Commun*. **1997**, 999-1000. b) M. T. Miller, P. K. Gantzel, T. B. Karpishin, *J. Am. Chem. Soc*. **1999**, *121*, 4292-4293. c) M. Schmittel, A. Ganz, D. Fenske, *Org. Lett*. **2002**, *4*, 2289-2292. d) M. Schmittel, H. Ammon, V. Kalsani, A. Wiegrefe, C. Michel, *Chem. Commun*. **2002**, 2566-2567. e) V. Kalsani, H. Amon, F. Jäckel, J. P. Rabe, M. Schmittel, *Chem. Eur. J*. **2004**, *10*, 5481-5492.

[5] B. Ralahy, U. Hahn, E. Wasielewski, J.-F. Nierengarten, *Eur. J. Inorg. Chem*. **2021**, 2625-2635.

Solvent-Responsive Morphologies in Supramolecular Dendrimer Assemblies: Controlling the Uncontrollable

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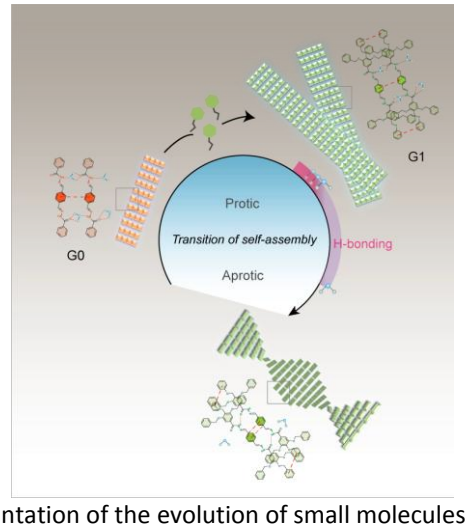
Inspired by helical molecular nanostructures found in biological systems, designing achiral molecules that can self-assemble into higher-order helical structures and unlocking the morphological transformation of self-assembly by tuning noncovalent molecular interactions is important in biomedical and chemical sciences.[1, 2] In this work, we have successfully integrated supramolecular dendrimer architectures into an achiral chromophore featuring aggregation-induced emission (AIE) properties, enabling robust emission in aggregated states. Specifically, two dibenzohydrazide-based dendrimers (G0 and G1) were thoughtfully synthesized, both demonstrating pronounced AIE characteristics. The pivotal role of hydrogen bonding and π-π stacking interactions in the self-assembly of G0 and G1 is revealed as the driving force behind the evolution of supramolecular morphology. Notably, the introduction of a polar protic solvent prompts a morphological shift from helical to fibrous structures. Comprehensive studies underscore the significant influence of hydrogen bonding on the morphological evolution of supramolecular architecture in dibenzohydrazide dendrimers. The demonstrated AIE characteristics exhibited by G0 and G1 hold immense promise across diverse applications, including imaging and optoelectronics. These findings pave the way for designing materials with finely tuned fluorescence and unlock avenues for hierarchical structures, presenting exciting opportunities in the field.



Scheme 1. Schematic representation of the evolution of small molecules into higher-order assemblies driven by supramolecular interactions

Acknowledgements

The authors thank SERB, DST and MoE for their financial support.

References

[1] S.I. Stupp, L.C. Palmer, *Chem. Mater.,* **2013**, *26*, 507-518.

[2] S. Fu, A. Pang, B.Z. Tang, *ACS Nano,* **2022,** *16* (8), 12720-12726.

Combining Imine Condensation Chemistry with [3,3] Diaza-Cope Rearrangement for One-Step Formation of Hydrolytically Stable Chiral Architectures

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Dynamic covalent chemistry (DCC) has, in recent years, provided valuable tools to synthesize molecular architectures of increasing complexity.[1] Our group took also advantage of imine DCC chemistry to prepare TPMA-based supramolecular cages for molecular recognition applications.[2] However, the versatility of this approach has as a major drawback: the intrinsic hydrolytic lability of imines, which hampers some applications. We present herein a synthetic strategy that combines the advantages of a thermodynamic-driven formation of a supramolecular structure using imine chemistry, together with the possibility to synthesize chiral hydrolytically stable structures through a [3,3]-sigmatropic rearrangement.[3] A preliminary mechanistic analysis of this one-pot synthesis, the scope of the reaction and the supramolecular applications of the newly synthesized structures are also discussed.

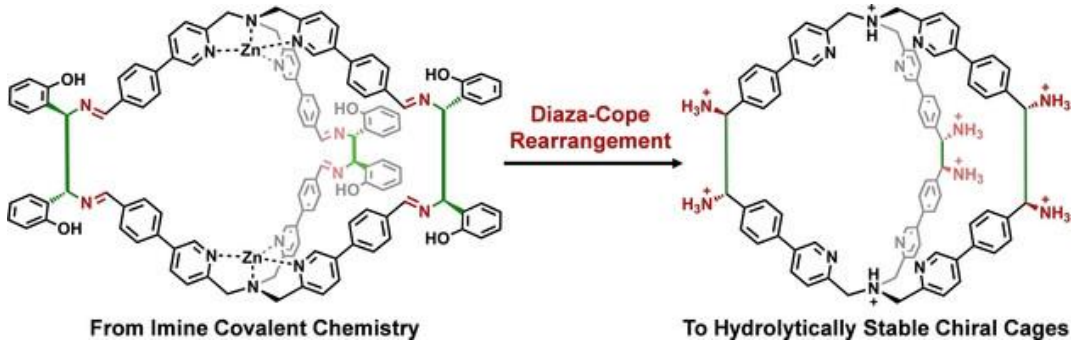

Figure 1. [3,3] Diaza-Cope rearrangement for chiral hydrolytically stable cage formation.

Acknowledgements

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References

[1] S. J. Rowan, S. J. Cantrill, G. R. L. Cousins, J. K. M. Sanders, J. F. Stoddard, *Angew. Chem. Int. Ed.* **2002**, *41*, 898-952; H. Wang, Y. Jin, N. Sun, W. Zhang, J. Jiang, *Chem. Soc. Rev.* **2021**, *50*, 8874-8886.
[2] C. Bravin, E. Badetti, F. A. Scaramuzzo, G. Licini, C. Zonta, *J. Am. Chem. Soc.* **2017**, *139*, 6456-6460; C. Bravin, J. A. Piękoś, G. Licini, C. A. Hunter, C. Zonta, *Angew. Chem. Int. Ed.* **2021**, *60*, 23871-23877.
[3] F. Begato, R. Penasa, K. Wurst, G. Licini, C. Zonta, *Angew. Chem. Int. Ed.* **2023**, *62*, e20230449.

Ruthenium Peptide Bioconjugates for Photoactivated Chemotherapy

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One of the most severe limitations of current anticancer chemotherapy are the serious side effects caused by toxic drugs affecting not only tumors but also healthy organs. Local activation of drugs by light irradiation of the tumor is a promising approach to control where the toxicity is delivered. Metal complexes are well suited for photoactivated chemotherapy (PACT), but their ability to enter cancer cells is often tuned by increasing lipophilicity, which leads to unselective uptake by passive transport.[1] To solve this issue, conjugation of metallodrugs to peptides is particularly promising,[2] as many receptors exist at the cell membrane that take up peptides selectively. Peptide conjugation also opens new possibilities to combine the action of the metallodrug to that of the peptide, some of which have cytotoxic properties. The applicability of many peptides in drug development, however, is limited by nonspecific enzymatic peptidase activity, which can lead to severe toxic reactions. For such peptides as well, conjugation to a metallodrug can be beneficial if the metal center in the prodrug limits peptide degradation.

In this work, we study the combination of biologically active anticancer peptides and photoactivatable Ru(II) complexes to achieve synergistic effects in a family of ruthenium-peptide bioconjugates for PACT treatment of cancer. By coordination of multiple Ru(II) complexes to the methionine residues of the peptide, the components cage each other in the dark, thus affording low toxicity, while light-induced cleavage of the ruthenium-thioether bonds releases two bioactive components, which kill cancer cells in a very efficient and side effect-free manner.

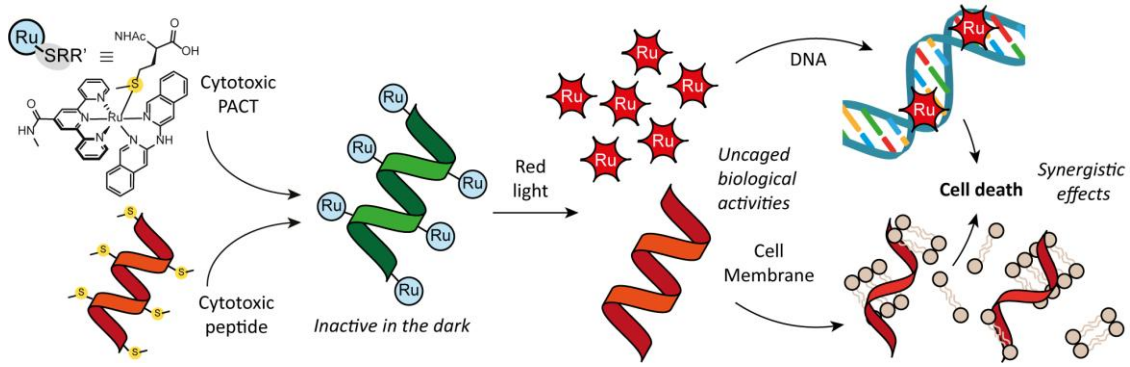

Figure 1. General concept of peptide-Ru(II) bioconjugates composition and action upon red light irradiation.

Acknowledgements

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References

[1] S. Bonnet, *J. Am. Chem. Soc*. **2023**, *145*, 23397–23415.

[2] L. Zhang, S. Bonnet et al., *J. Am. Chem. Soc.* **2023**, 145, 14963–14980.

TRIPTYCENE-FUSED PYRIDYLBENZIMIDAZOLES: SYNTHESIS, PROPERTIES AND USE IN COORDINATION CHEMISTRY

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Shape-persistent triptycene-based molecules have garnered increasing interest among supramolecular chemists and material scientists for the construction of more complex architectures such as covalent-organic frameworks (COFs) and organic or metal-organic cages.[1] In order to expand the family of functionalized triptycene-based building blocks, we developed a new series of triptycene-fused pyridylbenzimidazoles, in which the nitrogen atom of the pyridine linked to the benzimidazole moiety is systematically shifted from the ortho to the para-position. We have also varied the number of substituted blades bearing the functional motif from one to three. Initial coordination studies were therefore made using bis-(o-pyridil)benzimidazole tripticene as ligand to form self-assembled triple-stranded mesocates with Fe(II) and Zn(II) as octahedral metal centres. The rigidity of the molecular skeleton and the steric effect of triptycenes prevent the three ligand strands from wrapping around the two metal centres, precluding the formation of a helicate structure. The metal-induced self-assembly blocks the prototropic tautomerization of the benzimidazole protons, stabilizing the *syn* form of the partially adaptive ligand. In addition, NMR studies on the diiron(II) mesocate in deuterated methanol showed that the complex is paramagnetic at room temperature, and undergoes a thermal-induced one-step spin cross-over (SCO) during solution cooling with a $T_{1/2}$ of 243 K (Evans method).[2]

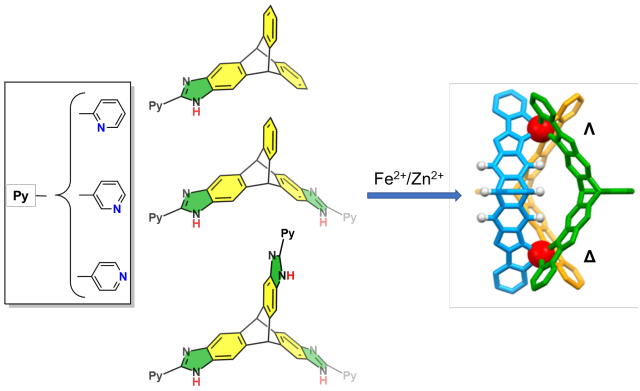

Figure 1. Family of triptycene-fused pyridylbenzimidazoles and M_2L_3 mesocate (M = Fe(II) or Zn(II)).

Acknowledgements

We acknowledge the Ministero dell'Università e della Ricerca (MUR) and the University of Pavia through the program "Dipartimenti di Eccellenza 2023–2027".

References

[1] Y. Zhao, S. Das, T. Sekine, H. Mabuchi, T. Irie, J. Sakai, D. Wen, W. Zhu, T. Ben and Y. Negishi, Angew. Chem. Int. Ed., **2023**, 62, e202300172; K. Tian, S. M. Elbert, X.-Y. Hu, T. Kirschbaum, W.-S. Zhang, F. Rominger, R. R. Schröder and M. Mastalerz, Adv. Mat., **2022**, 34, 2202290.

[2] R. W. Hogue, S. Singh and S. Brooker, Chem. Soc. Rev., **2018**, 47, 7303-7338.

SUPRAMOLECULAR ASSEMBLIES OF PSEUDOPOLYROTAXANE TYPE FROM POLY(ETHYLENE GLYCOL) AND POLY(N-ISOPROPYLACRYLAMIDE AND THEIR COPOLYMERS

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The supramolecular chemistry of polyrotaxanes, using reversible covalent bonds and specific polymers, makes it possible to obtain innovative, stimulable materials.[1] These supramolecular assemblies can be represented as a string of pearls. In this communication, the pearls used are cyclic cyclodextrin molecules which are non-cytotoxic and biodegradable, and which can slide on a polymer chain to form pseudopolyrotaxanes. The aim of this work was to obtain pseudopolyrotaxanes that could be thermally stimulated.[2] To achieve this goal, biocompatible pseudopolyrotaxanes including either an homopolymer, or a diblock copolymer were synthesized from a poly(N-isopropylacrylamide) (PNIPAM), a thermosensitive polymer[3], and/or an hydrophilic polymer, a poly(ethylene glycol) (POE), known for its biocompatibility with cyclodextrins allowing their good threading.[4] Several pseudopolyrotoxanes were successfully synthesized under different conditions, and their structures (number of threaded cyclic molecules as a function of the size of the chain, the starting stoichiometry cyclic molecule/polymer) were probed by using various characterization methods (SEC, NMR, XRD).

Acknowledgements

This work was funded be a Ph.D. grant from 2MIB Doctoral School (Université Paris-Saclay).

References

1. Harada, A., Takashima, Y. & Nakahata, M. Supramolecular Polymeric Materials via Cyclodextrin–Guest Interactions. *Acc. Chem. Res.* **47**, 2128–2140 (2014).
2. Kobayashi, Y. Precise synthesis of polyrotaxane and preparation of supramolecular materials based on its mobility. *Polym. J.* **53**, 505–513 (2021).
3. Pasparakis, G. & Tsitsilianis, C. LCST polymers: Thermoresponsive nanostructured assemblies towards bioapplications. *Polymer* **211**, 123146 (2020).
4. Harada, A., Takashima, Y. & Nakahata, M. Supramolecular Polymeric Materials via Cyclodextrin–Guest Interactions. *Acc. Chem. Res.* **47**, 2128–2140 (2014).

Dynamic stapled peptides for the inhibition of protein-protein interactions

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In the search for new target-directed strategies, the use of Dynamic Combinatorial Chemistry (DCC) has been expanding over the last few years. Thanks to DCC, large libraries of thermodynamically stable constructs can be generated by employing reversible reactions.[1] More interestingly, it is possible to explore the self-adaptative potential of such libraries simply by the addition of biological targets into the complex mixture, which could lead to the discovery of new therapeutics. In this project, we wish to implement DCC in the context of finding peptidic inhibitors for Protein-Protein Interactions (PPI). This strategy would allow the simultaneous and rapid screening of multiple constructs without facing difficulties related to rational design and synthesis. Therefore, we are currently working on a proof of concept that relies on the generation of dynamic libraries of stapled peptides for the identification of PPI inhibitors. The project focuses on the p53-HDM2/HDMX PPI, known to play a crucial role in cell-cycle regulation and apoptosis.

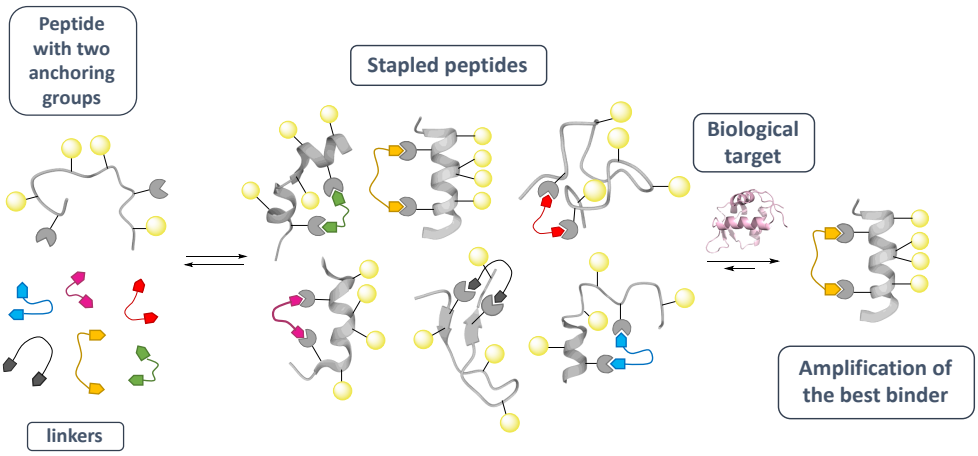

Figure 1. Generation of a library of stapled peptides by dynamic combinatorial chemistry and screening of the best binders in the presence of the biological target.

Acknowledgments

We thank the mass spectrometry MS3U platform (Sorbonne Université) for its services. We acknowledge the Doctoral School of Molecular Chemistry of Central Paris (ED406) and Sorbonne Université for fundings.

References

[1] A. Rodrigues, L. Rocard, R. Moumné, *ChemSystemsChem*, **2023**, 5, e202300011

Axially-Chiral Supramolecular Polymers from Highly Hindered Non-Planar Chiral Allenes

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(*P*) or (*M*) single molecule supramolecular fibers can be obtained during the self-assembly of axially chiral allenes, which place their four substituents in two perpendicular planes. This specific spatial distribution, in combination with the rigidity of the allenes, makes them great candidates to create chiral building blocks with potential self-assembling properties. Therefore, we designed a chiral allene with two *tert*-butyl groups in different planes and opposite directions to provide stability to the building block. In the other two positions of the allene, π-extended and planar ethylene phenylene moieties —substituted at the *para*-positions of the aromatic rings with ethylene diamides that bear gallic wedges with paraffinic chains— were introduced to favour the self-assembly of the axially chiral allene. Aggregation studies in MCH through different spectroscopic techniques such as UV-vis, ECD, IR or NMR, in addition to atomic force microscopy (AFM) and computational studies revealed the formation of single-molecule chiral fibers formed by the 1-D stack of the allene building blocks through a cooperative mechanism. This species evolves towards the formation of larger fibers obtained by self-assembly of the single ones. In these aggregates, an axial-to-axial helical induction mechanism emerges to generate the chiral fibers, whose handedness depends on the axial chirality of the allene: (*P*)-allene, (*M*)-aggregate; (*M*)-allene, (*P*)-aggregate.

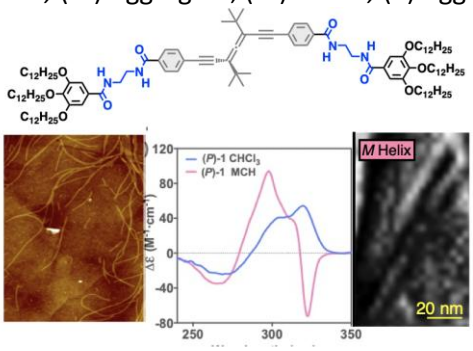

Figure 1. Structure of the allene employed in this work, variation of chiroptical properties and AFM images showing the self-assembled helical fibers.

Acknowledgements

Financial support from AEI (PID2022-136848NB-I00), Xunta de Galicia (ED431C 2022/21, Centro Singular de Investigación de Galicia acreditación 2019-2022, ED431G 2019/03) and the European Regional Development Fund (ERDF) are gratefully acknowledged. R. R and M. F. M. thanks AEI for a Juan de la Cierva Incorporación (IJC2020-042689-I), and a FPI contract respectively. M. L. S. thanks Xunta de Galicia for a predoctoral fellowship. We also thank Centro de Supercomputación de Galicia (CESGA) for computational resources.

References

[1] M. Lago-Silva, M. Fernández-Míguez, Z. Fernández, M. M. Cid, E. Quiñoá, R. Rodríguez, F. Freire. *Submitted*

Two-Dimensional Supramolecular Polymerization of a Bis-Urea Macrocycle into a Brick-Like Hydrogen-Bonded Network

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We report on a dendronized bis-urea macrocycle **1** self-assembling via a cooperative mechanism into two-dimensional (2D) nanosheets formed solely by alternated urea-urea hydrogen bonding interactions. The pure macrocycle self-assembles in bulk into one-dimensional liquid-crystalline columnar phases. In contrast, its self-assembly mode drastically changes in $CHCl_3$ or tetrachloroethane, leading to 2D hydrogen-bonded networks. Theoretical calculations, complemented by previously reported crystalline structures, indicate that the 2D assembly is formed by a brick-like hydrogen bonding pattern between bis-urea macrocycles. [1] This assembly is promoted by the swelling of the trisdodecyloxyphenyl groups upon solvation, which frustrates, due to steric effects, the formation of the thermodynamically more stable columnar macrocycle stacks. This work proposes a new design strategy to access 2D supramolecular polymers by means of a single non-covalent interaction motif, which is of great interest for materials development.

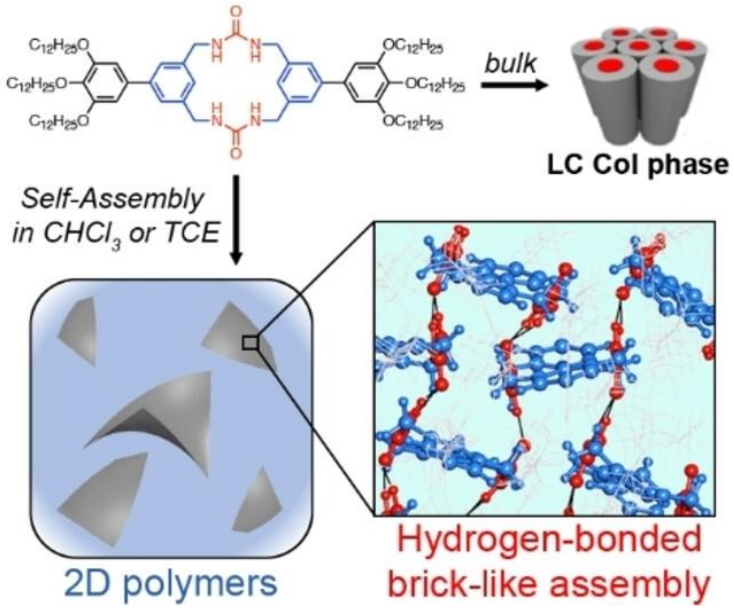

Figure 1. Dendronized bis-urea macrocycle forms columnar liquid-crystalline phases, while in solvents it self-assembles into two-dimensional (2D) nanosheets with a brick-like organization.

Acknowledgements

We acknowledge the MICINN/AEI of Spain, the GOIB and the National Science Foundation for financial support. L. R. is thankful to Govern de les Illes Balears for the PhD fellowship (FPI_039_2020).

References

[1] J. Yang, M. B. Dewal, D. Sobransingh, M. D. Smith, Y. Xu, L. S. Shimizu, J. Org. Chem. 2009, 74, 102–110.

Encapsulation of copper(I) bisphenanthroline complexes for tuning their luminescence properties

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The binding pocket of proteins provides a well-defined environment around its guest through supramolecular interactions that play a crucial role in the assembly's properties. For example, mutations in the sequence of the Green Fluorescent Protein modify the luminescence properties of the embedded chromophore[1].

The control of molecular properties with supramolecular chemistry leads us to examine the self-assembled hexameric resorcin[4]arene capsules as protein binding pockets' surrogates. Such organic capsules are known to encapsulate cationic species and, more recently, coordination complexes[2], modifying their catalytic and photophysical properties. The possibility to bias the chirality of this hexameric capsule seems an appealing strategy to get chiroptical properties including Circularly Polarized Luminescence.

This poster will present the synthesis of four new copper(I) bisphenanthroline complexes associated with a chiral counteranion, their encapsulation studies as well as the consequences of the encapsulation on their absorption and emission properties.

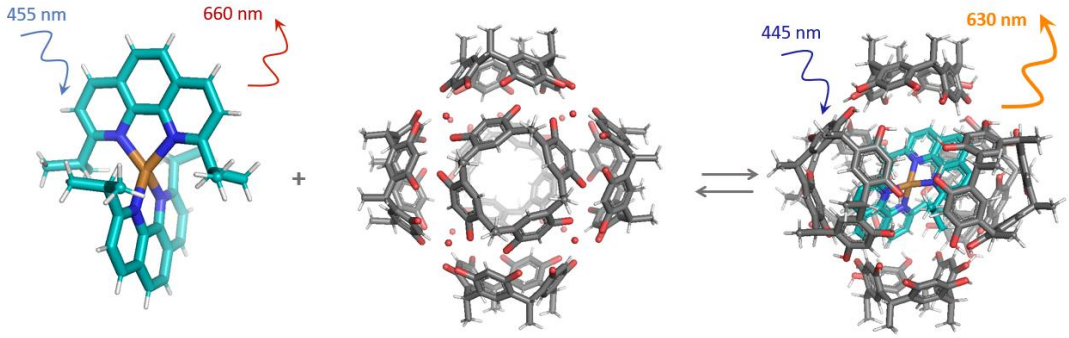

Figure 1. Tuning of photophysical properties by encapsulation of a copper(I) complex.

Acknowledgements

Doctoral School MTCI, Université Paris Cité, for the financial support.

References

[1] V. Sample, R. H. Newman, J. Zhang, *Chem. Soc. Rev.*, **2009**, *38*, 2852-2864.

[2] T. Zhang, L. Le Corre, O. Reinaud, B. Colasson, *Chem. Eur. J.*, **2021**, *27*, 434-443.

Dual Stimuli-Responsive Foldamers

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Stimuli-responsive foldamers demonstrate controlled switching behaviour upon the application of an external stimulus (e.g., light or redox chemistry) and they have excited great interest due to their wide-ranging applications in sensing, synthesis, materials chemistry and biological chemistry.[1,2] To date, the main focus has been placed on the development of foldamers that can respond to only one type of stimulus (e.g., only light).[1a] However, these singly stimuli-responsive foldamers can only display limited levels of operational complexity and, consequently, multi-stimuli-responsive foldamers have emerged as highly desirable targets.[3]

We report on novel, dual stimuli-responsive foldamers that exhibit the ability to individually respond to the two distinct stimuli of light and redox chemistry (Figure 1).[4] The reversible photo-driven conformational switching of these new azobenzene-based foldamers, between stable helix and random coil geometries, has been established using both ^{1}H NMR and circular dichroism (CD) spectroscopy (Figure 1b). Whilst cyclic voltammetry has been used to determine the reversibility of their chemical switching behaviour, between neutral ferrocene and charged ferrocenium states, upon regulated changes to the redox chemistry (Figure 1c).

We anticipate that these novel supramolecular scaffolds will play a key role in the future development of multi-addressable foldamers for sophisticated smart functions.

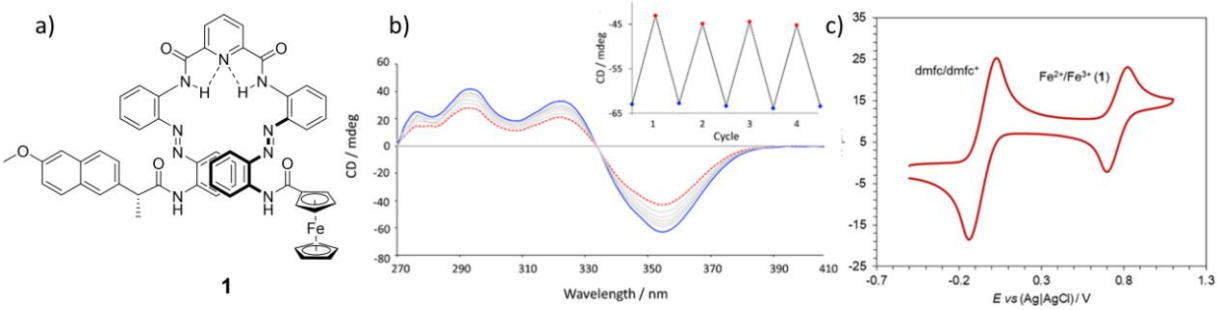

Figure 1. a) Dual stimuli-responsive foldamer **1** composed of light-responsive azobenzene units and a redox-active ferrocene unit b) CD spectra of **1** before irradiation (blue line) and at the photostationary state (red line) after irradiation with 365 nm for 10 min; inset shows fatigue cycling studies c) Cyclic voltammogram of **1** in dichloromethane with decamethylferrocene (dmfc) as an internal reference.

Acknowledgements

We acknowledge the Royal Society Research Grant [RGS\R1\231242], Leverhulme Trust Project Grant [RPG-2022-118] and UKRI Future Leaders Fellowship [MR/S035486/2].

References

[1] Z. Yu, S. Hecht, *Chem. Commun.*, **2016**, *52*, 6639-6653; B. Gole, B. Kauffmann, V. Maurizot, I. Huc and Y. Ferrand, *Angew. Chem. Int. Ed.*, **2019**, *58*, 8063-8067.
[2] B. A. F. Le Bailly, J. Clayden, *Chem. Commun.*, **2016**, *52*, 4852-4863.
[3] M. H. -Y. Chen, S. Y. -L. Leung, V. W. -W. Yam, *J. Am. Chem. Soc.*, **2019**, *141*, 12312-12321.
[4] A. R. Davis, J. O. Dismorr, L. Male, J. H. R. Tucker, S. J. Pike, *under review*.

Iminopyrrole-Based Self-Assembly: A Route to Intrinsically Flexible Molecular Links and Knots

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The subcomponent self-assembly approach is a powerful tool for constructing large architectures from relatively simple precursors. Reactions between aldehydes, amines, and metal salts involve formation of coordinative (N→metal) and covalent (N=C) bonds, and as the result leads to macrocycles, molecular cages, and mechanically interlocked molecules (MIMs).[1] In the literature there are numerous examples of links and knots that have a diiminopyridine[2,3] motif in their structure while the field of MIMs incorporating diiminopyrrole has been still unexplored.

We have shown that application of 2,5-diformylpyrrole in self-assembly reactions with diamines and Zn(II)/ Cd(II) salts allows the preparation of [2]catenane, trefoil knot, and Borromean rings. The intrinsically dynamic nature of the diiminopyrrole motif rendered all of the formed assemblies intramolecularly flexible.[4]

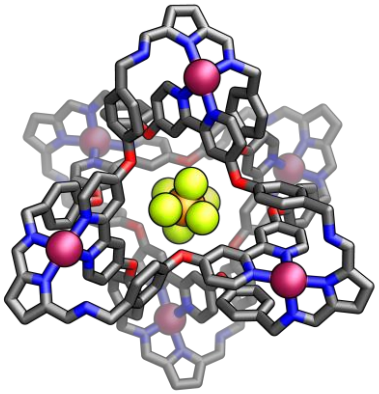

Figure 1. The X-ray molecular structure of Borromean rings with incorporated PF_6^-.

Acknowledgements

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References

[1] J. R. Nitschke, *Acc. Chem. Res.* **2007**, *40*, 103–112.
[2] K. S. Chichak, S. J. Cantrill, A. R. Pease, S.-H. Chiu, G. W. V. Cave, J. L. Atwood, J. F. Stoddart, *Science* **2004**, *304*, 1308–1312.
[3] T. Prakasam, M. Lusi, M. Elhabiri, C. Platas-Iglesias, J.-C. Olsen, Z. Asfari, S. Cianférani-Sanglier, F. Debaene, L. J. Charbonnière, A. Trabolsi, *Angew. Chem. Int. Ed.* **2013**, *52*, 9956–9960.
[4] A. Sarwa, A. Białońska, M. Sobieraj, J. P. Martínez, B. Trzaskowski, B. Szyszko, *Angew. Chem. Int. Ed.* **2024**, *63*, e202316489.

BIOMOLECULAR CHEMOTAXIS IN THE GRADIENT OF MACROMOLECULAR CROWDERS AND METAL IONS

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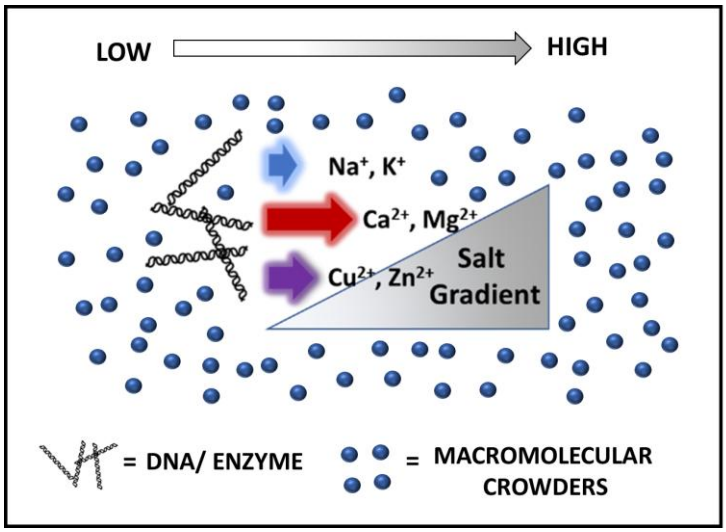
Colloidal and microbiological species propelled through various phoretic mechanism, such as – diffusiophoresis, osmophoresis, thermophoresis, electrophoresis etc. The surface of the colloidal object can sense the concentration or energy gradient surrounding it, resulting a flow across solid/liquid interface of the particle, and thus the particle moves in either towards or opposite direction of the gradient. In our study we reported the migrational behaviour and spatial distribution of biomolecules (i.e., calf thymus DNA & Alkaline phosphatase) in a gradient of different physiologically relevant monovalent and divalent cations and in macromolecular crowding. In case of DNA, we studied the migrational behaviour under two different conditions – (i) microfluidic and (ii) evaporating droplets. We have found migration of DNA is mostly towards low to high salt gradient for both mono- and divalent cations. In case of Ca^{2+} and Mg^{2+} drift is more as compared to other divalent ions like Cu^{2+} and Zn^{2+} as well as monovalent ions Na^{+} and K^{+}, under similar experimental condition we observed the Non-uniform coating in the gradient of metal ions, Cu^{2+} ions having the ability to suppress the coffee ring effect.[1] This process, which was governed by the effective charge and diffusion coefficient of the DNA–metal ion complex, can have potential applications in nucleic acid-based spatiotemporal surface patterning, biosensors, and dynamic bio-colloidal assembly and transport. In case of enzyme (i.e., Alkaline phosphatase), we studied the chemotactic behaviour of alkaline phosphatase (ALP) in the gradients of carbohydrates (glucose, fructose and sucrose) and metal ions, including cofactors (Zn^{2+} and Mg^{2+}), under microfluidic conditions. We have found that ALP migrates marginally away from the carbohydrate gradient, whereas for divalent metal ions, the direction is opposite and more prominent. This differential phoresis is due to the Hofmeister effect driven change in the ALP surface zeta potential and osmotic pressure imbalance.[3] We have also investigated the migrational behaviour of biomolecules in crowded media (i.e., PEG400, PEG4000, PEG9000). Gaining control over the chemotactic extent and direction of an enzyme in response to purely non-catalytic conditions will have potential application in designing environment-responsive nanomachines.



Anion-π interactions in confined space

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The crucial basis of supramolecular chemistry is the intermolecular forces, such as hydrogen bonding, van der Waals forces, coordination bonding or π-π interactions. Over the last two decades, anion-π interactions, relying on the bonding of anions on electron-deficient aromatic surface, have emerged as a new branch of supramolecular chemistry.[1] They have attracted a strong interest in various applications related to molecular recognition, membrane transport,[2] crystal engineering,[3] and catalysis,[4] while their role was demonstrated as relevant also in natural systems.[5]

In order to increase the association of the electron-rich species with the aromatic system, the quadrupole moment (Q_{zz}) must be increased by introducing strong electron-withdrawing substituents while maintaining the high polarizability ($\alpha_{//}$) of the molecular system. Even though, a cooperative effect with hydrogen bonding helps to enhance the formation of the anionic complex, the binding by a single π-acidic surface suffers from non-selective recognition of anionic species and limited Q_{zz}.

On this basis, we designed covalent organic cages with C_3 symmetry, where naphthalenediimides (NDI) are grafted to benzene triimide (BTI). Hence, we expect that the association of multiple π-acidic surfaces will provide binding cavities with high affinity for anionic guests and/or suitable for substrate positioning for confined catalysis.

In this communication, we will discuss the synthesis of tripodal electron-deficient cages and the study of their anion recognition properties.

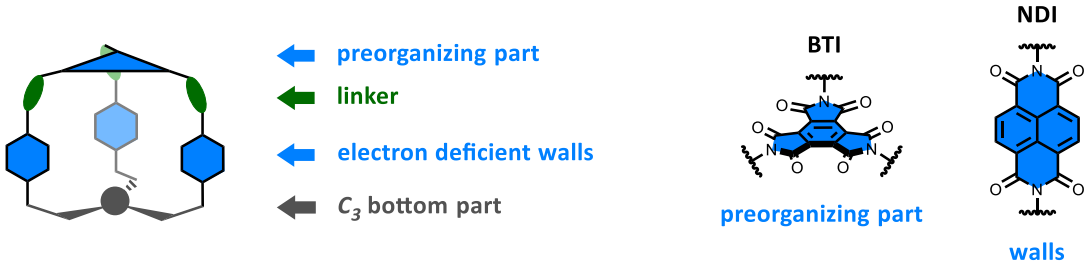

Figure 1. Schematic representation of the tripodal electron-deficient cages.

Acknowledgements

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References

[1] D. Quiñonero, C. Garau, C. Rotger, A. Frontera, P. Ballester, A. Costa, P.M. Deyà, *Angew. Chem., Int. Ed.*, **2002**, *41*, 3389 –3392.

[2] R. Plais, G. Clavier, J-Y. Salpin, A. Gaucher, D. Prim, *Eur. J. Org. Chem*., **2023**, *26*, e202201281.

[3] A. Bauzá, T.J. Mooibroek, A. Frontera, *CrystEngComm*, **2016**, *18*, 10-23.

[4] Y. Zhao, Y. Cotelle, L. Liu, J. López-Andarias, A-B. Bornhof, M. Akamatsu, N. Sakai, S. Matile, *Acc. Chem. Res.*, **2018**, *51*, 2255−2263.

[5] C. Estarellas, A. Frontera, D. Quiñonero, P.M. Deyà, *Angew. Chem. Int. Ed*., **2011**, *50*, 415 –418.

Crystal Structures of non-covalent Protein-Foldamer Hybrids

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Inspired by supramolecular protein architectures in nature, artificial protein assemblies with predisposed geometries are of great interest for applications in macromolecular recognition and as biocompatible nano-materials.[1] We aim to expand the library of natural macromolecular building blocks by fully synthetic, quinoline-based aromatic oligoamide foldamers (AOFs).

The ability of AOFs to bind proteins via non-covalent surface interactions has previously been demonstrated. Their chemical versatility through sidechain moieties not available in natural peptides, combined with their shape-persistency in water makes AOFs intriguing candidates to design robust and chemically diverse hybrid protein-foldamer assemblies.[2,3]

Starting from a small (~7.5 kDa) protein *CloneA* with a defined binding interface towards a specific pentameric AOF sequence Q_5, we target complex three-dimensional networks with controlled geometry and stoichiometry. To do so, we employ computational modelling and iterate through designs involving the fusion of oligomerization domains to the protein as well as symmetrizing the AOF.

Herein we present the first crystal structures of non-covalent protein-foldamer hybrids utilizing two types of C_2 symmetrical AOFs carrying the Q_5 epitope in complex with *CloneA* variations. The structures show highly symmetrical supramolecular networks in the solid state.

Our findings provide the basis to develop precise design rules and further establish synthetic foldamers as biocompatible building blocks in large well-ordered assemblies.

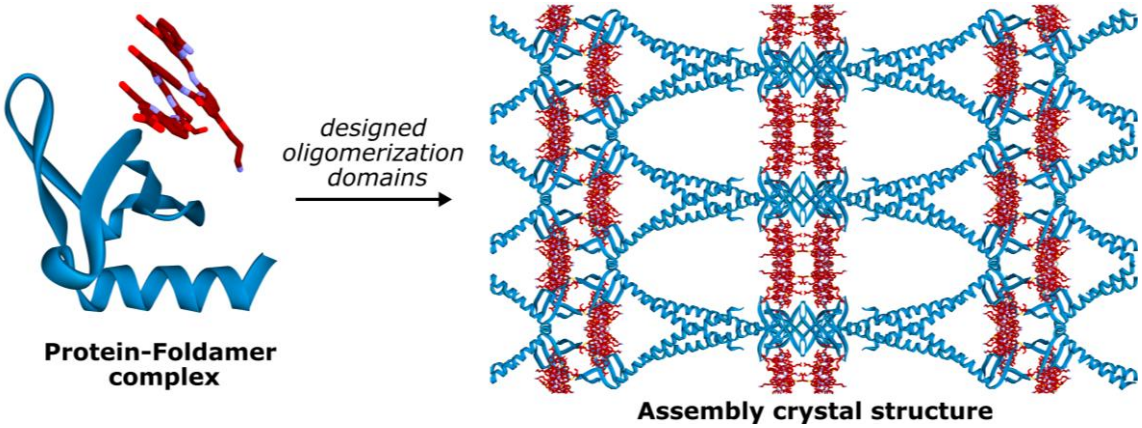

Figure 1. Crystal structure of the 1:1 complex of protein *CloneA* and the Q_5 foldamer (left). Fusion of the protein to a coiled-coil dimerization domain and introduction of C_2 symmetry to the AOF leading to a large tetragonal (SG: $I4_122$) assembly in the solid state (right).

Acknowledgements

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References

[1] I. W. Hamley, *Biomacromolecules* **2019**, *20*, 1829-1848.

[2] P. S. Reddy, B. Langlois D'Estaintot, T. Granier, C. D. Mackereth, L. Fischer, I. Huc, *Chem. Eur. J.* **2019**, *25*, 11042-11047.

[3] X. Hu, S. J. Dawson, P. K. Mandal, X. De Hatten, B. Baptiste, I. Huc, *Chem. Sci.* **2017**, *8*, 3741-3749.

Synthesis of proteomimetic structures based on foldamers

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The link between structure and activity is a key concept that led the way for the design of molecules aiming at interacting against or on behalf of proteins. In that regard, numerous researchers have been inspired by those biopolymers to design artificial architectures with a well-defined folding ability, called Foldamers.[1] Their structural diversity does not yet equal that of biomolecules. Indeed, the helix is by far the most frequently reported type of secondary structure among foldamers and there are comparatively much less examples of foldamers forming sheet-like structures.[2] This scarcity of foldamer-based sheet-like architectures may be due to their greater tendency to aggregate and precipitate when isolated.

Here we present a rational approach for the construction of synthetic multi-stranded β-sheets. Our strategy relies on the iterative coupling of a repetition unit designed to fold through intramolecular hydrogen bonds formation between diamine and diacid units (**Figure 1**). Short diamine and diacid strands are connected by a turn, named ^{D}Pro-DADME, that sets the linear strands at a distance and orientation allowing β-sheet formation.[3] A convergent multi-step synthesis in solution was elaborated to access up to 9-stranded molecules, containing both urea and amide junctions. The solubility of these objects in organic solvents and the absence of aggregation phenomenon enable conformational studies in solution by conventional NMR techniques, and in the solid state by XRD. The possibility to extend the number of strands composing these structures to access complex finite multi-stranded systems able to cover large surfaces or even to fold into synthetic β-barrel structures are currently under investigation.

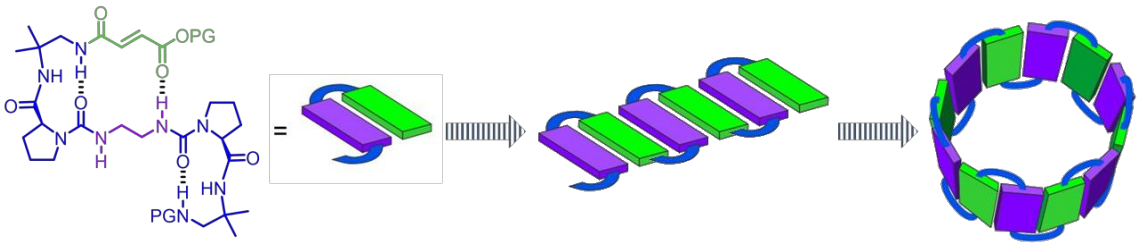

Figure 1. Chemical structure of our repetition unit and schematic representation of the strategy to obtain planar or macrocyclized structures.

References

[1] Gellman, S.H., *Acc. Chem. Res.*, **1998**, *31*, 173-180.

[2] a) Spencer, R., Chen, K.H., Manuel, G., J. S. Nowick, J.S., *Eur. J. Org. Chem.*, **2013**, 3523–3528; b) Ross, J.E., Knipe, P.C., Thompson, S., Hamilton, A.D., *Chem. Eur. J.*, **2015**, *21*, 13518-13521; c) Sebaoun, L., Maurizot, V., Granier, T., Kauffmann, B., Huc, I., *J. Am. Chem. Soc.*, **2014**, *136*, 2168-2174.

[3] Fisk, J.D., Powell, D.R., Gellman, S.H., *J. Am. Chem. Soc*. **2000**, *122*, 5443-5447.

ENCAPSULATED NEUTRAL RUTHENIUM CATALYST FOR SUBSTRATE SELECTIVE OXIDATION OF ALCOHOLS

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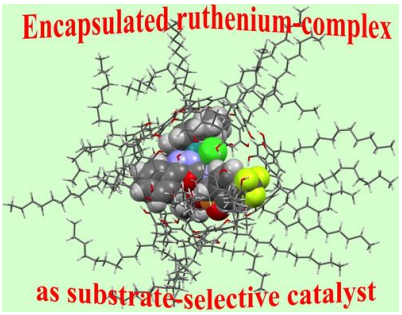
Catalysis with molecular containers is an emerging field due to its similarity to enzymes.[1] Supramolecular assemblies can provide large, confined spaces, as demonstrated by the self-assembled capsule discovered by Atwood.[2] The neutral complex dichloro-{diethyl[(5-phenyl1,3,4-oxadiazol-2-ylamino)-(4-trifluoromethyl-phenyl)methyl]phosphonate}(p-cymene)-ruthenium(II) was encapsulated inside this self-assembled hexameric host obtained upon reaction of 2,8,14,20-tetra-undecyl-resorcin[4]arene and water. The formation of an inclusion complex was inferred from a combination of spectral measurements (MS, UV/Vis spectroscopy, ^{1}H and DOSY NMR). The ^{31}P and ^{19}F NMR spectra are consistent with motions of the ruthenium complex inside the self-assembled capsule. Molecular dynamics simulations carried out on the inclusion complex confirmed these intracavity movements and highlighted possible supramolecular interactions between the ruthenium first coordination sphere ligands and the inner part (aromatic rings) of the capsule. The embedded ruthenium complex was assessed in the catalytic oxidation (using $NaIO_4$ as oxidant) of mixtures of three arylmethyl alcohols into the corresponding aldehydes. The reaction kinetics were shown to vary as a function of the substrates size, with the oxidation rate varying in the order benzylalcohol >4-phenyl-benzylalcohol >9-anthracenemethanol. Control experiments realized in the absence of hexameric capsule did not allow any discrimination between the substrates. This example corresponds to the first example of a neutral complex encapsulated in this self-assembly.[3]



Scheme 1. Picture of encapsulated complex inside the Atwood capsule.

Acknowledgements

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References

[1] O. Bristi, O. Reinaud, *Org. Biomol. Chem.,* **2015**, *13*, 2849-2865; J. Xu, H. Cheng, Z. Liang, D. Chunying, *Acc. Chem. Res,*. **2019**, *52*, 100-109; J. Yang, B. Chatelet, D. Hérault, J. P. Dutasta, A. Martinez, *Eur. J. Org. Chem.*, **2018**, 5618-5628.
[2] L. R. MacGillivray, J. L. Atwood, *Nature*, **1997**, *389*, 469-472.
[3] S. Hkiri, M. Steinmetz, R. Schurhammer, D. Sémeril, *Chem. Eur. J.*, **2022**, *28*, e202201887.

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 modellizations 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**).

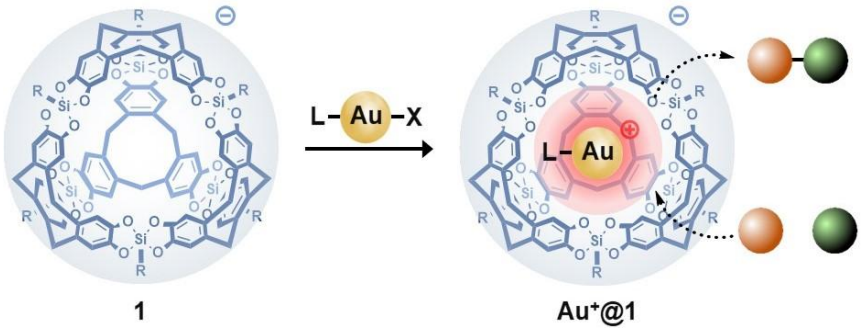

Figure 1. Concept: Using the confinement effect to alter the reactivity of gold complexes.

Acknowledgements

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References

[1] L. Rochigiani, M. Bochmann *Chem. Rev.* **2021**, *121*, 8364-8451.

[2] J. Rodriguez, G. Szalóki, E. D. Sosa Carizzo, N. Saffon-Merceron, K. Miqueu, D. Bourissou *Angew. Chem. Int. Ed.*, **2020**, *59*, 1511-1515; (b) G. Szalóki, J. Babinot, V. Martin-Diaconescu, S. Mallet-Ladeira, Y. Garcia-Rodeja, K. Miqueu, D. Bourissou *Chem. Sci*. **2022**, *13*, 10499-10505;

[3] M. Morimoto, S. M. Bierschenk, K. T. Xia, R. G. Bergman, K. N. Raymond, D. F. Toste *Nat. Catal*. **2020**, *3*, 969-984.

[4] J. V. S. Guerra, L. F. G. Alves, D. Bourissou, P. S. Lopes-de-Oliveira, G, Szalóki *J. Chem. Inf. Model*. **2023**, *63*, 3772-3785.

Chiral recognition by cyclodextrin regioisomers: exploiting asymmetrical bridging to shape the cavity

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Building only from a pool of L-amino acids, Nature makes protein capable of remarkable discrimination of enantiomers. Following a precise folding scheme, the asymmetric shape of the active site is dictated by the 3D-positioning of amino-acids one relative to the others. As organic chemists, can we build a similar system using only cyclic D-sugars such as cyclodextrins (CDs), and achieve shape-directed enantio-discrimination?

Previously developed catalytically active (NHC)-bridged CD-metal complexes display interesting chemo-, regio-, and stereo- selectivities.[1,2,3,4] It was found that a symmetrical 2-point bridging of α-CDs induce an helicoidal distortion of their cavity into a M-helix, accounting for the observed stereoselectivity.[2] Yet, no control over the distortion, nor over the stereochemical outcome of the catalysed reactions was possible. Pushing the concept forward, we want to gain control over the distortion of the cavity and access pseudo-enantiomeric shaped-cavities from 3-point bridging patterns using tripodal moieties such as tren groups.

We achieved the synthesis of two permethylated CD regioisomers with mirror-image 3-point bridging patterns, that readily complex Cu(II) inside their cavities. Preliminary results from circular dichroism spectra indicate that the pair of regioisomers can behave in the manner of enantiomers. Host-guest UV-vis-NIR titration in buffered medium, in presence of a serie of α-chiral carboxylates, revealed interesting inversion of stereoselectivity when 2-phenylbutanoate was used as guest (Figure 1). Next steps include exemplification with other chiral guests, in addition to molecular modelling to account for the observed preferences, as well as exploiting the two regioisomers for catalysis.

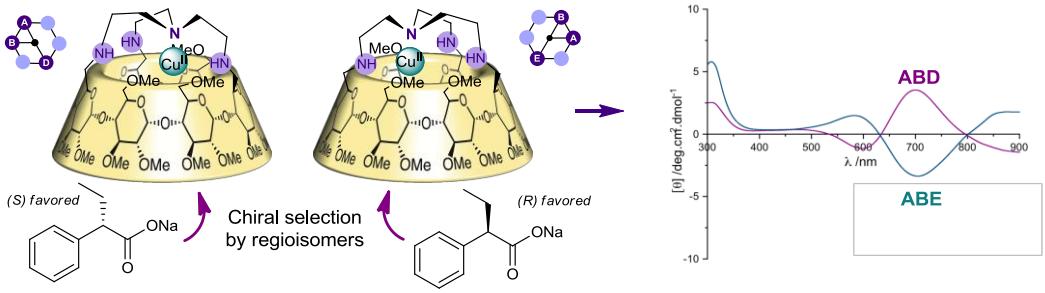

Figure 1. Scheme of chiral recognition of carboxylates by tren-bridged CD regioisomers, and circular dichroism spectra of the corresponding copper acetate complexes..

References

[1] M. Guitet, P. Zhang, F. Marcelo, C. Tugny, J. Jiménez-Barbero, O. Buriez, C. Amatore, V. Mouriès-Mansuy, J-P. Goddard, L. Fensterbank, Y. Zhang, S; Roland, M. Ménand, M. Sollogoub, *Angew. Chem. Int. Ed.*, **2013**, *52*, 7213–7218.

[2] P. Zhang, C. Tugny, J. Meijide Suárez, M. Guitet, E. Derat, N. Vanthuyne, Y. Zhang, O. Bistri-Aslanoff, V. Mouriès-Mansuy, M. Ménand, S. Roland, L. Fensterbank, M. Sollogoub, *Chem.* **2017**, *3*, 174–191.

[3] G. Xu, S. Leloux, P. Zhang, J. Meijide Suárez, Y. Zhang, E. Derat, M. Ménand, O. Bistri-Aslanoff, S. Roland, T. Leyssens, O. Riant, M. Sollogoub, *Angew. Chem. Int. Ed.* **2020**, *59*, 7591–7597.

[4] C. Tugny, N. del Rio, M. Koohgard, N. Vanthuyne, D. Lesage, K. Bijouard, P. Zhang, J. Meijide Suárez, S. Roland, O. Bistri-Aslanoff, M. Sollogoub, L. Fensterbank, V. Mouriès-Mansuy, *ACS Catal.* **2020**, *10*, 5964–5972.

Tuning the covalent chemistry of CO_2 capture by supramolecular effects

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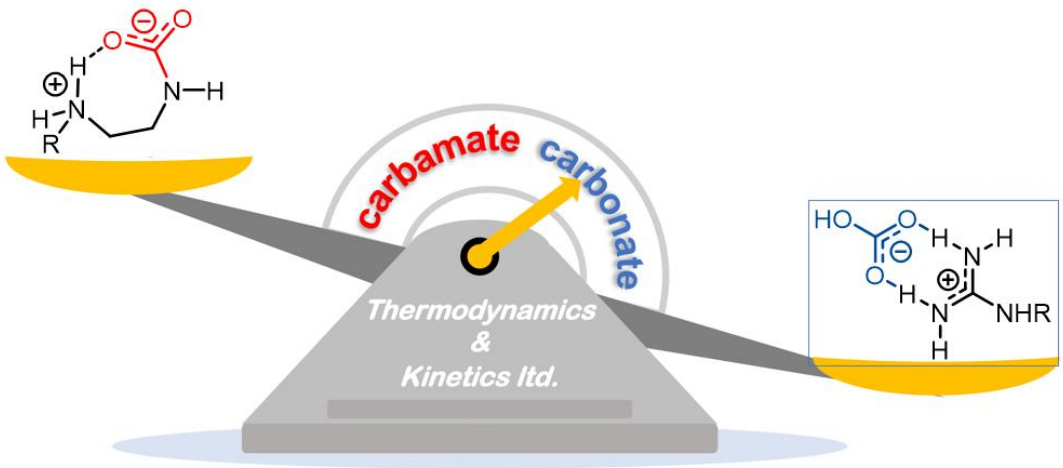
Among the various technologies aimed at reducing greenhouse gas emissions, post-combustion carbon capture utilizing industrial amines stands out as one of the most advanced. However, its widespread adoption is hindered by high costs. To address this issue, there is a need for amine formulations that possess both high capture capacity and rapid kinetics.[1]

Here, we investigate the potential of bis-guanidinium salts as supramolecular additives to facilitate the formation of hydrogenocarbonate while minimizing the formation of carbamates. As a result, the cyclic capacity of the amine absorbents is substantially increased while fast kinetics is preserved. Beyond the concept of tunable antiparallel covalent chemistry, this study underlines the role that supramolecular chemistry may play in environmental challenges such as carbon capture.



References

[1] F. Marocco Stuardi, F. MacPherson, J. Leclaire *Curr. Opin. Green Sustain. Chem.* **2019**, *16*, 71-76; J. Leclaire, D. J. Heldebrant *Green Chem.* **2018**, *20*, 5058-5081

Light-emitting liquid crystalline blends for organic lasers

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Interest in organic electronics has been increasing during the last decades, leading to the production of several devices based on organic semiconductors such as organic light-emitting diodes (OLEDs).[1] In parallel to OLEDs, the development of efficient organic lasers is still a challenge. Such devices are very interesting because they can generate a monochromatic and coherent light. Their structure is composed of a gain material that is responsible for the stimulated emission, coupled with a resonator and an energy source.

Organic lasers that use organic gain materials have existed for decades, but only in solution.[2] Now, the development of new solid-state gain materials has opened up the route to develop organic laser diodes (OLDs), which are based on the direct conversion of an electric current into laser light. The first evidence of an OLD was recently shown by the group of Prof. Adachi, using an amorphous material based on a pi-conjugated blue-emitting molecule as gain material.[3] However, this result was obtained with only one example of dye so far, with limitations such as a short device lifetime, and complex processability. In this context, the development of new, more efficient and easily processable gain materials is highly necessary. We are also motivated to design new lasing materials that can be compatible with both optical and electrical pumping.

To this end, we have developed novel, light-emitting liquid crystalline materials to be used as gain media. By using such systems, it is possible to easily tune the emissive properties by modification of the chemical structure. In addition, these materials enable donor-acceptor construction through FRET between moieties with different emitting wavelengths.
We will present the first series of liquid crystalline gain materials, their mesogenic and electronic properties as single components and also as blends. A special focus will be places on the study of the blends and their photophysical properties, especially in their amplified spontaneous emission (ASE) performances.

Acknowledgements

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References

[1] H. Uoyama, K. Goushi, K. Shizu, H. Nomura, and C. Adachi, Nature, 2012, 492, 234-238.
[2] N. Tessler, G. J. Denton, and R. H. Friend, Nature, 1996, 382, 695-697.
[3] A. S. D. Sandanayake T. Matsushima, F. Bencheikh, S. Terakawa, W. J. Potscavage, C. Qin, T. Fujihara, K. Goushi, J.-C. Ribierre, and C. Adachi, Apllied Physics Express 2019, 12, 061010

Photocontrolled self-assembly of azobenzene-based amphiphilic surfactants

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While the field of photoactive surfactants has been widely explored, only in recent years these materials have been investigated for the self-assembly of responsive nano-architectures (micelles, emulsion, foams).[1] To this end, researchers have extensively explored the integration of azobenzene moieties into amphiphiles to modify their aggregation behaviour upon light exposure.[2] Within this research field, a new family of minimalistic photo-switchable non-ionic amphiphilic molecules, referred as **AzoPEGs**, were developed[3]. Their structure, consisting of a short hydrophilic oligoethylene chain linked to a lipophilic azobenzene photoswitchable unit (Figure 1a), allow them to self-organize into monodisperse nanodroplets in water, with a size below 400 nm, at millimolar concentrations through a spontaneous emulsification process. Indeed, this simple motif enables the reversible self-assembly and disassembly of these nanoaggregates upon exposure to light, owing to the abrupt change in dipole moment between the different stereoisomeric forms of the Azo group (Figure 1b). The difference in polarity between the inner core of the nanoaggregates and the surrounding water makes them suitable as photoactivable nanocontainers for small, lipophilic molecules, with potential applications in controlled release and nanotechnology. In addition, the oligoethylene chain can be functionalised with moieties able to introduce additional functionalities in terms of reactivity and/or catalytic activity.

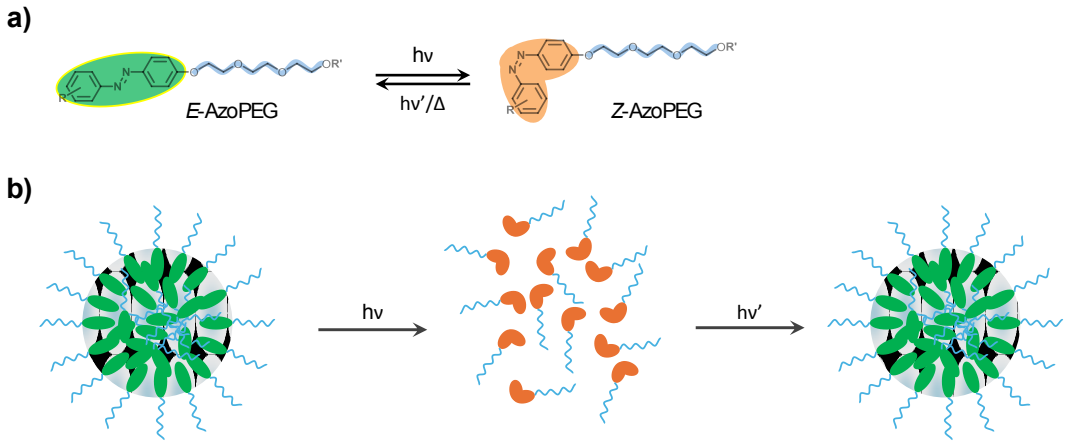

Figure 1. a) *E*-**AzoPEG** photo-isomerization reaction. b) Reversible self-assembly of *E*-**AzoPEG** nanoaggregates.

Acknowledgements

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References

[1] N. Basìlio and L. Garcìa-Rìo, *Curr. Opin. Colloid Interface Sci.*, **2017**, *32*, 29–38.
[2] R. F. Tabor, T. M. McCoy, Y. Hu and B. L. Wilkinson, *Bull. Chem. Soc. Jpn.*, **2018**, *91*, 932.
[3] M. Villa, G. Bergamini, P. Ceroni and M. Baroncini, *Chem. Commun.*, **2019**, *55*, 11860—11863.

Comparison of complexation properties of subetadex and mono-subetadex cyclodextrins on citalopram model molecule

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Cyclodextrins (CDs) have a number of important properties, such as chiral separation or the enhancing of water solubility. In our work, we investigated the complexation properties of sugammadex analogue CDs, subetadex (SBX) and mono-subetadex (monoSBX). These CDs are isomerically pure, persubstituted or monosubstitued with carboxythioether groups on the primary side. The structure and properties of these CDs can be determined more easily and accurately than in case of randomly substituted CDs.

Previous studies have demonstrated that SBX has significant solubility-enhancing and enantiomer recognition properties, but these features are pH-dependent.[1,2] Under acidic conditions chiral recognition, while under neutral conditions the non-selective inclusion complex formation is dominant. Based on these results, the complexation features are investigated at pH 7.4 using citalopram selective serotonin reuptake inhibitor (SSRI) antidepressant as a model compound.

In our research, the stability constants were determined by different methods (from phase-solubility isoterms, Hummel–Dreyer method by HPLC and capillary electrophoresis) and the structure of the complex was determined by NMR. Our aim was to gain a deep understanding of the complex structure that forms between SBX or monoSBX and citalopram, and to compare the stability constants obtained by these techniques.

Acknowledgements

The research was funded by the National Research, Development and Innovation Office (NKFIH FK-142721) and the National Laboratory (PharmaLab) grant RRF-2.3.1-21-2022-00015.

References

[1] Ujj, D., Kalydi, E., Malanga, M., Varga, E., Sohajda, T., Béni, S., Benkovics, G.: Sugam-madex analoguecyclodextrins as chiralselectors for enantioseparation of cathinone deriva-tives bycapillary electrophoresis. *J. Chromatogr. A* **2022**, 1683, 463506.

[2] Mayer, B.P., Kennedy, D.J., Lau, E.Y., Valdez, C. A.: Evaluation of polyanionic cyclodextrins as high affinity binding scaffolds for fentanyl. *Sci Rep* **2023**. 13, 2680.

Tailor-made BTAs for better-performing supramolecular helical catalysts

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Sergeants-and-soldiers" effect [1] refers to the ability of a small amount of chiral monomers (the "sergeants") to fully control the main chain helicity of polymers mainly composed of achiral monomers (the "soldiers"). This phenomenon is widely known for non-functionalized supramolecular polymers and may occur under diluted conditions as long as the coassembly process is sufficiently strong. The lookout for the "best" sergeant, the one which would allow to form stable stacks (avoiding chain-chapping or sequestration [2]) in several conditions and with low loadings, is still a hot topic of research especially when it comes to apply "sergeants-and-soldiers" mixtures to asymmetric catalysis. In our group, the "sergeants-and-soldiers" effect has been widely applied in supramolecular catalysis with helical assemblies of benzene-1,3,5-tricarboxamide (BTA) monomers.[3]

Up to now the "sergeant" derived from the dodecyl ester of Leucine (**1**) was found to efficiently intercalate into the stacks of the BTA ligand (**3**), leading to the highest level of enantioselectivity comparatively to other "sergeants", tested to date. However, the selectivity drops off upon dilution, what forces to work with relatively high catalytic loading. Thus, in an attempt to move towards a more efficient "sergeant", we herein demonstrate that a little change in its molecular structure (such as the replacement of the ester by an ether function (**2**)) allows to maintain a good selectivity under diluted conditions as a probable consequence of the higher stabilization of the coassemblies.[4]

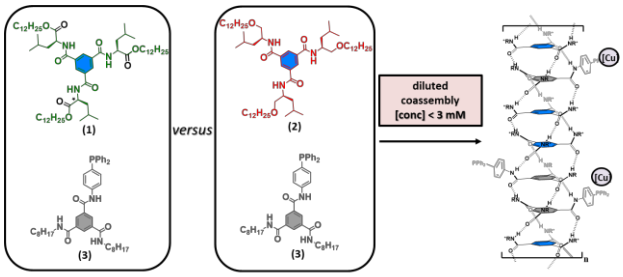

Figure 1. Supramolecular co-assemblies with BTA herein studied.

Acknowledgements

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References

[1] Li, Y.et al. L. *J. Am. Chem. Soc.*, ***2020***, *142, 5676-5688*. [2] Weynadt, E. *et al. Organic Materials* **2020**, *2,* 129 – 142. [3] Martinez-Aquirre, M. A. et al. *Angew. Chem. Int. Ed*., **2021**, *60*, 4183-4191. [4] A. Valverde-González et al. to be submitted.

Transformations and self-sorting in azulene-based coordination cages

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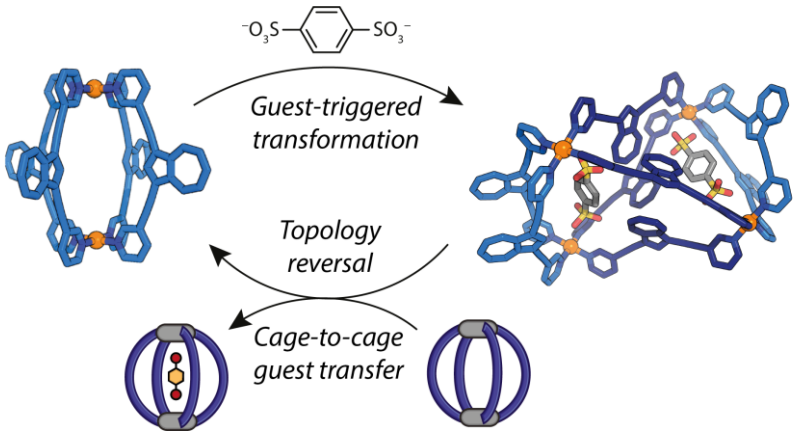
Coordination cages are often seen as purely synthetic mimics of biological receptors enzymes, possessing nanoscopic cavities capable of binding guest molecules, and extensive work has been published on the catalytic properties of coordination cages.[1] However, peptidic receptors can often undergo strong 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.



References

[1] Y. Xue *et al. Coord. Chem. Rev.* **2021**, *430*, 213656

[2] A. Walther *et al. J. Am. Chem. Soc.* **2023**, *145*, 25365

Domain swapping in abiotic foldamers

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Driven by curiosity and creativity, chemists have demonstrated that some folding patterns found in peptides and proteins can be reproduced in completely abiotic oligomers. Abiotic oligomers also have features of their own, such as folding in an organic medium. By connecting two well-defined helices formed by aromatic oligoamides of 8-aminoquinoline-2-carboxylic acid with well-designed linkers, anti-parallel and parallel helix-turn-helix tertiary structures have been investigated. [1, 2] Additional hydroxy groups have been placed on one face of the helix-turn-helix structure to create complementary arrays of hydrogen-bond donors and acceptors that, we hoped, would promote the formation of dimers of tertiary structures, i.e. genuine abiotic quaternary structures (Figure 1c). Whereas the crystal structure of the modified foldamer sequence differs from the initial design. Instead, it revealed a novel domain-swapped dimer (DSD, Figure 1a) structure which is rarely observed in abiotic structures but common in proteins. In the DSD structure, the intramolecular interaction interface in the initial design does not form and turns out to be intermolecular interactions and promotes dimerization.

The ^{1}H-NMR spectra and CD spectra of the domain swapping dimer in different proportions of DMSO/chloroform show that the molecule undergoes two transitions. We assign the first transition to the dissociation of the DSD structure and the sequence folds back to the tertiary structure (Figure 1b). Further addition of DMSO resulted in the intramolecular hydrogen bond being disrupted and leading to an opened linear monomer. [2]

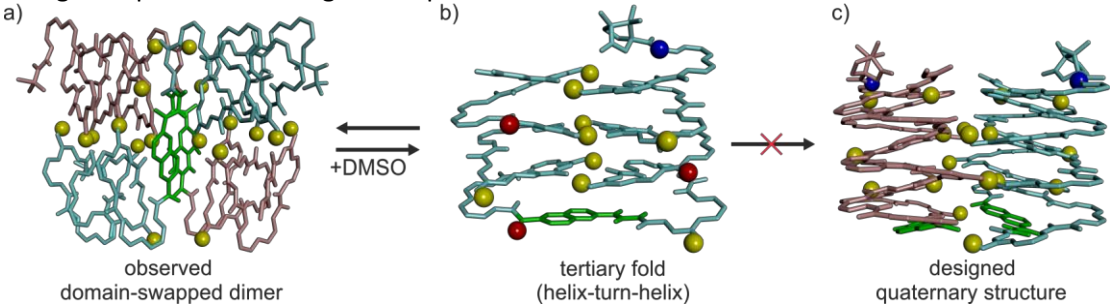

Figure 1. a) The simplified views of the crystal structure of domain-swapped dimer. b) Modified helix-turn-helix tertiary structure. [2] Extra hydroxy groups are introduced on one face of the structure to create complementary arrays of hydrogen bond interface that could promote the aggregation of two tertiary structures. c) The energy-minimized model of two identical helix-turn-helix structures dimerized through the hydrogen bond interface that has been introduced. Individual molecules are shown in light blue and pink tube representation. Hydroxy protons are shown as yellow balls. Linkers are shown in green. For clarity, only the outer rim of the helices is shown.

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References

[1] S. De, B. Chi, T. Granier, T. Qi, V. Maurizot, I. Huc, *Nat. Chem.* **2018**, *10*, 51.

[2] D. Mazzier, S. De, B. Wicher, V. Maurizot, I. Huc, *Angew. Chem. Int. Ed.* **2020**, *59*, 1606.

Cucurbit[8]uril Mediated Supramolecular and Photocrosslinked Double Network Hydrogel Matrices for 3D-Bioprinting

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Printing of biologically functional constructs is significant for applications in tissue engineering and regenerative medicine. Designing bio-inks remains challenging due to the multifaceted requirements such as cytocompatibility, printability and shape fidelity.[1] In order to promote matrix and materials stiffness, while not sacrificing stress relaxation mechanisms which support cell spreading, migration and differentiation[2], we report a double network bio-ink design. Therefore, star-shaped polyethylene glycols short peptides and photoactive end groups are synthesized, and used to prepare three-dimensional networks with cucurbit[8]uril (CB[8]) through supramolecular host-guest-complexation. The hydrogel obtained shows fast relaxation and thus supports the proliferation and differentiation of cells. Upon irradiation, the mechanical properties of the hydrogel can be rapidly adapted via selective photochemical dimerization of stilbazolium within CB[8][3], leading to double networks with increased form stability while retaining the dynamic nature of the hydrogels. This modular approach opens new design opportunities for extrudable and cell-friendly dynamic biomaterials for applications in 3D-bioprinting.

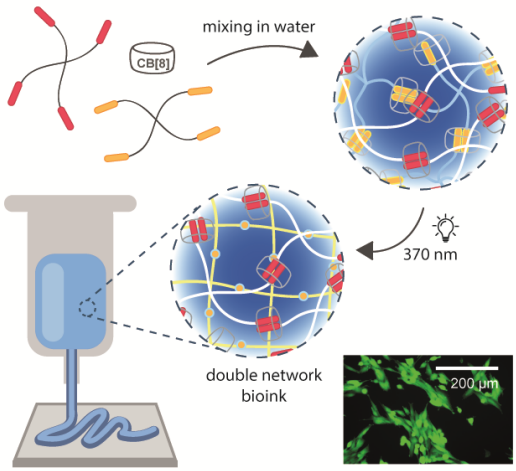

Figure 1. Schematic representation of double network bio-ink formation based on cucurbit[8]uril host-guest chemistry.

Acknowledgements

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References

[1] D. Chimene, K. K. Lennox, R. R. Kaunas, A. K. Gaharwar, *Ann. Biomed. Eng.* **2016**, *44*, 2090.
[2] O. Chaudhuri, L. Gu, D. Klumpers, M. Darnell, S. A. Bencherif, J. C. Weaver, N. Huebsch, H. P. Lee, E. Lippens, G. N. Duda, D. J. Mooney, *Nat. Mater.* **2016**, *15*, 326.
[3] L. Zou, M. J. Webber, *Chem. Comm.* **2019**, *55*, 9931.

Remote induction of asymmetric catalysis with Aib-derived chiral foldamers

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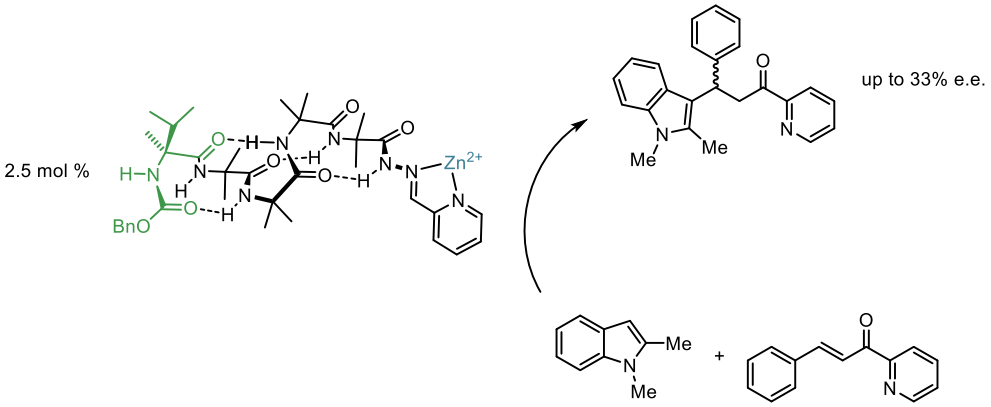
Communication between biocatalytic networks is crucial to cell function, including networks in different compartments. This cellular compartmentalisation by membranes permits the separation of incompatible catalytic conditions. A similar incompatibility often occurs when attempting to link aqueous biocatalysis with chemocatalysis that has been optimised in organic solvents.

Molecular information relays developed in the Webb group could provide an exciting solution to this problem. These relays transmit information along multi-nanometre distances, which allows them to operate simultaneously in aqueous and hydrophobic environments. At their core is an amphiphilic α-aminoisobutyric acid (Aib) foldamer that adopts well-defined helical conformations. The use of a chiral controller (green) at the N-terminus induces a change in screw-sense of the 310 helix which can be felt at the C-terminus.

The presented work reports new systems in which helical chirality is induced from a remote chiral controller at the C-terminus, producing an enantioselective catalysis output at the N-terminus of an Aib derived foldamer



Scheme 1. Aib-foldamer catalyzed enantioselective Friedel Crafts alkylation reaction

References

[1] F. G. A. Lister, B. A. F. Le Bailly, S. J. Webb, J. Clayden, Nat. Chem. 2017, **9**, 420 - 425.

[2] M. De Poli, W. Zawodny, O. Quinonero, M. Lorch, S. J. Webb, J. Clayden, Science, 2016, **352**, 376 - 380.

Mechanical disruption of β-Amyloid fiber analogs by out-of-equilibrium operation of light-driven molecular motors

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Diphenylalanine peptide (FF) is well-known to form highly stable β-amyloid fibers. The difficulty to disrupt these aggregates is associated with numerous pathologies such as Alzheimer's disease.[1] The mechanical work produced by the rotation of artificial molecular motors has already been amplified in our group to influence the macroscopic properties of soft materials.[2,3] In this work, we incorporated light-driven artificial molecular motors in carboxybenzyl-protected-FF (Z-FF) supramolecular hydrogels that form β-amyloid-like fibers. Interestingly, the mechanical work generated during the constant rotation of the molecular motor under UV light is sufficient to disrupt the β-amyloid fibers. This disruption was visible macroscopically as a gel-to-sol transition. In the absence of light, the system fully recovers its original microstructure. This unique reversible gel-sol transition phenomenon was studied by several techniques (rheology, TEM, AFM, CD, and SAXS) proving that the disruption of the β-amyloid fibers originates solely from the work generated by the out-of-equilibrium rotation of the molecular motor.[4] These results highlight the potential of molecular motors to generate nanoscale mechanical work that targets biologically relevant structures, with expected applications in nanotechnologies and nanomedecine.

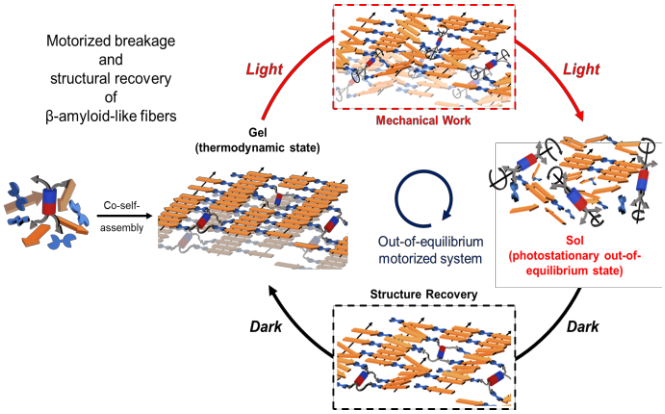

Figure 1. Schematic representation of the out-of-equilibrium motorized system based on supramolecular hydrogels.[4]

Acknowledgements

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References

[1] J. D. Harper, P. T. Lansbury, *Annu. Rev. Biochem.* **1997**, *66*, 385–407.
[2] Q. Li, G. Fuks, E. Moulin, M. Maaloum, M. Rawiso, I. Kulic, J. T. Foy, N. Giuseppone, *Nat. Nanotechnol.* **2015**, *10*, 161–165.
[3] J. T. Foy, Q. Li, A. Goujon, J.-R. Colard-Itté, G. Fuks, E. Moulin, O. Schiffmann, D. Dattler, D. P. Funeriu, N. Giuseppone, *Nat. Nanotechnol.* **2017**, *12*, 540–545.
[4] D. Daou, Y. Zarate, M. Maaloum, D. Collin, G. Fleith, D. Constantin, E. Moulin, N. Giuseppone, *Adv. Mater.* just accepted; DOI 10.1002/adma.202311293.

Synthetic Approaches and Collaborative Workflow for Sensitive Molecular Catalyst Design and Characterization at Electrode Interfaces

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Electrode-immobilized molecular catalysts can be challenging to characterize due to their low concentrations and incompatibility with standard molecular characterization tools. However, surface-sensitive spectroscopic techniques like X-Ray Photoelectron Spectroscopy (XPS) and Sum Frequency Generation (SFG) have unlocked new interdisciplinary pursuits to understand the molecular environment and properties of attached metal complexes.[1]
A particular challenge of synthesizing and characterizing some metal-based catalysts or their intermediates is their decomposition in the presence of air and water. This difficulty remains when making and studying molecular monolayers of these catalysts on electrode surfaces as air and water must be excluded from the synthesis through to the final spectroscopic measurement, which is often not an available setup. Moreover, if spectroscopic data indicates molecular decomposition, one needs to be able to distinguish whether it is due to incompatibility between the attached molecule and the interface, or to the handling, storage, or the measurement itself.

This poster will discuss cross-institutional collaborations to design, prepare, and handle sensitive covalently attached molecular monolayers on electrode interfaces. We will describe air-free functionalization protocols informed by inorganic synthesis, material science, and limiting parameters in surface-sensitive spectroscopy measurements. This discussion includes instrument accessory, glassware, and electrochemical cell design for specialized measurements of sensitive samples, with an emphasis on available materials and ease in handling in air-free environments.

Acknowledgements

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References

[1] A. Ge, B. Rudshteyn, P. E. Videla, C. J. Miller, C. P. Kubiak*, V. S. Batista*, and T. Lian*, *Acc. Chem. Res.* **2019**, *52*, 5, 1289–1300.

Persistent Organic Room-Temperature Phosphorescence in Chiral Phthalimide Derivatives: The Dramatic Impact of Heterochiral vs Homochiral interactions

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Room temperature phosphorescence (RTP) from purely organic compounds (*i.e.* without any metal), and related photophysical aspects linked to the management of triplet excited-states have become a crucial issue for several areas of research, ranging from optoelectronics, non-linear optics to photocatalysis, and bioimaging.[1] Recently, the possibility to obtain RT circularly polarized (CP) phosphorescence with chiral organic emitters has also attracted significant interest due to the potential access to different states of CP-light (either left or right).[6-12]

In this congress, I would like to present our contributions regarding this area of research, notably by illustrating how the enantiopurity of a chiral material offers a unique possibility to explore the impact of intermolecular interactions on the efficiency of photophysical properties and/or electronic conduction without altering its molecular electronic properties. Our findings show that comparing RTP between racemic and enantiopure crystals can bring further information on the intermolecular interactions impacting the triplet exciton stabilization and migration, which needs to be optimized for designing efficient organic RTP molecular materials.

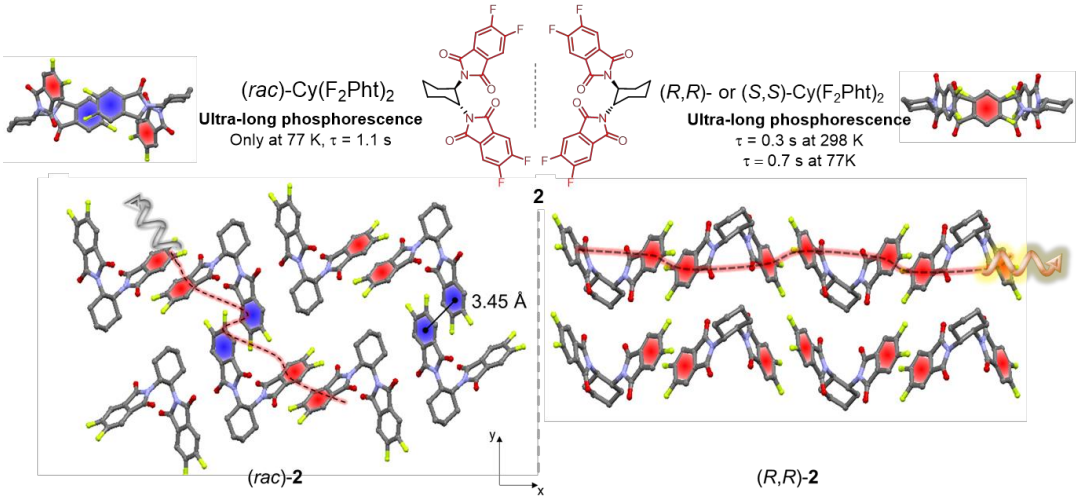

Figure 1. Chemical structures of *RR*-**Cy(F₂Pht)₂** and *SS*-**Cy(F₂Pht)₂**; and comparison of their X-ray crystallographic structures at the molecular and supramolecular levels with different views of intermolecular interactions between dimers (red for H-type aggregates, and blue for J-ones).

References

[1] H. Ma, Q. Peng, Z. An, W. Huang and Z. Shuai, *J. Am. Chem. Soc.*, 2019, **141**, 1010-1015; D. Nidhankar, Goudappagouda, V. C. Wakchaure and S. S. Babu, *Chem. Sci.*, 2021, **12**, 4216-4236.; S. Hirata, *Applied Physics Reviews*, 2022, **9**, 011304.

[2] Z. An, C. Zheng, Y. Tao, R. Chen, H. Shi, T. Chen, Z. Wang, H. Li, R. Deng, X. Liu and W. Huang, *Nat Mater*, 2015, **14**, 685-690; L. Favereau, C. Quinton, C. Poriel, T. Roisnel, D. Jacquemin and J. Crassous, *J. Phys. Chem. Lett.*, 2020, **11**, 6426-6434; X. Wu, C.-Y. Huang, D.-G. Chen, D. Liu, C. Wu, K.-J. Chou, B. Zhang, Y. Wang, Y. Liu, E. Y. Li, W. Zhu and P.-T. Chou, *Nat. Commun.*, 2020, **11**, 2145.

SUPRAMOLECULAR HYDROGELS OF GALACTONAMIDES: CELL CULTURE, 3D PRINTING and METALLOGELS

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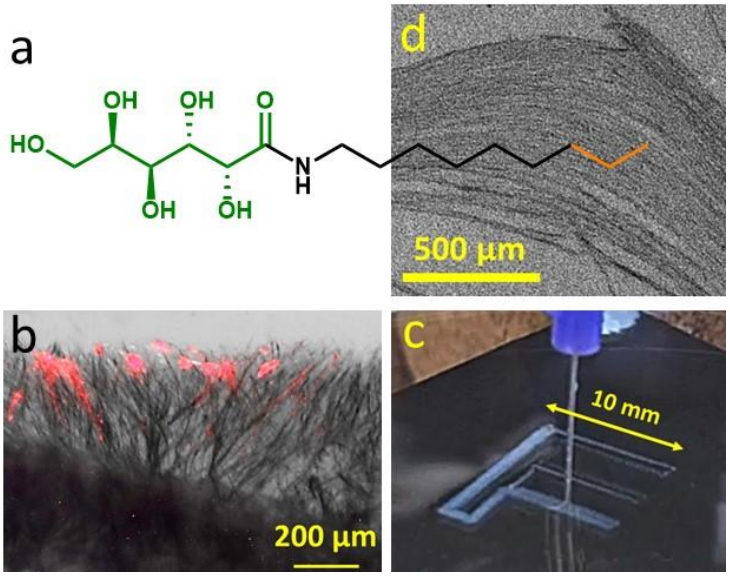
N-alkyl-D-galactonamides are simple carbohydrate derivatives (Fig. a) that give supramolecular hydrogels due to the self-assembly of these molecules in supramolecular fibers (Fig. d) [1]. After tackling with the fragility of these non-covalent hydrogels, we show that these hydrogels can be used as scaffolds for cell culture for several weeks. By developing methods to observe the interior of these very soft gels, it was possible to highlight the development of the cells in clusters within the hydrogel (Fig. b), which is strongly impacted by the fibrillar network.

These molecules are also well adapted to shape the gels by wet spinning or 3D printing (Fig. c) [2-3]. The very fast self-assembly of the molecules during the solvent switch involved in the process lead to the formation of well-defined self-standing structures, such as gel noodles or 3D printed gels. An insight into the microstructure of the wet spun fibers or the one of the 3D printed gels highlighted the relationship between the solubility of the molecules and the microstructure and organization of the self-assembled fibers.

Finally, N-alkyl-D-galactonamides form complexes with molybdate species. This complexation gives rise to a new series of hydrogels with properties very different from the ones of the free molecules. The sol-gel transition, the rheology, the structure of the supramolecular fibers (Fig. d), the structure of the complex and the arrangement of the molybdate within these fibers have been highlighted. It opens new perspectives for these molecules that give metallogels and therefore, that can be used for organizing organic-inorganic supramolecular structures.



References

[1] A. Chalard, et al. Simple Synthetic Molecular Hydrogels from Self-Assembling Alkyl-galactonamides as Scaffold for 3D Neuronal Cell Growth. *ACS Appl. Mater. Interfaces* **2018**, 17004.

[2] Andriamiseza, F. et al. *J.* 3D Printing of Biocompatible Low Molecular Weight Gels*, Coll. Interf. Sci.* **2022**, *617*, 156 and Wet Spinning and 3D Printing of Supramolecular Hydrogels, *Colloids Surf. A,* **2023**, *673*, 131765.

[3] Drew, E. N.; Piras, C. C.; Fitremann, J.; Smith, D. K. Wet-Spinning Multi-Component Low-Molecular-Weight Gelators to Print Synergistic Soft Materials. *Chem. Commun.* **2022**, *58* (79), 11115–11118.

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