Journées de Chimie Supramoléculaire

May 22-23, 2025

STRASBOURG

BOOK OF ABSTRACTS

Jean-Marie Lehn Foundation

Université de Strasbourg

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Welcome words

The Congress "*Journées de Chimie Supramoléculaire*" (JCS) is a part of the scientific activity of the Supramolecular Chemistry Group (Supr@SCF) of the French Chemical Society (SCF). Starting from 2019, the moment the Supr@SCF group has been created, scientific meetings bringing all the chemists sharing an interest for various aspects of supramolecular chemistry are organized every year.

The next meeting, JSC2025, will be held in Strasbourg in May 22-23, 2025, at the European School of Chemistry, Polymers and Materials (ECPM). The event is organized by the Supr@SCF group together with the Foundation of Jean-Marie Lehn from the University of Strasbourg.

There will be four invited lectures. Additionally, oral communications (12) as well as flash communications (15) will be proposed to young scientists, post-docs and PhD students. A poster session will be also organized.

This event is an opportunity for the supramolecular chemistry community to meet and share their results. As supramolecular chemistry is highly interdisciplinary research area, we hope that each of you will find a lot of inspiration and enjoy this event.

We look forward to meeting you in Strasbourg, the capital of Europe.

Iwona Nierengarten, Henri-Pierre Jacquot de Rouville, Giulio Ragazzon, Aline Nonat

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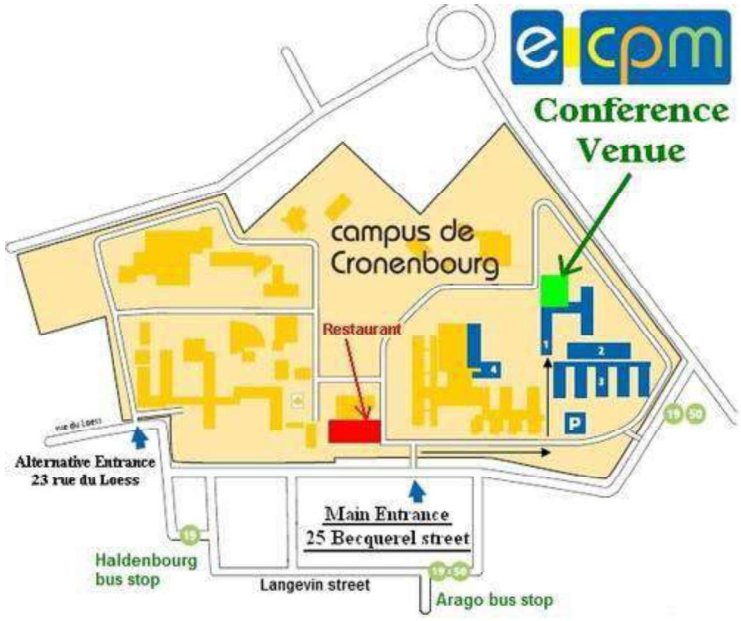

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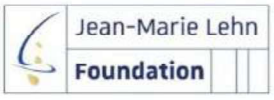

Program

Thursday May 22, 2025

from 13:00	***Registration***	
13:45-14:00	Welcome Words	
14:00-14:40	**Session Chair Giulio Ragazzon**	**Plenary: Dr. Ling PENG** **2024 André Collet prize laureate** ***Modular and adaptive dendrimer nanotechnology-based nanomedicine***
14:40-14:55		OC-1: **Svetlana SAMOKHVALOVA** *Electricity-driven formation, movement and destruction of complex coacervates*
14:55-15:10		OC-2: **Yannick GEIGER** *Dissolved or assembled reactants? The case of the Formose reaction*
15:10-15:25		OC-3: **Sitthichok KASEMTHAVEECHOK** *Controlled redox activation of supramolecular halogen bond organocatalyst*
15:25-15:30		FC-1: **Nihal HADJ SEYD** *Dissymmetric molecular tweezers for multifunctional systems*
15:30-15:35		FC-2: **Baptiste CHABAUD** *Stimuli-responsive host-guest interactions: the impact of surface chemistry on supramolecular assembly*
15:35-15:40		FC-3: **Dietmar GLINDEMANN** *PTFE ("TEFLON") sealing ring for hermetic greaseless glass joints*
15:40-16:10		**Coffee Break**
16:10-16:25	**Session Chair Iwona Nierengarten**	OC-4: **Irene REGENI** *Ruthenium peptide bioconjugates for photoactivated chemotherapy*
16:25-16:40		OC-5: **Sébastian GOEB** *Redox-responsive coordination cage*
16:40-16:55		OC-6: **Dan-Dan SU** *Tubular chiral pillar[n]arene open-end or capped-end nanotubes for highly selective water/proton permeation*
16:55-17:00		FC-4: **Yohan ZARATE** *Mechanical disruption of β-Amyloid fiber analogs by out-of-equilibrium operation of light-driven molecular motors*
17:00-17:05		FC-5: **Fidan RAHMATOVA** *Prebiotic pathways for lipid acylation*
17:05-17:10		FC-6: **Angelina JOCIC** *Spiro-bridged N-heterotriangulenes as building blocks for functional materials*
17:10-17:15		FC-7: **Léa LEFRANCOIS** *Polyaromatics detection by gold electrode grafted with acridinium receptor*
17:15-17:45		**Plenary: Dr. Anne NIJS** ***Behind the scenes of scholarly publishing: insights from Chemistry Europe***
17:45-19:45	**Poster Session** **Buffet**	

Friday May 23, 2025

8:35-9:15	Session Chair HP J. de Rouville	**Plenary: Dr. Clément FALAISE** **2024 Christiane Dietrich-Buchecker prize laureate** ***The chaotropic effect: unlocking new possibilities in the supramolecular chemistry of large inorganic polyanions***
9:15-9:30		OC-7: **Deborah ROMITO** *An amino acid, a calcium salt and CO_2: not the beginning of a joke, but a complex supramolecular catalytic system*
9:30-9:45		OC-8: **Loïc GROSLAMBERT** *Chalcogen bonds involving tellurium derivatives: understanding the nature of these interactions"*
9:45-10:00		OC-9: **Marc GINGRAS** *"The sulfur dance" around arenes and heteroarenes - the reversible nature of nucleophilic aromatic substitutions*
10:00-10:05		FC-8: **Marie POUJADE** *Fluorescence detection of chlordecone in water by hemicryptophane cages*
10:05-10:10		FC-9: **Ioan STROIA** *Highly confined water flow through macrocyclic self-assembled artificial water channels*
10:10-10:15		FC-10: **Krishnakavya Thaipurayil MADANAN** *Mg^{2+}-driven selection of natural phosphatidic acids in primitive membranes*
10:15-10:20		FC-11: **Max PERLOT** *Synthesis of gram-scale nitrogen-containing cryptophanes for trapping toxic thallium(I) ions*
10:20-10:50		**Coffee Break**
10:50-11:05	Session Chair Aline Nonat	OC-10: **Christophe MICHON** *(NHC-olefin)-nickel nanoparticles in micelles: a cooperative and reusable catalyst for effective hydrogenations and reductive-aminations in water*
11:05-11:20		OC-11: **Arthur DAVID** *Highly charged octacationic photoluminescent homo[2]catenanes*
11:20-11:35		OC-12: **Ivan V. KHARIUSHIN** *Supramolecular dyads as photogenerated qubit candidates*
11:35-11:40		FC-12: **Erik MISSELWITZ** *Octacyano-substituted tridecacyclene: a non-benzenoid cyanocarbon with low-lying LUMO and multistage redox properties*
11:40-11:45		FC-13: **Jorge MARCO-GUIMBAO** *Enhancing tin perovskite solar cells performance through innovative fullerene derivatives for minimized interfacial voc losses*
11:45-11:50		FC-14: **Aline MAKHLOUTAH** *Synthesis of photoswitches and photoswitchable lipids for light-controlled therapeutic applications*
11:50-11:55		FC-15: **Ambroise MOUHANNA** *Molecular tweezers based on bioinspired units*
11:55-12:35		**Plenary: Dr. Andrey KLYMCHENKO** ***Self-assembled fluorescent organic nanoparticles for biosensing***
12:35-13:00	**Awards** **Closing Remarks**	

INVITED LECTURES

Dr. Ling PENG

Aix-Marseille Université – CNRS, CINaM

2024 André Collet prize laureate

Dr. Ling Peng carried her undergraduate study in polymer chemistry with Prof. Chen Rongshi at Nanjing University in China, her PhD program in organic chemistry with Prof. Albert Eschenmoser at Swiss Federal Institute of Technology in Zurich, Switzerland, and her postdoctoral research in pharmacy with Prof. Maurice Goeldner at Louis Pasteur University of Strasbourg in France. She obtained a CNRS position in 1997. She is currently Directrice de Recherche de Classe Exceptionnelle (DRCE) and head of a research team at CINaM (Aix-Marseille University). Dr. Ling PENG has been working actively at the interface of chemistry and biology, and in particular, developing functional dendrimers for biomedical applications, molecular probes for exploring biological events and nucleoside analogues for drug discovery. Her research team is labelled by La Ligue contre Le Cancer in France since 2016. Dr. Ling PENG is a Distinguished Member of the French Chemical Society since 2019. She was awarded with the Dr et Mme Henri Labbé Prize of the French Academy of Sciences in 2017 and the Grand Prize of the French Chemical Society Sud PACA in 2024.

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Modular and adaptive dendrimer nanotechnology-based nanomedicine

Ling Peng

Centre Interdisciplinaire de Nanoscience de Marseille, Équipe Labellisée par La Ligue, Aix-Marseille Université, CNRS, Marseille, France. E-mail: ling.peng@univ-amu.fr

The application of nanotechnology is widely expected to bring breakthrough in medicine for disease treatment and diagnosis. Dendrimers are ideal precision materials for elaborating nanomedicine by virtue of their well-defined structure, multivalent cooperativity and nanosize per se. We have pioneered modular and adaptive self-assembling dendrimer nanosystems[1] for the delivery of anticancer drugs,[2] nucleic acid therapeutics[3] and imaging agents[4] for cancer detection and treatment. Remarkably, these supramolecular dendrimer nanosystems are able to exploit the in situ tumor-secreted extracellular vesicles for effective delivery and deep penetration in tumor tissue, while overcoming tumor heterogeneity and dynamic evolution.[2] Also, we have recently developed self-assembling dendrimers against infectious diseases caused by multidrug-resistant pathogens.[5] Our findings offer a new perspective for harnessing the unique advantageous features of supramolecular dendrimers chemistry to reach the ultimate goal of nanomedicine.

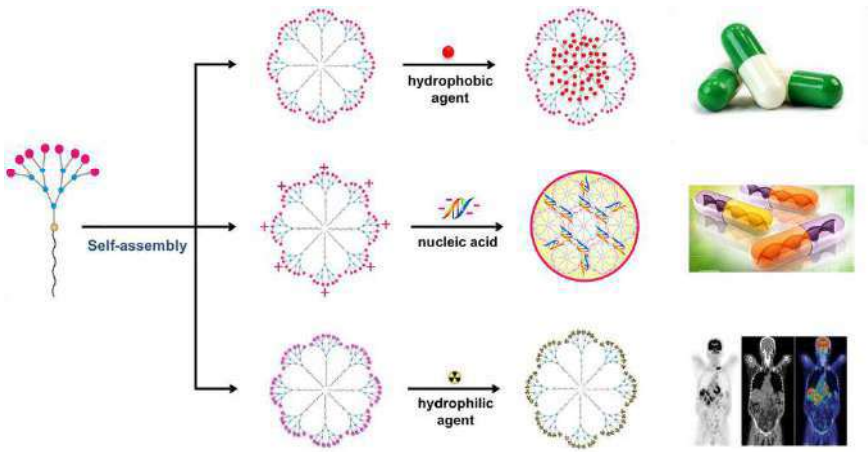

Figure: Self-assembling supramolecular dendrimers for biomedical applications

Acknowledgements. *This work was supported by the Ligue Nationale Contre le Cancer, EU Horizon Europe Cancer Mission "HIT-GLIO" (No. 101136835), EU H2020 NMBP "SAFE-N-MEDTECH" (N° 814607) and EU H2020 EuroNanoMed program (iNanoGun, antineuropatho, Nan-4-TUM).*

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[1] a) Z. Lyu, et al, *Acc Chem Res* **2020**, *53*, 2936; b) J. Chen, et al, *Acc Mater Res* **2022**, *3*, 484
[2] a) Y. Jiang, et al, *PNAS,* **2023**, *120*, e2215308120; b) T. Wei, et al, *PNAS*, **2015**, *112*, 2978
[3] a) J. Chen, et al, *PNAS,* **2023**, *120*, e2220787120; b) J. Chen, et al, *Nat. Protoc.* **2021**, *16*, 327.
[4] a) Z. Lyu, et al, *PNAS*, **2024**, *121*, e2322403121; b) P. Garrigue, et al, *PNAS,* **2018**, *115*, 11454
[5] a) N. Zhang, et al, *Sci Adv*, **2024,** *10*, eadn8117; b) D. Dhumal, et al, *Nanoscale*, **2022**, *14*, 9286

Dr. Clément FALAISE

Institut Lavoisier de Versailles (ILV)

2024 Christiane Dietrich-Buchecker prize laureate

Clément Falaise obtained his PhD degree in 2014 at the University of Lille, under the supervision of Thierry Loiseau (UCCS), and he was working on the coordination chemistry of tetravalent actanides. He then joined the group of May Nyman (Oregon State University) where his work focused on understanding the mechanisms of formation of uranyl nano-buildings in aqueous solution, then the group of Stéphane Cordier (ISCR) to develop supramolecular systems based on luminescent clusters. Then, he joined the CNRS in 2017 at the Lavoisier Institute of Versailles where his research is focused on the physico-chemistry of inorganic polyanions (polyoxometallates, metal clusters, boron clusters) in aqueous solution. His work has been promoted through around sixty publications and various research contracts (ANR, MOMEMTUM-CNRS, EMERGENCE@INC). Since 2021, he has been a member of the national committee for scientific research (CoNRS, section 14).

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The Chaotropic Effect: Unlocking New Possibilities in the Supramolecular Chemistry of Large Inorganic Polyanions

Arnaud Tillet,[a] Nathalie Leclerc,[a] Mohamed Haouas,[a] Soumaya Khlifi,[a] Emmanuel Cadot,[a] and Clément Falaise*[a]

[a] Institut Lavoisier de Versailles, Université Paris-Saclay, Versailles, France; clement.falaise@uvsq.fr

In 2015, the groups of Stoddart[1] and Nau[2] discovered that large inorganic polyanions, specifically boron clusters and polyoxometalates, exhibit an unexpected yet remarkable affinity for cyclodextrins in water, opening new avenues in supramolecular chemistry. This high affinity is now recognized as a hitherto underestimated driving force, the *chaotropic effect*. Our team has contributed to clarifying the nature of this water-mediated phenomenon and to mastering its potential in several innovative directions: (i) designing host–guest systems (see figure),[3,4] (ii) constructing highly ordered hybrid architectures with large internal cavities,[5] (ii) trapping elusive entities,[6] and (iv) directing the self-assembly of polyanions with non-ionic surfactants into vesicles (see figure).[7]

In the first part of this presentation, I will highlight our most significant discoveries regarding the application of the chaotropic effect in the chemistry of polyoxometalates and metal-atom clusters. Following this, I will introduce some recent, unpublished findings, including a simple chemical system that spontaneously forms well-ordered nanotubes with an inner diameter of 16 nm (see figure).

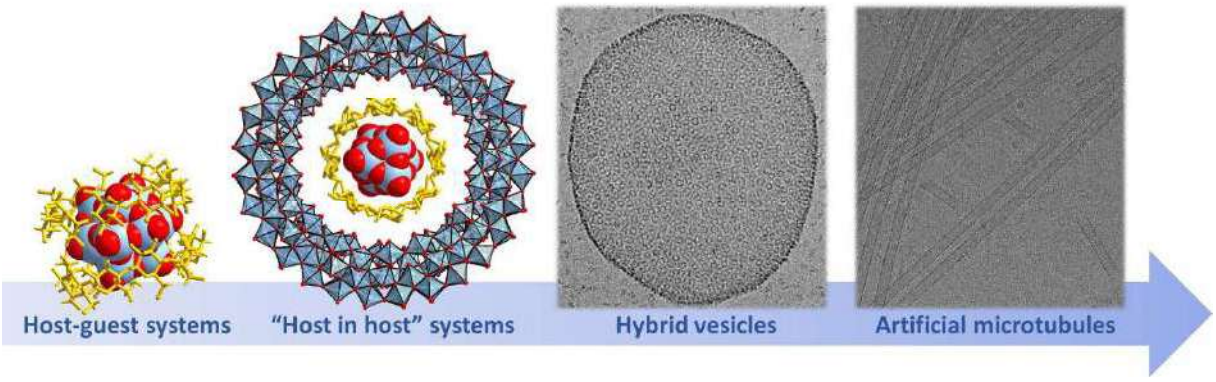

Figure: Supramolecular assemblies resulting from inorganic polyanions and non-ionic organic substances in water.

[1] Y. Wu *et al. J. Am. Chem. Soc.* **2015**, 137, 4111; [2] K. Assaf *et al. Angew. Chem. Int. Ed.* **2015**, 54, 6852; [3] C. Falaise *et al. Angew. Chem. Int. Ed.* **2021**, 60, 14146; [4] M. Segado-Centellas *et al. Chem. Sci.* **2024**, 15, 15849, [5] S. Khlifi *et al. J. Am. Chem. Soc.* **2022**, 144, 4469; [6] C. Falaise *et al. J. Am. Chem. Soc.* **2018**, 140, 11198; [7] C. Falaise *et al. J. Am. Chem. Soc.* **2024**, 146, 1501

Dr. Andrey KLYMCHENKO

Faculté de Pharmacie, Université de Strasbourg

Dr. Andrey Klymchenko obtained his PhD degree in 2003 from Kyiv National University. He worked as post-doctoral fellow in the University of Strasbourg and Catholic University of Leuven. Then, he joined CNRS in 2006, received CNRS Bronze Medal in 2010 and was promoted to Director of Research in 2014. In 2015, he obtained the ERC consolidator grant BrightSens to work on fluorescent nanoparticles for ultrasensitive detection of cancer markers. In 2021, he received Prix du Dr et de Mme Henri LABBE from French Academy of Sciences and was elected member of Academia Europaea. He is leading the “Photoactive Materials and Bioimaging” group at the Faculty of Pharmacy of the University of Strasbourg. His research interests include functional fluorescent molecules and nanomaterials for biosensing, imaging and in vitro diagnostics. He is a co-founder of start-up BrightSens Diagnostics focused on molecular in vitro diagnostics based on fluorescent nanoparticles and AstraNICE dedicated to fluorescent biomaterials for image-guided surgery. He is a co-author of over 260 peer-reviewed articles and 12 patents.

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Self-assembled fluorescent organic nanoparticles for biosensing

Andrey S. Klymchenko

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Email: andrey.klymchenko@unistra.fr

Self-assembled fluorescent organic nanoparticles (NPs) emerged as an attractive platform for designing functional nanomaterials, including fluorescent biosensors. Particularly promising are dye-loaded polymer[1] and lipid[2] NPs, inspired from the field of drug delivery.

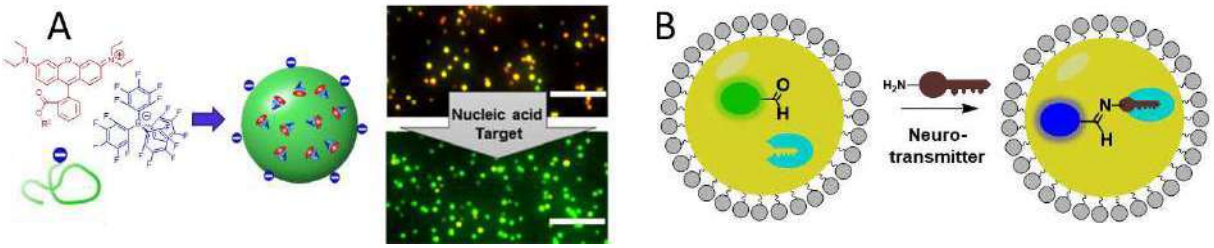

Figure 1. Self-assembled polymer (A) and lipid (B) NPs used for biosensing.

To assemble polymeric NPs of controlled size from 10-40 nm, we developed an approach of nanoprecipitation of hydrophobic polymers bearing a few charged groups.[3] To ensure dye encapsulation with minimal aggregation-caused quenching, bulky hydrophobic counterions were proposed as nano-spacers within dyes.[4] Close dye proximity with minimal aggregation ensured ultrafast dye-dye energy migration rendering NPs unprecedented light-harvesting properties[5] and enabled long-range energy transfer breaking the Forster law.[6] Their functionalization with DNA yielded nanoprobes for amplified detection of RNA/DNA markers (Fig. 1A) of cancer[7] and viral diseases.[8]

In the second approach, we developed fluorescent lipid NPs,[2] which are self-assembled from reagents generally recognized as safe. Their good stability in vivo[9] suggested them as promising nanocarrier of contrast agents and drugs as well as nanoreactor for biosensing. Using *in situ* dynamic covalent chemistry, we developed approaches for drug/dye capture and release.[10] Moreover, combining molecular recognition with dynamic imine chemistry, we introduced a concept of artificial receptor for neurotransmitter sensing.[11]

[1] A. H. Ashoka, I. O. Aparin, A. Reisch, A. S. Klymchenko, *Chemical Society Reviews* **2023**, *52*, 4525.
[2] A. S. Klymchenko, F. Liu, M. Collot, N. Anton, *Adv. Healthcare Mater.* **2021**, *10*.
[3] A. Reisch, et al., *Adv. Funct. Mater.* **2018**, *28*, 1805157.
[4] A. Reisch, et al., *Nature Commun.* **2014**, *5*, 4089.
[5] K. Trofymchuk, et al., *Nat. Photonics* **2017**, *11*, 657.
[6] D. S. Biswas, et al., *Advanced Materials* **2023**, *35*, 2301402.
[7] a) N. Melnychuk, et al., *Angew. Chem. Int. Ed.* **2020**, *59*, 6811; b) S. Egloff, et al., *Biosens. Bioelectron.* **2021**, *179*, 113084.
[8] E. Cruz Da Silva, et al., *Small* **2024**, e2404167.
[9] R. Bouchaala, et al., *J. Control. Release* **2016**, *236*, 57.
[10] a) F. Liu, et al., *Angew. Chem. Int. Ed.* **2021**, *60*, 6573; b) F. Liu, N. Anton, Y. Niko, A. S. Klymchenko, *ACS Applied Bio Materials* **2023**, *6*, 246.
[11] B. Kozibroda, J.-M. Lehn, A. S. Klymchenko, *Angewandte Chemie International Edition* **2025**, e202419905.

Dr. Anne NIJS

Managing Editor of ChemistryEurope

Editor of EurJOC

Anne Nijs studied chemistry at Rheinisch-Westfälische Technische Hochschule Aachen (Germany) and obtained her PhD in 2011 under the supervision of Carsten Bolm working in the area of asymmetric transition-metal catalysis. She joined Wiley-VCH in September 2011 to work for *Chemistry—A European Journal*. In 2016, she moved to the *European Journal of Organic Chemistry* as Deputy Editor and since July 2018 she has been serving as the Editor-in-Chief of the journal. In 2024, she took over the role of Managing Editor of *ChemistryEurope*.

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Behind the Scenes of Scholarly Publishing: Insights from Chemistry Europe

Anne Nijs*[a]

[a] Wiley-VCH, Rotherstrasse 21, 10245 Berlin, Germany. anijs@wiley.com

Founded in 1995, Chemistry Europe is an association of 16 chemical societies from 15 European countries, representing over 75,000 chemists. It publishes a family of high-quality scholarly chemistry journals, covering a very broad range of disciplines.

Its mission is to evaluate, publish, disseminate, and amplify the scientific excellence of chemistry researchers from around the globe in high-quality publications. It supports its members at every stage of their careers as they strive to solve the challenges that impact humankind. In all its work, Chemistry Europe values integrity, openness, diversity, cooperation, and freedom of thought.

This talk will explore the publishing process from the perspective of an editor. It will highlight Chemistry Europe as the publishing association behind leading journals such as *Chemistry—A European Journal*, *European Journal of Organic Chemistry*, and the new title *ChemistryEurope*. The presentation will offer insights into how the Editorial Office operates. It will also touch on recent developments in Open Science and Open Access. Questions on scholarly publishing are very welcome!

ORAL COMMUNICATIONS

Electricity-driven formation, movement and destruction of complex coacervates

Svetlana Samokhvalova, [a] **Kalliopi Fourli,** [a] **Luis Calahorra Río,** [b] **Guillermo Monreal Santiago*** [a]

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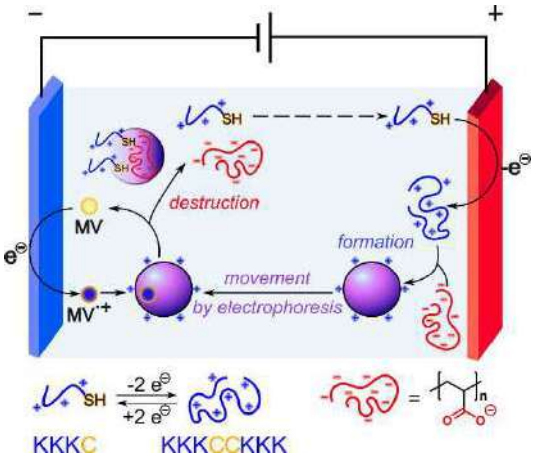
[b] Instituto de Química Orgánica General, Madrid, Spain

Coacervates are aqueous phases formed through liquid-liquid phase separation (LLPS). They are often used as mimics of membraneless organelles (MLOs) – liquid droplets that play different roles in cellular biology. [1] Since MLOs are dynamic (forming transiently, moving, changing properties, and responding to stimuli), there is a growing interest in bringing coacervates out-of-equilibrium as well.[2] Complex coacervates contain oppositely-charged polyelectrolytes, which makes them particularly susceptible to external electric fields.[3] Herein, we present a method that provides spatio-temporal control over complex coacervates utilizing electricity.

In this project, we use an electrochemical potential to drive the out-of-equilibrium formation, movement and destruction of coacervate droplets, mimicking the dynamic properties of MLOs. Opposite electrochemical reactions control the formation and destruction of coacervates, while electrophoresis drives their mobility in the electric field. Since no chemical "waste" is produced during electrochemical oxidation and reduction, the system can maintain a formation-destruction regime for several hours.



Formation, movement and destruction of complex coacervates, controlled by electrochemistry and electrophoresis.

Acknowledgements. *This work is supported by the USIAS Fellowship, within the French national program "Investment for the future"(IdEx-Unistra). K.F thanks the CSC Graduate School funded by the French National Research Agency (CSC-IGSANR-17-EURE-0016) for a Master fellowship.*

[1] Donau, C. et al., *Nat Commun*, **2020**, 11, 5167.
[2] Slootbeek, A. D et al., *Chem. Commun*. **2022**, 58 (80), 11183–11200.
[3] Agrawal, J. F. et al., *PNAS* **2022**, 119, 32, e2203483119.

Dissolved or assembled reactants? The case of the Formose reaction

Yannick Geiger*[a,b], Sinan Bascil,[b] Alex Blokhuis*[c] & Joseph Moran[b]

[a] Chemistry of Complex Matter (CMC), University of Strasbourg, France. Email: y.geiger@unistra.fr
[b] Institut de Sciences et d'Ingénierie Supramoléculaires (ISIS), University of Strasbourg, France
[c] Instituto IMDEA Nanociencia, Madrid, Spain

By default, chemicals in a reaction mixture are supposed to be in solution-phase when there is no evident sign of phase separation, such as a hazy or milky appearance of the mixture resulting from solid particles or liquid droplets. Though, this can be deceiving: small molecules can aggregate to assemblies large enough to behave like a separate phase, but still small enough not to cause any visible turbidity.[1] This can have a profound impact on equilibria in complex systems, as exemplified by the Formose reaction. It is a reaction network that forms a combinatorial explosion of sugars from formaldehyde, catalysed by Ca^{2+} and basic pH (cf. Figure 1) and which is discussed in the context of the origin of life (prebiotic formation of sugars and nucleic acids).[2] Despite being discovered over 150 years ago,[3] the reaction network as a whole is still not understood.[4] Recent results from Dynamic Light Scattering (DLS) and other analytical techniques suggest that the sugars are in aggregated form instead of solution-phase, which might be a key factor that has been overlooked so far.

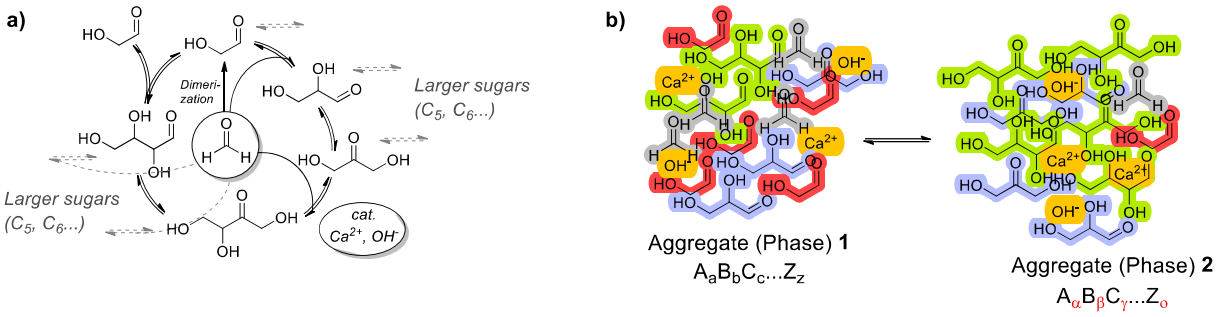


Figure 1. a) Autocatalytic Breslow cycle, which is at the heart of the Formose reaction. The depicted sugars can add to further formaldehyde, C_2 or higher sugars to make larger sugars (C_5, C_6…, grey dashed arrows); b) illustration of Formose constituents assembled into large aggregates. Here, equilibria are not between individual molecules but between phases, i. e. ensembles of aggregates of same composition and fix constituent ratio.

Acknowledgements. *This work was supported by the European Research Council (ERC) grant 101001752 (J.M.).*

[1] A. Blokhuis†*, Y. Geiger†, S. Otto*, *Manuscript in preparation.*
[2] Q. P. Tran, R. Yi, A. C. Fahrenbach, *Chem. Sci.* **2023**, *14*, 9589.
[3] A. Butlerow, *C. R. Acad. Sci.* **1861**, *53*, 145.
[4] A. Briš, M. G. Baltussen, G. L. Tripodi, W. T. S. Huck, P. Franceschi, J. Roithová, *Angew. Chem. Int. Ed.* **2023**, *63*, e202316621.

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Controlled Redox Activation of Supramolecular Halogen Bond Organocatalyst

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Among non-covalent interactions, halogen bonding (XB) has attracted attention in the scientific community due to its softer, more directional, and larger size than its hydrogen bonding analog (HB).[1] This allows various opportunities for fine-tuning this interaction to achieve the desired function in solution such as molecular recognition[2] and organocatalysis.[3] Additionally, the use of redox active system allow us to tune the σ-hole strength upon oxidation/reduction and thus trigger catalysis.[4] In this presentation, we will illustrate our last result regarding the design of redox active halogen bond catalysts based on ferrocene derivatives. Investigation of their redox properties revealed a high reversibility of the oxidation process and stability of XB in the oxidized state. Such findings allowed us to further investigate the stability of the activated catalytic system using UV-vis and NMR spectroscopies and tested as catalysts in Friedel-Crafts alkylation reaction in the presence of a chemical oxidant.

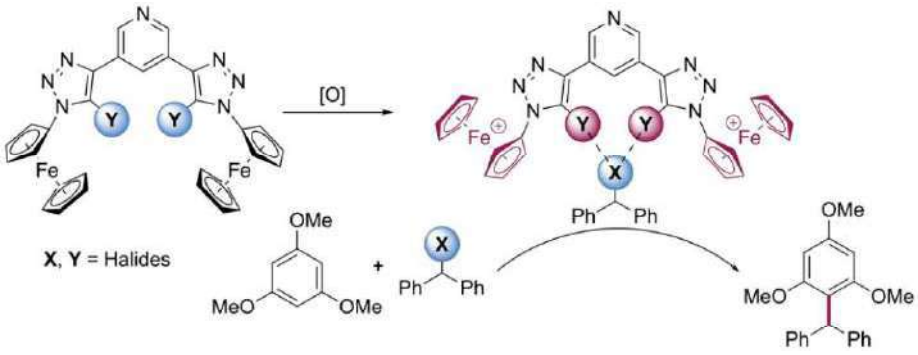

Figure 1. Halogen bond organocatalyst based on ferrocene derivatives for catalytic Friedel-Crafts alkylation reaction.

Acknowledgements. *The Laboratoire d'Électrochimie Moléculaire (LEM) is gratefully acknowledged.*

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Ruthenium Peptide Bioconjugates for Photoactivated Chemotherapy

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Anticancer peptides (ACPs) are naturally derived molecules with anti-proliferative properties that are active toward cancer cells, making them promising candidates for new chemotherapeutics. However, their clinical application faces two major challenges: susceptibility to in vivo degradation by proteases and limited selectivity, often affecting healthy cells as well. A potential strategy to enhance the stability and specificity of ACPs is photoactivated chemotherapy (PACT),[1] in which a non-active prodrug is converted into a cytotoxic drug upon light irradiation. Polypyridyl-ruthenium complexes are particularly well-suited for this approach, as they undergo ligand exchange when irradiated with visible light.[2]

In this work, we conjugated the anticancer peptide Mastoparan-X (MPX) to one or more red light-activated ruthenium complexes. By coordinating multiple Ru(II) complexes to the peptide's methionine residues, the components mutually cage each other in the dark, minimizing toxicity. Upon light activation, cleavage of the ruthenium-thioether bonds releases two bioactive components that efficiently kill cancer cells without side effects. Additionally, we explored the structure–function relationship of the conjugates by designing variants that increasingly disrupt the peptide's original secondary structure.

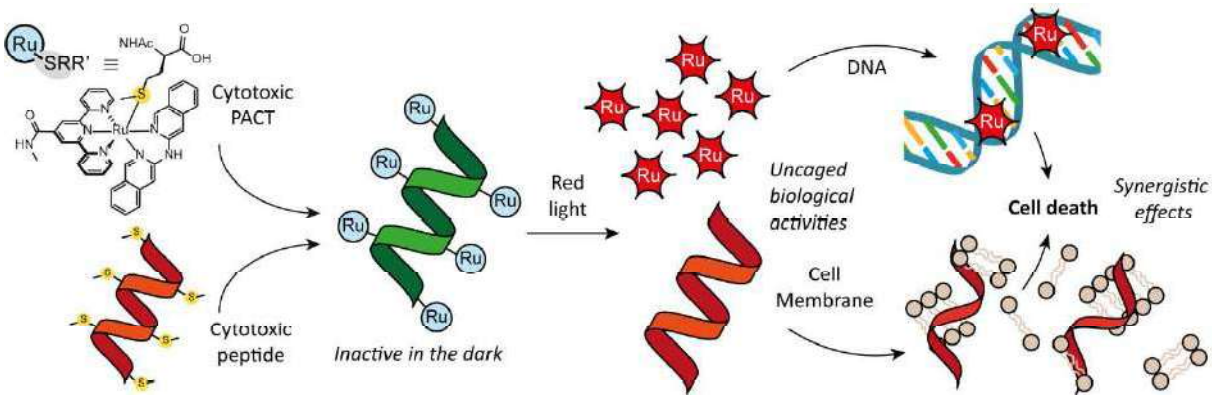

Figure 1 : General concept of peptide-Ru(II) bioconjugates composition and action upon red light irradiation.

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Redox-Responsive Coordination Cages

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Coordination cages[1] are dynamic architectures capable of stimuli-triggered transformations due to the reversible nature of metal–ligand bonds.[2] This adaptability makes them promising candidates for selective molecular recognition, switchable catalysis, and transformable materials. Various external stimuli, including light, anion templating, or concentration changes, can trigger structural reconfiguration in these metal–organic assemblies. Building on our efforts to design redox-active discrete structures via coordination-driven self-assembly for controlled guest binding and release,[3] we present a novel strategy to convert discrete assemblies into distinct architectures upon redox stimulation (Figure 1). Central to these structures is the π-extended tetrathiafulvalene (exTTF) unit, well known for its remarkable geometric and electronic properties, including facile oxidation accompanied by pronounced conformational change. By exploiting these properties, we show how redox-triggered transformations can influence the topology and structure of supramolecular assemblies, offering new perspectives for stimuli-responsive materials.

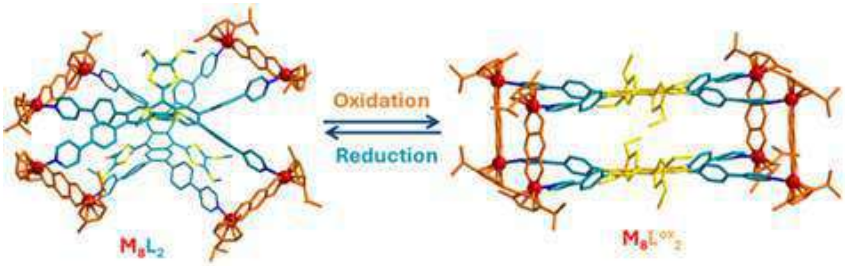

Figure 1. X-Ray crystal structures of coordination architectures based on the exTTF motif illustrating a transformation occurring upon redox stimulation

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Tubular Chiral Pillar[n]arene --- Open-end or Capped-end Nanotubes for Highly Selective Water/Proton Permeation

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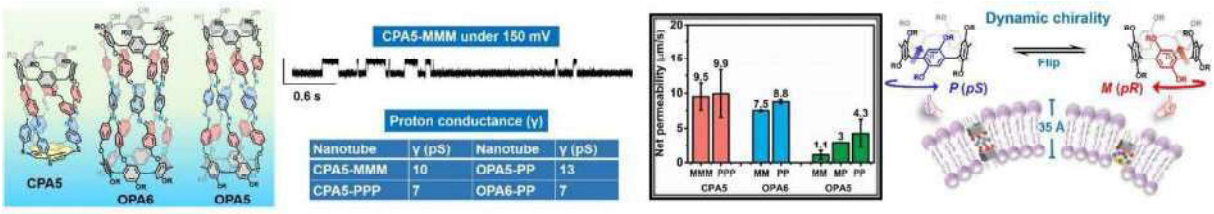
Artificial water channels (AWCs) have been reported in recent years to mimic natural channel aquaporins (AQPs), allowing selective water translocation through the unique hollow architecture.[1] Pioneered by Ogoshi's synthetic route and explored by Hou in transmembrane water transport, pillar[n]arenes (PA) attract much attention to construct AWCs due to their ideal pillar-shaped structure and tunable narrow constriction.[2] These studies have provided a well-founded knowledge for understanding the water transport mechanism of PA, which have inspired us to deeply explore the effect of chiral selectivity on bilayer membrane partition. Herein, we present three kinds of nanotubes, open-end PA5 or capped-end CPA5, and open-end PA6 tubular structures.[3] It revealed that OPA6 present an enhanced water flow rate of 10^7 water molecules/channel/second compared to OPA5. While the CPA5 showed an unexpected performance with the value of 10^8 water molecules/channel/second. These nanotubes allow water accommodation with the narrow pores of ~3 Å, then achieve the water transition along the tubular channel across bilayer. In addition, the different water transport ability of chiral nanotubes (M form and P form) emphasize an increased permeability of P-form and a chiral response to the insertion through the chiral L-lipid bilayer lipid membrane. The results described herein may pave the way for a deep understanding of the transport mechanism of pillar[n]arene water channels.



Scheme 1. pillar[n]arene nanotubes, their water permeability and channel opening possibility.

Acknowledgements. *This project was supported by Agence Nationale de la Recherche, project ANR-22-CE09-0006-03, CORNERSTONE*

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An amino acid, a calcium salt and CO_2: not the beginning of a joke, but a complex supramolecular catalytic system

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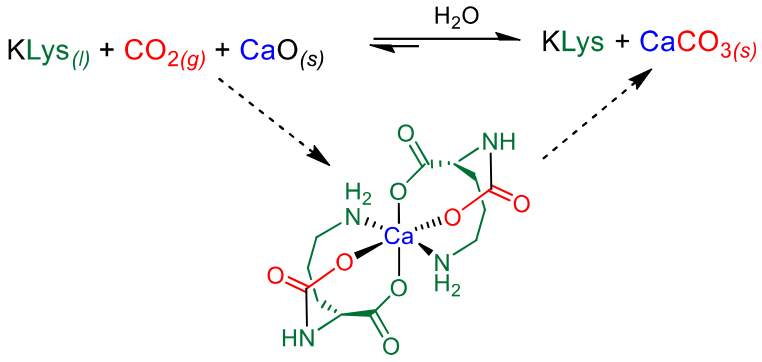
As the years go by, carbon capture, utilization and storage (CCUS) processes have increasingly focused on the development of atom-efficient chemical pathways involving the CO_2 capture and conversion.[1] To further improve the applicability of this technology, a significant surge of interest has been developed towards coupling CO_2 scrubbing by amines to alkaline metals mineralization pathways.[2] Notably, the aim of this study consists in using a renewable non-toxic amino acid (being lysine) to capture CO_2, in the presence of alkaline industrial residues, to recover calcium carbonate. At first, the dynamic covalent and non-covalent molecular subsystem obtained from two components (aqueous lysine and CO_2) has been compositionally characterized by ^{13}C qNMR analyses. While investigating the full three component (lysine-CO_2-CaO model entity), an unexpected and unprecedented Ca-lysine-CO_2[3] coordination complex could be identified and may act as a key intermediate in the accelerated mineralization process. Series of experiments have been conducted to entirely identify the key parameters leading to the formation and conversion of this non-covalent complex.



Schematic representation of the reactive system and proposed chemical structure of the Ca-lysine-CO_2 ternary adduct studied in this work.

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Chalcogen bonds involving tellurium derivatives: Understanding the Nature of These Interactions"

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[a] Institut de chimie de Strasbourg, COSyS, UMR 7177 CNRS-Université de Strasbourg, France
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Interactions based on σ-hole on halogen or chalcogen atoms have recently emerged. They have been recognized as non-covalent interaction and rationalized using the concept of σ-hole.[1] Covalently bonded chalcogens often exhibit an area with a positive electrostatic potential along the σ* orbitals allowing them to interact with a Lewis Base. Compared to halogen, chalcogen atoms like tellurium are able to promote multiple σ-holes favouring σ-hole interactions (Figure 1A). Tellurium derivatives proved to be very effective as catalysts due to their strongest Lewis acidity compared to Selenium and Sulphur, but their use in catalysis is still scarce.

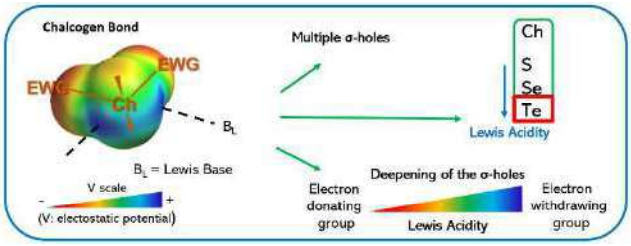

Figure 1A: Generalities concerning chalcogen bond and σ-holes

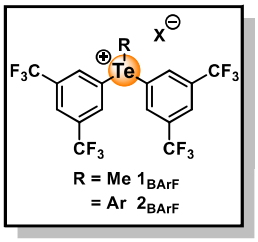

Figure 1B: Examples of Telluroniums salts

Nevertheless, applications based on ChBs have developed rapidly in recent years and significant progress has been made in the field of crystal engineering, biology and catalysis.[2] However, their involvement in stereoselective processes remains relatively unexplored.[3] Furthermore, the study of these interactions has been very limited in solution due to the weakness of these interactions and in particular due to competitive interactions such as solvation. Thus, a better understanding of these interactions in solution would be of crucial interest, particularly for developing effective organocatalysts.[4] Telluronium salts developed in our laboratory (Figure 1B) have shown very interesting catalytic properties.[5] A series of telluronium salts was synthesized and evaluated in various reactions[6] (Friedel-Craft reaction, bromolactonization of ω-unsaturated carboxylic acids and Aza-Diels-Alder reaction such as Povarov-type reaction[7]).

This communication will highlight that, beyond their interesting catalytic potential, these telluronium salts also exhibit remarkable physicochemical properties, including their ability to promote the formation of supramolecular assemblies. Numerous studies, both in the solid state and in solution, have provided deeper insights into these non-covalent interactions, enhancing our understanding of them.

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"The sulfur dance" around arenes and heteroarenes - the reversible nature of nucleophilic aromatic substitutions

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We disclose the features of a category of reversible nucleophilic aromatic substitutions in view of their significance and generality in dynamic aromatic chemistry.[1] Exchange of sulfur components surrounding arenes and heteroarenes may occur at 25°C, in a process that one may call a "sulfur dance". These S_NAr systems present their own features, apart from common reversible reactions utilized in dynamic covalent chemistry (DCC). By varying conditions, covalent dynamics may operate to provide libraries of thiaarenes with some selectivity, or conversion of a hexa(thio)benzene asterisk into another one. The reversible nature of S_NAr is confirmed by three methods : a convergence of the products distribution in reversible S_NAr systems, a related product redistribution between two per(thio)benzenes by using a thiolate promoter, and from kinetic/thermodynamic data. A four-component dynamic covalent system further illustrates the thermodynamically-driven formation of a thiacalix[2]arene[2]pyrimidine by sulfur component exchanges. This work stimulates the implementation of reversible S_NAr in aromatic chemistry and in DCC.

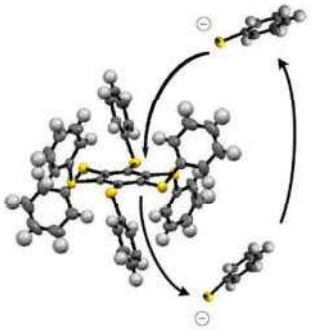

Fig. 1: sulfur exchanges by S_NAr

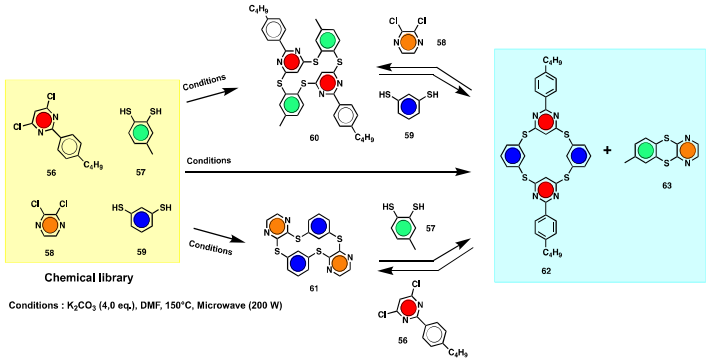

Fig. 2 : Dynamic exchange of sulfur components through reversible S_NAr reactions

Acknowledgements. *Financial support (ANR-20-CE07-003; Aix-Marseille Univ. - A*Midex), USIAS, the Institute for Advanced Study of the University of Strasbourg (JML) and the CNRS UMR 7006 ISIS (JLS). French-Italian University for a doctoral contract to MV (C2-141-Vinci);*

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(NHC-olefin)-nickel nanoparticles in micelles: a cooperative and reusable catalyst for effective hydrogenations and reductive-aminations in water

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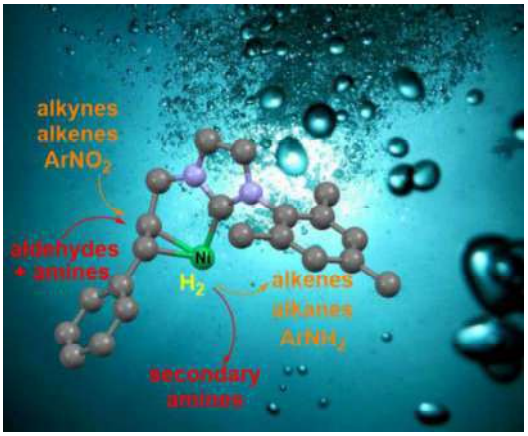
The present challenges in the application of nanoparticles (NPs) in catalysis are the tuning of the catalytic properties as well as the NPs stabilization in order to avoid agglomeration which ultimately results into the loss of their catalytic activity. Different strategies have been explored including the use of: surfactants and micellar catalysis, supports (with different metal-support interactions) or various organic ligands.[1] However, NHC ligands[2] have been much less applied to the stabilization of nanoparticles of Earth-abundant first row transition metals like nickel[3] which are now the priority in catalysis due to economic, environmental and societal reasons. Herein, we report the development of nickel NPs coordinated to NHC-olefin ligands[3] and self-assembled with a double layer of surfactant for catalytic hydrogenations and reductive aminations in water only.[4] The catalyst can be reused without any loss of activity and, thanks to H-bonding interactions, it cooperatively activates various functions.



Acknowledgements. *Financial supports from University of Strasbourg Institute for Advanced Study (USIAS) and the European Campus of the Upper Rhine region (EUCOR) are gratefully acknowledged.*

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Highly Charged Octacationic Photoluminescent Homo[2]Catenanes

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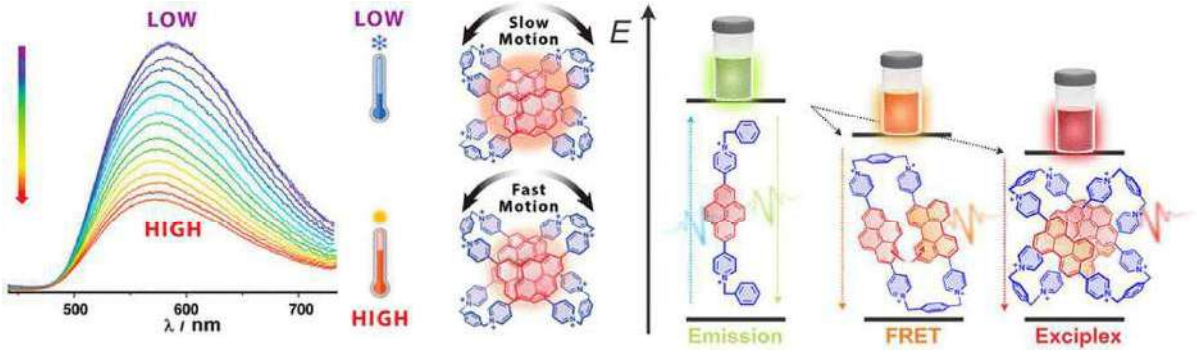
Mechanically interlocked molecules (MIMs)[1] exhibit unique properties, including their dynamic behavior, which can be exploited to develop innovative molecular machines.[2] In this context, we explored the fluorescence behavior of homo[2]catenanes incorporating polycyclic aromatic hydrocarbons, focusing on their motion-induced change in emission (MICE) and energy transfer properties.

Our first investigation[3] is centered on a dynamic pyrene-based homo[2]catenane, whose fluorescence is modulated by temperature-dependent co-conformational changes. These studies reveal that circumrotational and translational motions significantly influence exciplex emission. Notably, the emission variation is reversible across multiple heating and cooling cycles on account of the homo[2]catenane's co-conformational motion, highlighting the potential for temperature-sensing applications in biomedicine and materials science. The second investigation[4] deals with energy transfer mechanisms in bischromophoric homo[2]catenanes and cyclophanes incorporating anthracene, pyrene, and perylene units. These molecules exhibit Förster resonance energy transfer (FRET) and exciplex formation depending on their structure. The tunable nature of these interactions offers new perspectives for designing advanced photonic devices and bioimaging tools. Hence, our work highlights the impact of mechanical bonds on photoluminescence and energy transfer. These findings pave the way for further applications of MIMs in responsive molecular probes and optoelectronic materials.



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Journées de Chimie Supramoléculaire
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Supramolecular Dyads as Photogenerated Qubit Candidates

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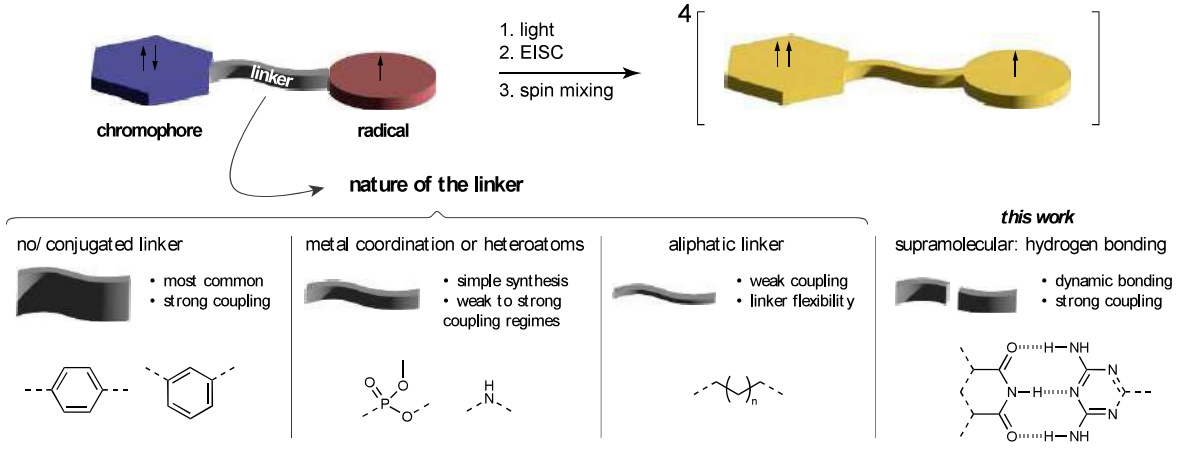
Light-induced multi-spin systems have received increased attention recently due to their exceptional properties and their potential for applications in molecular spintronics. Assemblies consisting of a chromophore, a linker, and a stable radical, are excellent model systems to investigate spin-spin interactions and high-spin states.[1] Light excitation generates a triplet state at the chromophore moiety, which may interact with the stable organic radical. In particular, the quartet states formed in these molecules after photoexcitation were shown to have the right optical and magnetic properties to serve as spin qudits (multi-level qubits). Several studies on covalently-linked chromophore-radical pairs suggest that the exchange interaction, which is considered a through-bond interaction, governs the formation of quartet states.[1]



A major challenge in the field is the scalability of the molecular qubit systems. Here, we provide evidence that supramolecular approaches might hold the key to solve this issue. We use perylene diimides and nitroxide radicals designed to self-assemble in solution via hydrogen bonding and demonstrate, using electron paramagnetic resonance spectroscopy, the formation of quartet states that can be manipulated coherently using microwaves.[2] This unprecedented demonstration that non-covalent bonds can enable spin mixing advances supramolecular chemistry as a valuable tool for exploring, developing, and scaling up materials for quantum information science.

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https://doi.org/10.1038/s41557-024-01716-5

FLASH COMMUNICATIONS

Dissymmetric Molecular Tweezers for Multifunctional Systems

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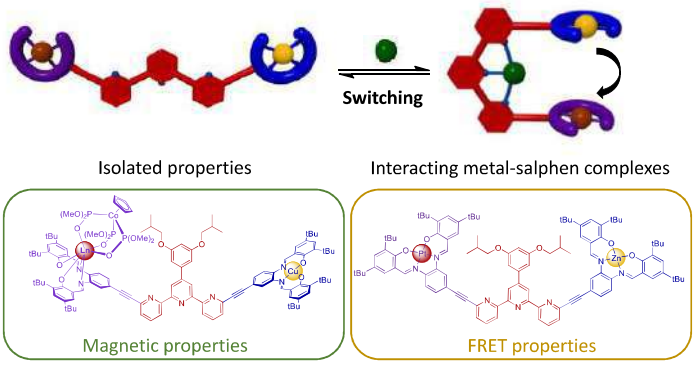
Molecular tweezers are a unique class of switches that can reversibly shift from an open to a closed state upon application of a chemical, electro- or photo-chemical stimulus.[1] Our group has successfully developed a family of switchable molecular tweezers based on a terpy(M-salen)$_2$ architecture. A coordination stimulus has been used to modulate luminescent,[2] magnetic,[3] catalytic[4] or self-assembly[5] properties depending on the M-salen moities. We aim to reach advanced multifunctional systems by developing dissymmetric molecular tweezers bearing two different metallic ions. Our objective is to modulate the luminescence properties of heteronuclear tweezers by controlling through space energy transfer between the two metal-salphen units thanks to the mechanical motion of the tweezers. 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 observed independent luminescence properties of both moieties. However, the spatial proximity of the closed state resulted in an exaltation of Pt-salphen emission associated with a decrease in Zn emission in agreement with an efficient energy transfer from the Zn to the Pt-salphen. More sophisticated systems incorporating 4f lanthanide ions are also investigated to combine luminescence and magnetic properties. The synthesis and studies of the heterometallic tweezers will be presented.



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Stimuli-responsive host-guest interactions: the impact of surface chemistry on supramolecular assembly

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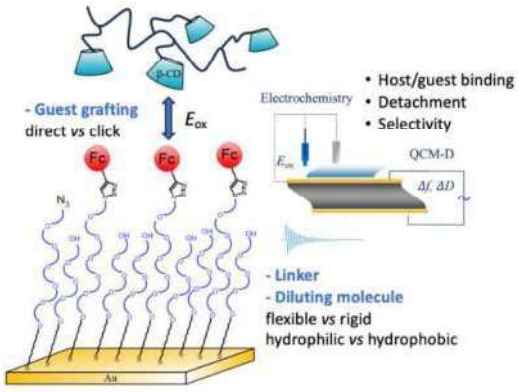
Stimuli-responsive host-guest interactions on both planar and nanoscale surfaces play a crucial role in various applications across health, environmental, and materials sciences. Our group has explored how surface chemistry influences host/guest assembly on surfaces and its responsiveness to external stimuli. In particular, we studied redox-active ferrocene (Fc)/β-cyclodextrin (β-CD) pair, leveraging electrochemistry for quantitative surface characterization, including areal density, 2D organization, and click chemistry efficiency.[1] Our findings demonstrate that the architecture and functionality of guest monolayers are influenced by the nature of the linkers connecting the guest molecules to the surface, as well as by the choice of diluting molecules used to tune their density.[1] Additionally, using quartz crystal microbalance with dissipation monitoring (QCM-D) coupled with electrochemistry, we revealed how these parameters affect the interaction between Fc-functionalized surfaces and multivalent β-CD probes.[1] Building on this, we are now investigating how surface chemistry affects the superselectivity, i.e. the ability of multivalent probes to sharply differentiate between ligand areal densities.[2] In this study, we combine QCM-D with surface plasmon resonance (SPR) to examine how the efficiency and selectivity of host/guest binding as well as conformation of multivalent host molecules depend on the 2D organization and flexibility of surface-attached guests. This research aims to provide insights into optimizing supramolecular host/guest systems, particularly in enhancing specificity, selectivity, and reversibility of host-guest assembly for applications in material and biomedical sciences.



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PTFE ("TEFLON") Sealing Ring for hermetic greaseless Glass Joints

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There is a prejudice that PTFE (often called "TEFLON") is too inelastic to be a hermetic sealant for greaseless conical joints. Therefore, teaching books recommend threaded or flanged "O-ring joints" for hermetic manipulation of air- and moisture sensitive chemicals if joint grease is no option.[1,2]
Here we show (Figure 1) that the common ground conical glass joint can be sealed relatively hermetic and at low cost with a narrow flat PTFE sealing ring (less than 1 mm wide and 0.1 mm thick.[3]
The low weight of the Sealing Ring (less than 10 mg PTFE) makes it environmentally friendly.
The sealing ring is high-vacuum tight (air leakage rate 10-8… 10-6 mBar*Liter/sec), solvent tight (loss of ethyl acetate out of containers < 0.1 mg/day) and resistant to fluctuation of temperature (freezing-thawing-heating cycles). The reusable PTFE sealing ring prevents stuck joints, is thin enough to be used with all joint clamps and is fixed elastically (without groove) on the glass joint.

Figure 1. Left: PTFE-sealing ring fixed elastic (no groove necessary). Middle: Sealing ring intransparent without pressure. Right: Sealing ring transparent under sealing pressure.

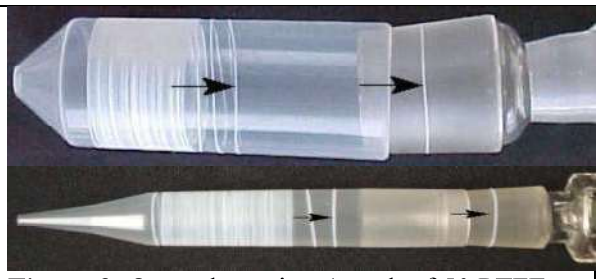

Figure 2. One sales unit = 1 pack of 50 PTFE-sealing rings on a plastic adapter (polypropylene) fitting the size of the glass joint (examples fitting joint 29mm and 14mm)
Sold worldwide by all major laboratory distributors
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Mechanical disruption of 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.

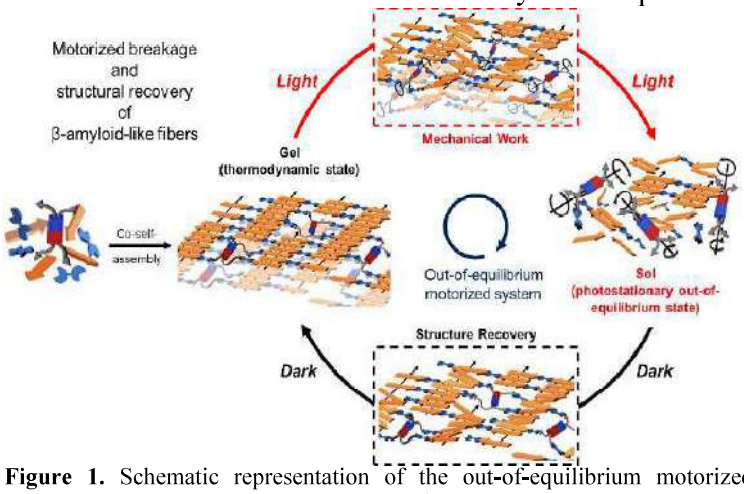

Figure 1. Schematic representation of the out-of-equilibrium motorized system based on supramolecular hydrogels.[4]

Acknowledgements.
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A novel prebiotic pathway for lipid acylation

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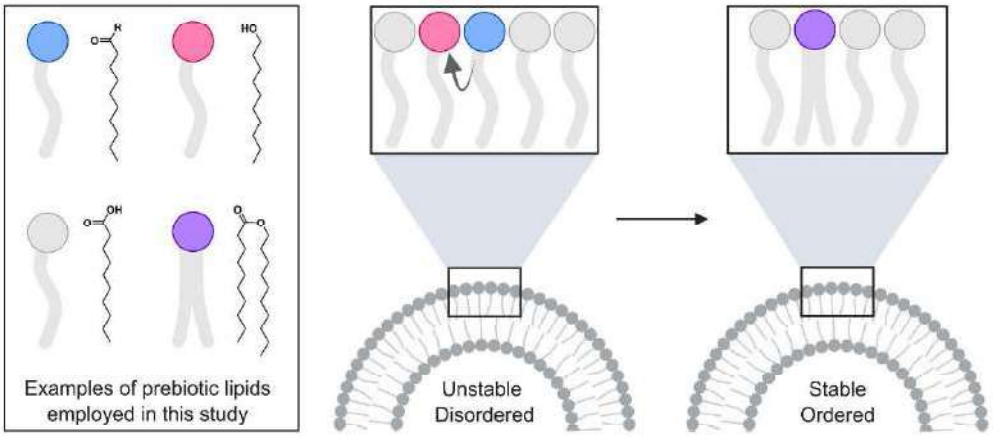
The emergence of protometabolism on early Earth required prebiotically plausible pathways to synthesize and modify key biomolecules, including lipids. Inspired by pioneering work demonstrating the self-assembly-driven non-enzymatic synthesis of natural phosphatidylcholines,[1] we show that primitive membranes can similarly facilitate acylation reactions at neutral pH, using acyl imidazoles as efficient, prebiotically relevant acylating agents.[2] We demonstrate the efficient acylation in membrana of diverse prebiotic substrates, including lysophospholipids with different headgroups,[3] monoester/ether glycerols, and alcohols of varying chain lengths. By employing primitive membranes as both reaction templates and organizational scaffolds, we reveal a potential pathway for prebiotic acyl-group transfer, driven by chemical reactivity rather than enzymatic control, which could have mimicked early biochemical steps toward protocell membrane diversification. Our findings bridge non-enzymatic synthesis on a large library of substrates with primitive membrane-mediated chemistry, offering insights into how spontaneous chemical processes might have led to the functional complexity of early cells.



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Spiro-bridged *N*-Heterotriangulenes as Building Blocks for Functional Materials

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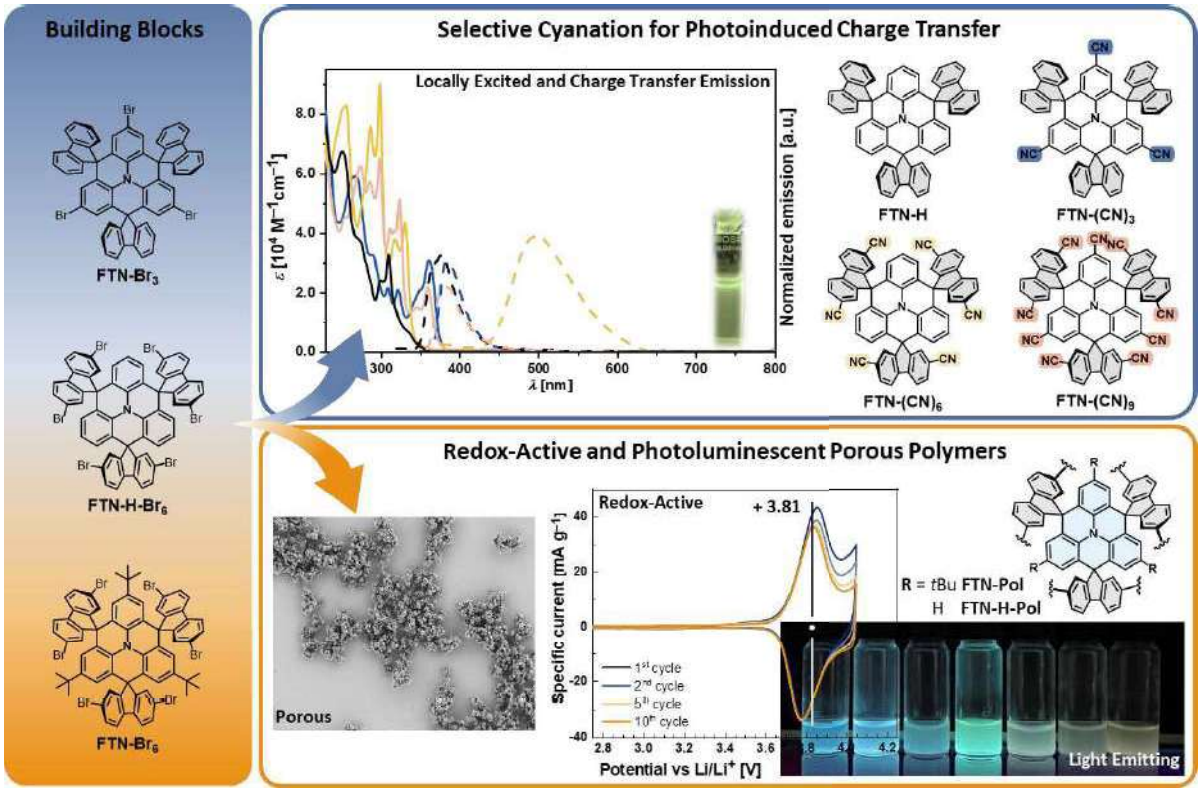
In 2020, our group reported a nitrogen-centered trispirocyclic *N*-heterotriangulene in which the central triphenylamine moiety is bridged via sp^3-carbon spirofluorene units.[1]
To investigate the impact of functionalization on the optoelectronic and structural properties, we have established selectively brominated spirocyclic building blocks allowing the synthesis of a series of compounds differing in the number and position of the electron-withdrawing cyano groups. Depending on the substitution pattern, the compounds display dramatically altered optoelectronic and redox properties which were studied in detail by optical spectroscopy and quantum chemical calculations.[2]
Due to the inherent rigidity of the brominated spirocyclic scaffolds, nickel-mediated *Yamamoto* coupling reactions afforded novel electron-rich conjugated microporous polymers with impressive thermal and structural stability and appealing photophysical properties. In addition, fully reversible oxidation at +3.81 V (vs. Li/Li^+) in composite electrodes and excellent cycling stabilities were observed when implementing the polymer as cathode material in lithium-ion batteries.[3]



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Polyaromatics Detection by Gold Electrode Grafted with Acridinium Receptor

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Over the past decades, acridinium moieties gained interest as recognition units in artificial supramolecular receptors.[1] Their electro-deficiency allows interactions with electron-rich aromatic guest molecules. The switchable properties of acridinium units (through application of chemical, redox stimuli)[2,3,4] leads to multi-responsive receptor in order to detect polyaromatic compound by electrochemistry.

In this work, a new macrocycle incorporating a semi rigid spacer, two acridinium moieties and a flexible chain was synthesized. The latter includes a disulfide bond for the grafting on gold surface (Figure 1).[5] Following efficient grafting of the macrocycle on a gold bead electrode, the electrochemical detection of polyaromatics was studied. Surprisingly, a selective detection of proflavine from a complex mixture of polyaromatics was observed.

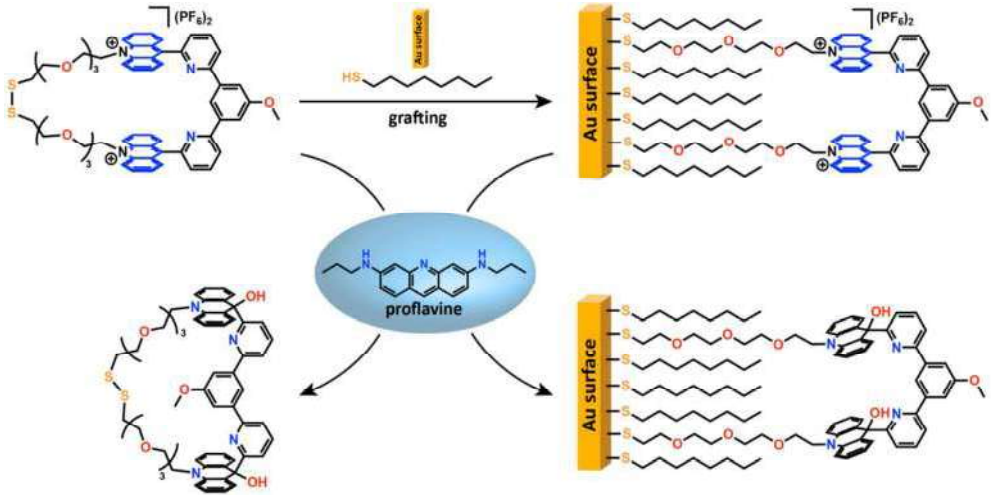

Figure 1: *Proflavine detection by an acridinium receptor, in solution and on gold surface.*

Acknowledgements

The CNRS, the university of Strasbourg and the Agence Nationale pour la Recherche (project ANR ACROSS).

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Fluorescence detection of chlordecone in water by hemicryptophane cages

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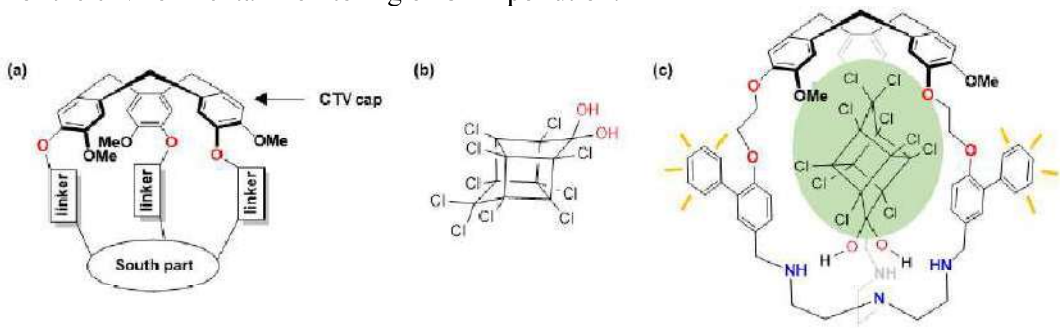
Chlordecone (CLD) is an insecticide with a perchlorinated bishomocubane structure, used in the French West Indies between 1972 and 1993 before being banned due to its toxicity and persistence in the environment[1], which today leads to massive environmental pollution and high levels of impregnation of the local population. Our group has designed supramolecular receptors based on hemicryptophanes, capable of selectively encapsulating chlordecone both in organic solvent[2] and in water for depollution purposes[3]. Our aim is to develop efficient fluorescent hemicryptophane cages, enabling rapid detection of chlordecone in water, easy to implement by French West Indian laboratories and less expensive than current systems, based on GC or HPLC analysis techniques coupled to a mass spectrometer. Hemicryptophane cages proved particularly effective for CLD detection at environmental concentrations, showing high association constants and increased fluorescence upon CLD encapsulation[4]. This paves the way for the development of an affordable high throughput detection system for the environmental monitoring of CLD pollution.



(a) General structure of hemicryptophane cages (b) Structure of chlordecone (c) Structure of developed hemicryptophane with fluorescent linkers for chlordecone encapsulation

Acknowledgements. *This project has received funding from the Préfecture de Martinique, under the auspices of Plan Chlordécone III, action remediation (2019). The authors acknowledge the French National Research Agency (ANR), the Region Guadeloupe and the Collectivité Territoriale de Martinique for their financial support of the CHLOR2NOU project n°ANR22-CHLD-0005-01. M.P.'s PhD work was funded by CEA.*

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Highly confined water flow through macrocyclic self-assembled artificial water channels

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Although nature has developed Aquaporins (AQPs) as specialized transmembrane channels to selectively and efficiently facilitate rapid water movement across cell membranes, artificial replacement of AQPs has emerged as an innovative solution to enable large-scale applications (e.g., for efficient industrial seawater desalination), applications otherwise inaccessible with natural channels due to their high-cost production, low stability and problematic processability.[1] Herein we disclose a series of self-assembled macrocyclic artificial water channels (Figure 1) that show a unique water dynamic along the highly confined pore, finely translated to satisfactory high-water permeabilities and salt and proton rejection. We have addressed three main structural features to finely modulate the π-π stacking as well as the water uptake and dynamic movement along the channel: *i)* macrocycle cavity (from confined cavities in **I-III** to large cavity of **V**), *ii)* graphed substituents (R=H, Ph, *t*-Bu) modulating stacking orientation (*i.e.*, syn and/or anti, Figure 1b), and *iii)* the nature of amide moiety (i.e., X=N vs. CH) and bridge half (i.e. **I** vs **II** vs **III**). All these together combined with the simplicity of these macrocycles (2 efficient synthesis steps) open the avenues toward improved reverse osmosis water desalination (in progress in our group), and AQPs channel replacement therapy.[2]

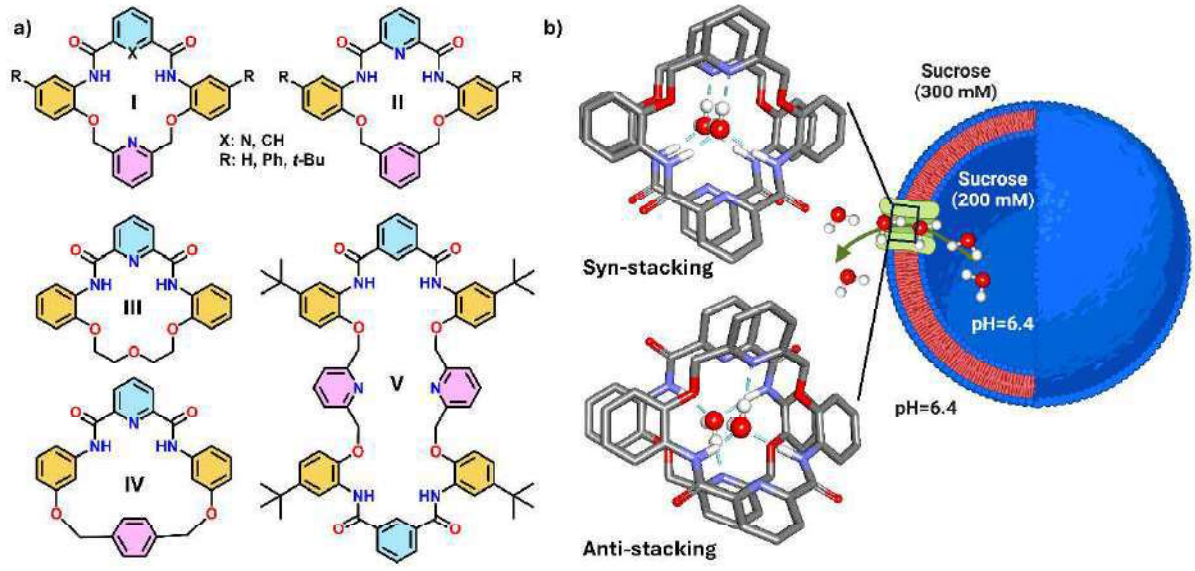

Figure 1. The structure of macrocycles **I-V** (a) self-assembling in channel-like architectures by π-π stacking in syn- and/or anti-orientations and facilitating water transmembrane transport along bilayer membrane (b).

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Mg^{2+}-driven selection of natural phosphatidic acids in primitive membranes

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Biological membranes are composed exclusively of phospholipids comprising glycerol-1-phosphate or glycerol-3-phosphate. By contrast, primitive membranes would have likely been composed of heterogeneous mixtures of phospholipids, including non-natural analogues comprising glycerol-2-phosphate, as delivered by prebiotic synthesis. Thus, it is not clear how the selection of natural phospholipids could have come about. Here we show how differences in supramolecular properties, but not molecular properties, could have driven the selection of natural phosphatidic acids in primitive membranes. First, we demonstrate that at the molecular level it is unlikely that any prebiotic synthesis or hydrolysis pathway would have enabled the selection of natural phosphatidic acids. Second, we report that at the supramolecular level, natural phospholipids display a greater tendency to self-assemble in more packed and rigid membranes than non-natural analogues of the same chain length. Finally, taking advantage of these differences, we highlight that Mg^{2+}, but not Na^{+}, K^{+}, Ca^{2+} or Zn^{2+}, drives the selective precipitation of non-natural phosphatidic acids from heterogeneous mixtures obtained by prebiotic synthesis, leaving membranes proportionally enriched in natural phosphatidic acids. Our findings delineate a plausible pathway by which the transition towards biological membranes could have occurred under conditions compatible with prebiotic metal-driven processes, such as non-enzymatic RNA polymerization.

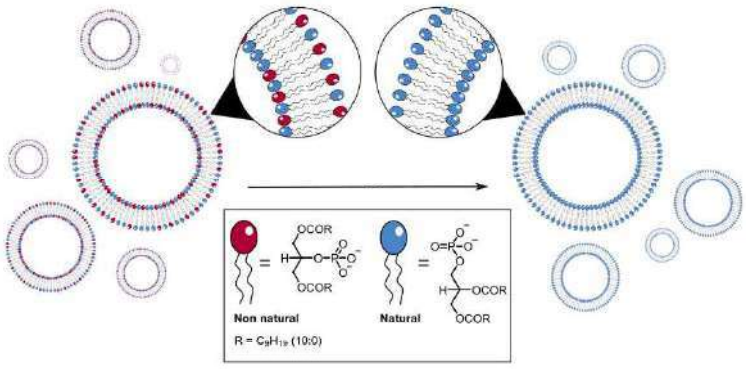

Figure 1. Schematic representation of selection and enrichment of primitive membranes with natural phospholipids

Synthesis of Gram-scale Nitrogen-Containing Cryptophanes for Trapping Toxic Thallium(I) Ions

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The contamination of ecosystems by thallium(I) ions is a major environmental issue, largely driven by human activities such as coal power generation and mineral extraction. Even at low concentrations, this highly toxic metal poses serious risks to humans and wildlife. Detecting, trapping, and removing its ionic form Tl(I) from contaminated water is therefore crucial.[1,2] One promising solution is the use of cryptophanes, a family of synthetic organic receptors, whose binding properties can be efficiently tuned by structural and functional modification.[3] Mostly, cryptophanes which are decorated by phenolate functions exhibit a good affinity toward Tl(I) only in basic medium and are not selective (high association constants for K^+ ions).[4]

However, other heteroatoms such as nitrogen or sulfur were not investigated as much as oxygen while it could be a solution to encapsulate cations at neutral pH. Promising results with the first nitrogen-containing cryptophane suggest that aromatic amine enhance selectivity and efficiency towards thallium(I) ions. Unfortunately, this study has often been delayed due to the synthetic challenges involved in the introduction of heteroelements into the cryptophane skeleton.[5,6]

In this regard, we have developed new approaches to obtain nitrogen-containing cryptophanes on gram-scale with a perfect diastereoselective synthesis (*anti*). Several protecting groups for nitrogen have been investigated and their impacts on synthesis highlighted. This platform will be used to obtain a new amphoteric cryptophane, whose thallium-binding properties will be assessed in water at neutral pH.

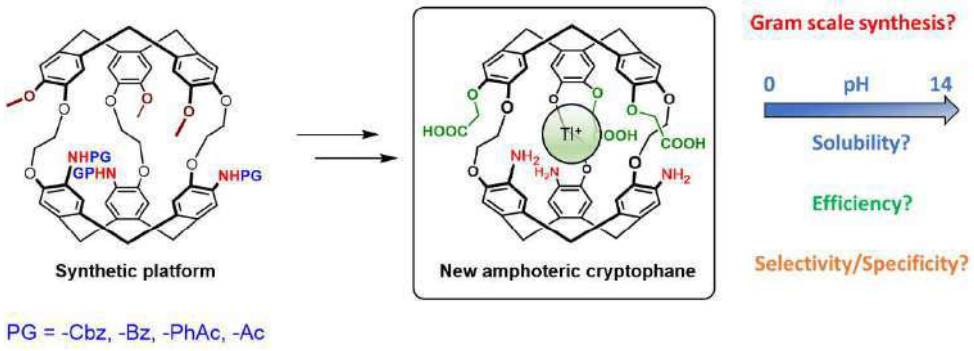

Figure 1: Optimized multi-step synthesis of an amphoteric cryptophane for trapping Tl(I) ions in water.

Acknowledgements. *Doctoral School of Chemistry of Lyon (ED 206) and The French National Research Agency (ANR) are acknowledged for financial support (Project ANR-21-CE07-0006 ENARECANIONS).*

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Octacyano-substituted tridecacyclene: A non-benzenoid cyanocarbon with low-lying LUMO and multistage redox properties

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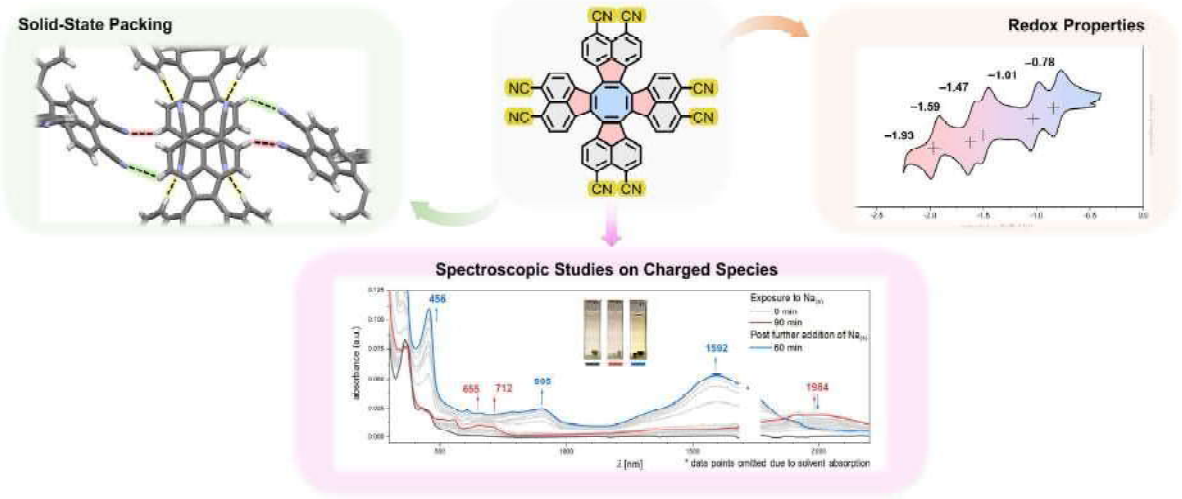
The attachment of cyano groups to diverse π-conjugated scaffolds, yielding the family of so-called cyanocarbons, affords electron-deficient compounds with unique self-assembly properties to form highly-organized architectures.[1] Incorporation of non-benzenoid rings into the sp^2-carbon frameworks of polycyclic aromatic hydrocarbons offers a complementary approach to achieve new classes of electron-accepting compounds with peculiar geometries and packing in the solid state.[2]

In this contribution, we introduce a non-benzenoid cyanocarbon obtained through decoration of the 5- and 8-membered ring-containing tridecacyclene scaffold with multiple strongly electron-withdrawing cyano groups. In the crystal, the saddle-shaped scaffold arranges in a zigzag packing motif governed by an interplay between the geometry of the central cyclooctatetraene moiety and the hydrogen bonding mediated by the dipolar cyano groups. In electrochemical studies, the compound undergoes five reversible reductions in a particularly narrow potential window of 1.15 V in CH_2Cl_2. The first reduction occurs at –0.78 V (vs. Fc/Fc^+) which corresponds to a remarkably low-lying LUMO of –4.32 eV. Chemical reduction with sodium metal afforded the mono- and dianionic species, which were comprehensively investigated using both spectroscopic and theoretical methods.[3]



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Enhancing Tin Perovskite Solar Cells Performance through Innovative Fullerene Derivatives for Minimized Interfacial Voc Losses

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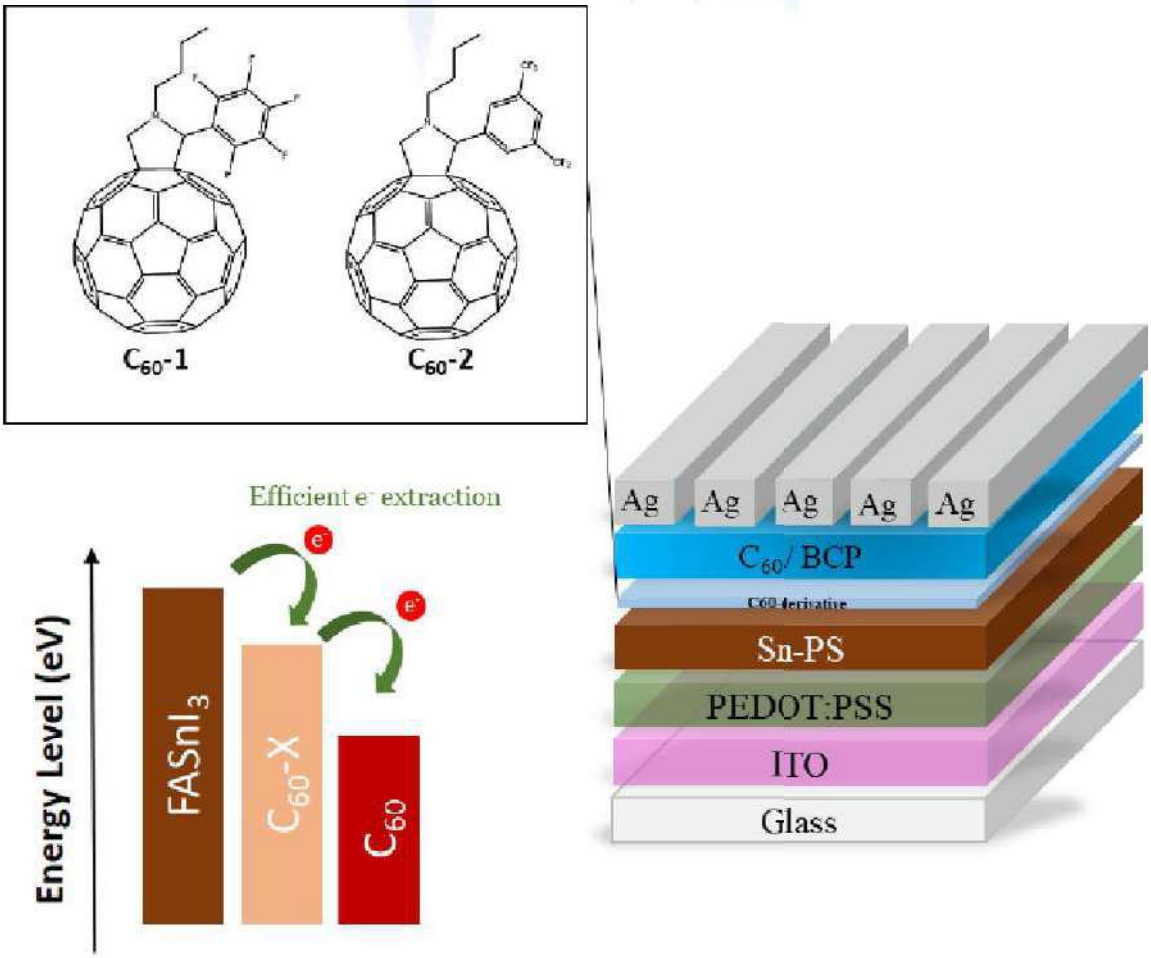
Abstract:
Tin halide perovskite solar cells (Sn-PSCs) are a promising alternative to their lead-based analogues due to their favorable optoelectronic properties. However, the offset between the perovskite conduction band and the LUMO level of the standard C60 remains a major bottleneck for their development, hindering the charge extraction and limiting the overall device performance. In this work, we designed and synthesized two novel fullerene derivatives, namely C60-1 and C60-2, functionalized with different fluorine-rich moieties, and incorporated them as interlayers between the perovskite and the C60 electron transport layer (ETL). These derivatives demonstrated suitable LUMO levels to effectively alleviate the energy level misalignment at the perovskite/ETL interface, minimizing the undesirable charge recombination and enhancing the charge extraction processes. As a result, the best-performing Sn-PSCs showed power conversion efficiencies of up to 10.5% and 11.0% for the devices incorporating C60-1 and C60-2, respectively. Moreover, the new compounds increased the operational stability of the unencapsulated devices in harsh ambient conditions (60% RH and 25°C). As a result, devices containing C60-1 and C60-2 retained up to 80% of their initial performance after 15.5 and 18.4 hours, respectively. These results highlight the potential of fullerene chemistry's versatility to mitigate carrier losses at the

interfaces while simultaneously improving both the performance and stability of Sn-PSCs, paving the way for future advancements in their design and development.



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Synthesis of Photoswitches and Photoswitchable Lipids for Light-Controlled Therapeutic Applications

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Photoswitchable lipids (photolipids) are emerging as a powerful tool for the precise, light-assisted manipulation and study of lipid function including membrane biophysics (permeability, fluidity…) and receptor activation.[1] In particular, a photolipid with a serine polar head can target TIM-3, a transmembrane receptor protein highly expressed on Natural killer (NK) cells, leading to a promising immunotherapeutic approach.[2] Herein, we will first present the synthesis of two photolipids featuring either a phosphatidylcholine polar head (Switch-PC) or a phosphatidylserine one (Switch-PS), designed for membrane-targeting application or TIM-3 activity modulation, respectively, and a photoswitchable unit in the lipid tail. As the photoswitch, we used a biomimetic 2,6-disubstituted-γ-pyrone analogue of cyclocurcumin,[3,4] that undergoes reversible E/Z photoisomerization under UV light. Notably, this chromophore can theoretically be excited in the optical biological NIR-I window (650-900 nm) using a two-photon absorption approach (TPA), allowing for deeper tissue penetration. Second, we will describe the evaluation of the photoswitching properties of Switch-PC in Giant Unilamellar Vesicles (GUVs), serving as model membrane systems. Finally, we will discuss the development of new easily accessible styryl-heterocycle photoswitches with interesting properties expanding the limits of these systems.

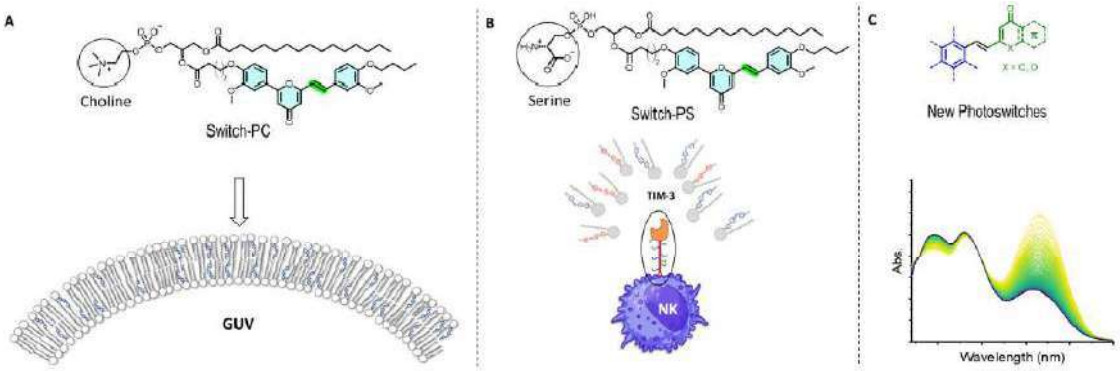

Figure 1: A- Switch-PC and its use in GUVs, B- Switch-PS targeting TIM-3 in NK cells, and C- General structure and properties of a new family of photoswitches.

Acknowledgements. *A.M. would like to acknowledge the LUE-Immunopass for her postdoctoral grant.*

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Molecular tweezers based on bioinspired units

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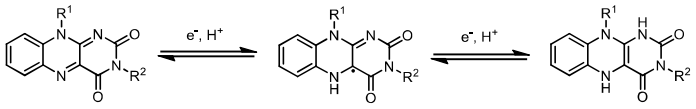
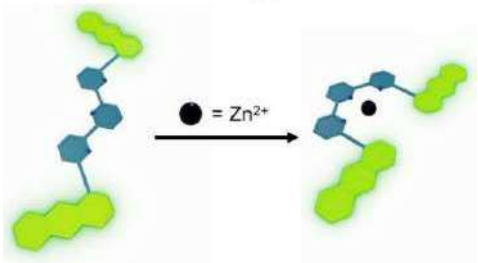
Commutability is a desirable property and a large number of species have been synthetized with the aim to commute different properties such as luminescence, electrochemical potential or catalytic activity. Among these, tweezers are interesting structures which can switch between an open form and a closed form upon application of a stimulus. Many commutable units have been developed to respond to different stimuli (light, electric potential, acidity, etc.). Coordination is another useful stimulus as it avoids equilibrium and enables to switch completely from one state to another. The group of G. Vives has developed several tweezers based on terpyridine units.[i] By coordination with a zinc cation, different properties of these tweezers were modulated, according to the units fixed on the terpyridine.

Our laboratory is interested in the study of flavins and their derivatives.[ii] In biological systems and particularly oxido-reductases such as flavoenzymes, the isoalloxazine core of flavins is used for electron transport because it has three stable oxidation states. Moreover, artificial isoalloxazines and their analogs have promising photophysical properties and can be used as photocatalysts, either through photoinduced electron transfer or energy transfer.[iii]



In the context of a collaboration between our groups, tweezers incorporating bioinspired analogs of flavins redox cofactors attached to a commutable terpyridine unit have been prepared. We will present the study of their coordination abilities with different zinc salts, along with their photophysical and electrochemical properties.[iv]



Acknowledgements. *Financial support from the ANR (project MULTIFUN), in collaboration with GOBS group, IPCM, Paris*

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POSTER PRESENTATIONS

Azaphosphatrane Confined in Enantiopure Hemicryptophane : Towards Enantioselective Catalysis

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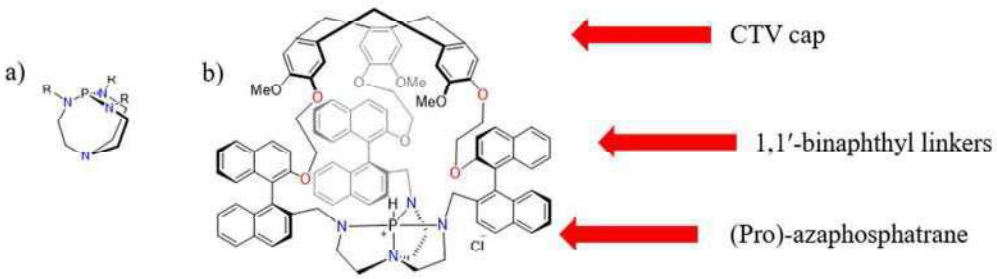
Pro-azaphosphatranes (**Scheme 1, a**), also named Verkade's superbases, were discovered in 1989 by Verkade. These species are highly basic with a pKa around 32 in CH_3CN. Pro-azaphosphatranes have been used as basic and nucleophilic catalysts in various transformations, such as isocyanurate formation or Strecker reaction.[1] **Azaphosphatranes**, pro-azaphosphatrane's acidic counterparts are stable species that could be used to generate reactive pro-azaphosphatrane in a single step.[2]

Previously in the team[3], we reported an endohedral functionalized cage displaying catalytic activity in Morita-Baylis-Hillman (MBH) reactions between cyclohexenone and prochiral activated benzaldehyde through the formation of Frustrated Lewis Pair (FLP) system between pro-azaphosphatrane and the $TiCl_4$ Lewis acid. The crucial role of the molecular cavity on catalytic performance was highlighted ; open analogues being much less efficient. Our objective is to enhance chirality around the active site by introducing chiral linkers.

On this basis, the goal of this work is to functionalize the azaphosphatrane moiety with the enantiopure **CTV** cap, via three enantiopure 1,1′-binaphthyl linkers, creating a hemicryptophane cage with various stereogenic units (**Scheme 1, b**). The synthesis of the cage will be presented along with the study of its corresponding pro-azaphosphatrane base as potential catalyst for enantioselective reactions.



Scheme 1. (a) General structure of pro-azaphosphatrane and (b) structure of developed azaphosphatrane encaged in an enantiopure hemicryptophane

Acknowledgements. *This work was supported by A*Midex (LiHaMiCo)*

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Guest Exchange by a Partial Energy Ratchet in Water

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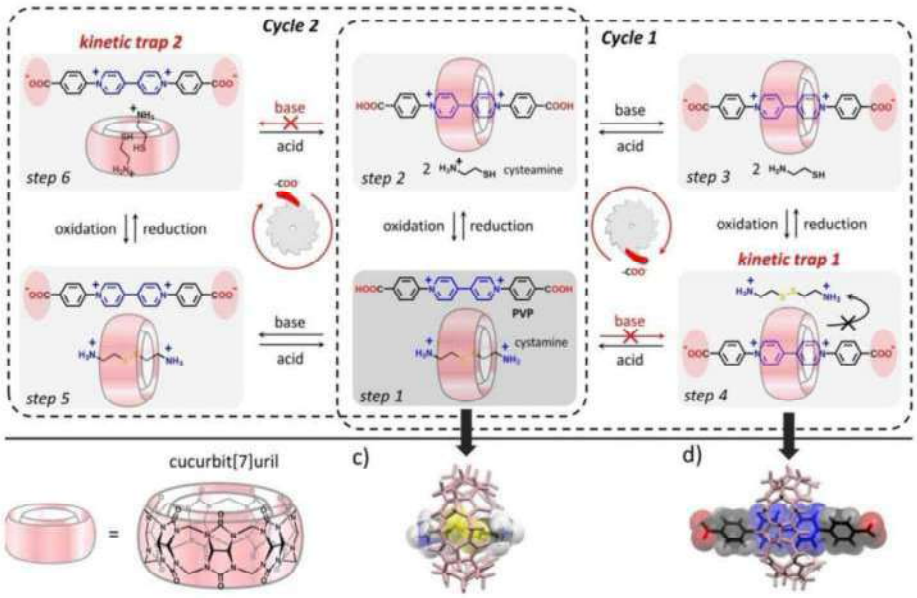
[b] Institute of Chinese Medical Sciences, University of Macau, China

Molecular machines are ubiquitous in nature and function away from equilibrium by consuming fuels to produce appropriate work. Chemists have recently excelled at mimicking the fantastic job performed by natural molecular machines with synthetic systems soluble in organic solvents.[1,2,3] In efforts toward analogous systems working in water, we show that guest molecules can be exchanged in the synthetic macrocycle cucurbit[7]uril by involving kinetic traps, and in such a way as modulating energy wells and kinetic barriers using pH, light, and redox stimuli.[4] Ditolyl-viologen can also be exchanged using the best kinetic trap and interfaced with alginate, thus affording pH-responsive blue, fluorescent hydrogels. With tunable rate and binding constants toward relevant guests, cucurbiturils may become excellent ring molecules for the construction of advanced molecular machines working in water.



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Computational study of fluorinated organocatalysts for hydrosilanes' activation through non-covalent interactions and applications in catalytic hydrosilylations

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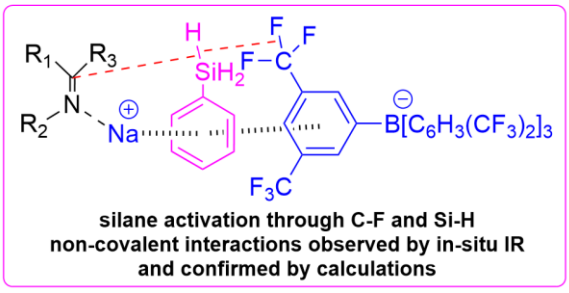
The reduction of organic functional groups bearing one or more unsaturations C=X (X being an heteroatom) like carbonyl, ester, amide, imine... can be performed through catalytic hydrosilylations using main-group or metal based catalysts[1] as well as organocatalysts[2] or bases.[3] Our study aims to develop a new and original concept of hydrosilane activation through non-covalent interactions between the C-F and Si-H bonds of a fluorinated species and a hydrosilane.[4] A comprehensive quantum chemical investigation for hydrosilane activation has been done on different aldimines and ketimines, employing density functional theory (DFT) calculations. The free energy barrier values (ΔG) in hydrosilane activation are reported for different imines in the presence of the $NaBArF_{24}$ catalyst. This transition state elucidates the distinct contributions of the ion pair components of the catalyst: the sodium cation stabilizes the nitrogen of the imine, a behavior also observed in molecular dynamics simulations using the semiempirical GFN2-xTB method, while the phenyl ring of the BArF anion stabilizes the phenyl group of $PhSiH_3$ through π-stacking interactions. A comprehensive analysis by various computational tools such as Bader's theory of atoms-in-molecules (AIM), natural bond orbital (NBO) analysis and non-covalent interaction (NCI) plots is also done to prove the hypothesis.



silane activation through C-F and Si-H non-covalent interactions observed by in-situ IR and confirmed by calculations

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"DCM-like" fluorophores conjugated to thermoresponsive polymer: toward thermometric photothermal agent

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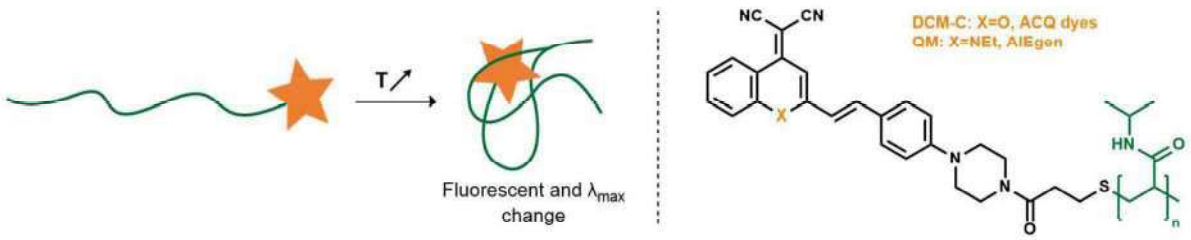
Fluorescent molecular thermometers are essential tools to measure the temperature at the nanoscale in biomedical applications. They hold promise in photothermal therapy (PTT) by providing real-time temperature feedback via fluorescence imaging during irradiation, addressing the challenges of precise and noninvasive temperature control to optimize therapeutic efficiency and minimize side effects. Consequently, photothermal agents capable of fluorescence-based temperature monitoring are gaining interest.[1] "DCM-like" compounds, including dicyanomethylene-4H-chromene (DCM-C) and quinoline malonitrile (QM), are push-pull fluorescent dyes characterized by an environment-sensitive (polarity, viscosity, or aggregation mode) luminescence response. In addition, by varying the acceptor core from DCM-C to QM, they can switch from "Aggregation Cause Quenching" (ACQ) to "Aggregation Induced Emission" (AIE) dyes.[2] They can also be effective as light-to-heat converters when fluorescence/photoisomerization deactivation channels are reduced.[3]

Within this work, fluorescents polymerics thermometers were developed by covalently linking DCM-C and QM dyes to biocompatible poly(N-isopropylacrylamide) (PNIPAM), a thermosensitive LCST (Lower Critical Solution Temperature) polymer capable of achieving phase-transition from a freely soluble to an insoluble at a certain threshold temperature. This transition alters the dye's environment and thus its luminescence properties. We varied the nature of the dyes from DCM-C to QM and the attachment site on the polymer (end-chain/side-chain) in order to identify the most suitable structure to achieve an optimal readout of the threshold temperature by fluorescence. Temperature-dependent optical properties were evaluated by steady-state photophysical technics, giving significant fluorescence change upon passing the transition-phase temperature. In order to link the luminescence variation to the dye's type (polarity/viscosity probe, ACQ/AIE), specific photophysical characterization of free dyes and dyes-polymer conjugated were also conducted. These encouraging results serve as guide for the future design of polymeric thermometric photothermal agent for in vivo applications.



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Multifunctional graphene-family nanomaterials for combined phototherapy and chemotherapy

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Graphene oxide (GO), one of the most studied members of the graphene family materials, can be exploited as a photothermal agent to convert light energy into heat and cause hyperthermia, leading to thermal ablation of tumor cells[1]. In addition to this property, GO has a large specific surface area that allows many therapeutic drugs or photosensitizers to be loaded onto its surface by covalent and non-covalent methods[2]. Photothermal therapy (PTT) and photodynamic therapy (PDT) have shown great potential as effective treatments against cancer[3]. However, a single approach has some limitations, and the combination of PTT and PDT can lead to a synergistic effect with greater therapeutic efficiency[4]. In this context, we synthesized GO doubly functionalized with folic acid (FA) and a boron dipyrromethene (BODIPY) derivative for combined targeted PTT/PDT. The GO-FA-BODIPY conjugate was characterized by thermogravimetric analysis, Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy. In vitro experiments allowed to assess its potential for the targeted elimination of cancer cells.

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Synthesis, characterization of chiral carbon dots

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Chiral carbon dots (Ch-CDs) are an emerging class of nanomaterials characterized by unique three-dimensional asymmetry[1], making them promising candidates for applications in catalysis[2], sensing[3], and molecular recognition[4]. In this study, we synthesized Ch-CDs via a solvothermal method using L-/D-tryptophan (Trp) as chiral precursors and perylenetetracarboxylic dianhydride as an achiral conjugated component. The resulting Ch-CDs exhibited well-defined spherical morphologies with diameters ranging from 4 to 6 nm.

To explore structure-property relationships, we further functionalized the Ch-CDs through amide reactions, introducing ligands with varying electronic effects. Interestingly, contrary to expectations, electron-donating ligands did not induce a significant red shift in fluorescence. This phenomenon is likely attributed to the predominant influence of the CDs' extensive conjugated core, which governs their optical properties. Additionally, in solution, ligand mobility and non-radiative energy dissipation further constrained their impact on fluorescence. These findings highlight the limitations of fine-tuning CDs optical properties through small-molecule surface modifications and provide valuable insights for the rational design of Ch-CDs in future applications.

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Carbon nanotube and 2D material loaded double network hydrogels for photocontrolled drug release

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The high water content and biocompatibility of amino-acid-based supramolecular hydrogels have generated growing interest in drug delivery research[1,2]. Nevertheless, the existing dominant approach of constructing such hydrogels, the exploitation of a single amino acid type, typically comes with several drawbacks such as weak mechanical properties and long gelation times, hindering their applications[3]. Here, we design a near-infrared (NIR) light-responsive double network structure, containing amino acids and different synthetic or natural polymers, *i.e.,* polyacrylamide, poly(*N*-isopropylacrylamide), agarose, or low-gelling agarose[4]. The hydrogels displayed high mechanical strength and high drug-loading capacity. Adjusting the ratio of Fmoc-Tyr-OH/Fmoc-Tyr(Bzl)-OH or Fmoc-Phe-OH/Fmoc-Tyr(Bzl)-OH, we could drastically shorten the gelation time of the double network hydrogels at room and body temperatures. Moreover, introducing photothermal agents (graphene oxide, carbon nanotubes, molybdenum disulfide nanosheets, or indocyanine green), we equipped the hydrogels with NIR responsivity. We demonstrated the light-triggered release of the drug baclofen, which is used in severe spasticity treatment. Rheology and stability tests confirmed the positive impact of the polymers on the mechanical strength of the hydrogels, while maintaining good stability under physiological conditions. Overall, our study contributed a novel hydrogel formulation with high mechanical resistance, rapid gel formation, and efficient NIR-controlled drug release, offering new opportunities for biomedical applications.

Acknowledgements. *We wish to acknowledge the Centre National de la Recherche Scientifique (CNRS) and the International Center for Frontier Research in Chemistry (icFRC). The authors wish to thank Cathy Royer for TEM analyses. We gratefully acknowledge Rym Soltani, Céline Corcelle and Riccardo Pinotti for the preparation of oxidized CNTs, and Yilin He for helping with the exfoliation of MoS_2. S. Xiang is indebted to the CSC for supporting his PhD.*

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Mg^{2+}-driven selection of natural phosphatidic acids in primitive membranes

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Biological membranes are composed exclusively of phospholipids comprising glycerol-1-phosphate or glycerol-3-phosphate. By contrast, primitive membranes would have likely been composed of heterogeneous mixtures of phospholipids, including non-natural analogues comprising glycerol-2-phosphate, as delivered by prebiotic synthesis. Thus, it is not clear how the selection of natural phospholipids could have come about. Here we show how differences in supramolecular properties, but not molecular properties, could have driven the selection of natural phosphatidic acids in primitive membranes. First, we demonstrate that at the molecular level it is unlikely that any prebiotic synthesis or hydrolysis pathway would have enabled the selection of natural phosphatidic acids. Second, we report that at the supramolecular level, natural phospholipids display a greater tendency to self-assemble in more packed and rigid membranes than non-natural analogues of the same chain length. Finally, taking advantage of these differences, we highlight that Mg^{2+}, but not Na^{+}, K^{+}, Ca^{2+} or Zn^{2+}, drives the selective precipitation of non-natural phosphatidic acids from heterogeneous mixtures obtained by prebiotic synthesis, leaving membranes proportionally enriched in natural phosphatidic acids. Our findings delineate a plausible pathway by which the transition towards biological membranes could have occurred under conditions compatible with prebiotic metal-driven processes, such as non-enzymatic RNA polymerization.

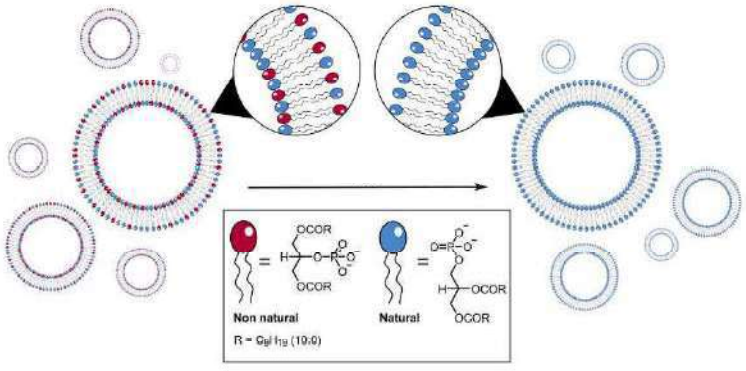

Figure 1. Schematic representation of selection and enrichment of primitive membranes with natural phospholipids

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Fluorescence detection of chlordecone in water by hemicryptophane cages

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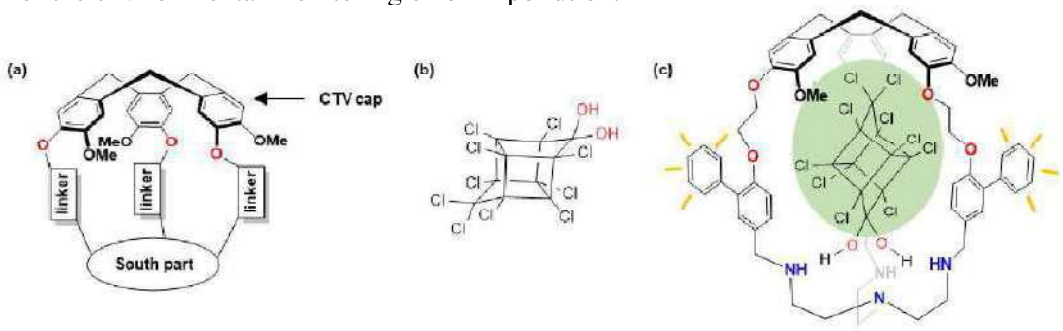
Chlordecone (CLD) is an insecticide with a perchlorinated bishomocubane structure, used in the French West Indies between 1972 and 1993 before being banned due to its toxicity and persistence in the environment[1], which today leads to massive environmental pollution and high levels of impregnation of the local population. Our group has designed supramolecular receptors based on hemicryptophanes, capable of selectively encapsulating chlordecone both in organic solvent[2] and in water for depollution purposes[3]. Our aim is to develop efficient fluorescent hemicryptophane cages, enabling rapid detection of chlordecone in water, easy to implement by French West Indian laboratories and less expensive than current systems, based on GC or HPLC analysis techniques coupled to a mass spectrometer. Hemicryptophane cages proved particularly effective for CLD detection at environmental concentrations, showing high association constants and increased fluorescence upon CLD encapsulation[4]. This paves the way for the development of an affordable high throughput detection system for the environmental monitoring of CLD pollution.



(a) General structure of hemicryptophane cages (b) Structure of chlordecone (c) Structure of developed hemicryptophane with fluorescent linkers for chlordecone encapsulation

Acknowledgements. *This project has received funding from the Préfecture de Martinique, under the auspices of Plan Chlordécone III, action remediation (2019). The authors acknowledge the French National Research Agency (ANR), the Region Guadeloupe and the Collectivité Territoriale de Martinique for their financial support of the CHLOR2NOU project n°ANR22-CHLD-0005-01. M.P.'s PhD work was funded by CEA.*

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Supramolecular self-assembly driven by both chaotropic effect and electrostatic interactions of a three-component system comprising giant polyoxometalate, cyclodextrin and cations

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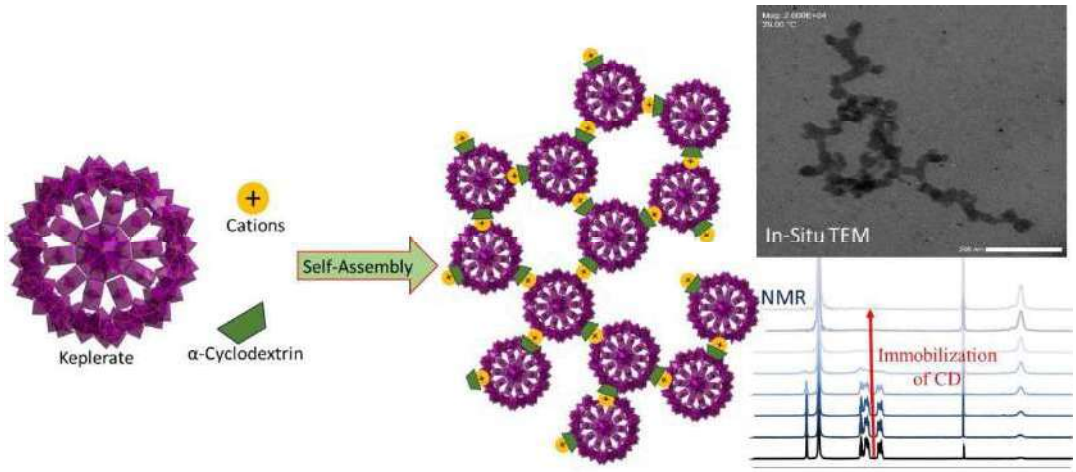
Polyoxometalates (POM) are a class of inorganic compounds well-known for their complexation ability of hydrophobic materials. These interactions are attributed to the chaotropic effect, a solvent effect driving supramolecular complexations in aqueous solutions.[1] Cyclodextrins (CD) are organic macrocycle widely studied for their inclusion/complexation properties due to their hydrophobic cavity and in this context, POM - CD systems were able to form a wide variety of supramolecular complexes.[2] So far complexation with POM mostly took place with γ-CD leading to highly stable supramolecular adducts.

In this communication, we show how the smallest α-CD exhibit striking strong interactions with the giant spheroidal POM, the so-called Keplerate type ion, abbreviated Mo_{132}.

Surprisingly, the interaction process, which can lead to large nano-aggregates appears precisely mediated by a third component, corresponding to cations such as NH_4^+, K^+, Ca^{2+}, Ba^{2+}.

This three-component supramolecular system i.e. α-CD / Mo_{132} / cation has been studied by NMR, 2D-NMR (DOSY), SAXS and in-situ TEM. Furthermore, some structural models involving POM, α-CD and Ba^{2+} will be discussed.



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New hydrogen bonding motifs for anion binding catalysis

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Inspired by nature, supramolecular catalysis exploits non-covalent interactions to accelerate chemical transformations.[1] Indeed, weak bond interactions have attracted great interest and in particular anionic bond plays an important role in the field of catalysis.[2] This type of catalysis can be accomplished using H-bonding, as well as halogen bonding, and chalcogen bonding. In each case, the binding of an anion is pivotal to promoting a chemical reaction in which ionic or ionizable substrates could be susceptible to nucleophilic attack. In this context, the aim of the present work is to study the properties and catalytic performance of 1,8-diaminocarbazole-based receptors. A family of structurally related diaminocarbazole receptors has been prepared using a convergent and high-yielding synthesis, their catalytic activity has been evaluated along with DFT calculations and binding constants toward different anions.

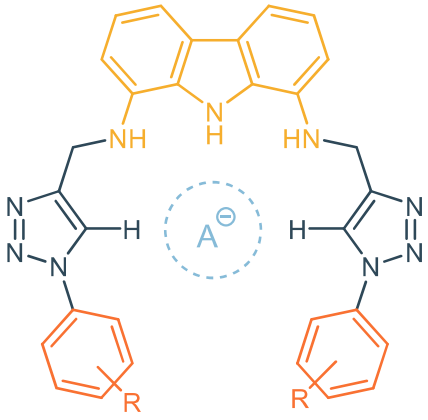

Figure caption. General structure of the receptors based on a 1,8-diaminocarbazole scaffold.

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Alkynylgold(I) C_3-Chiral Concave Complexes

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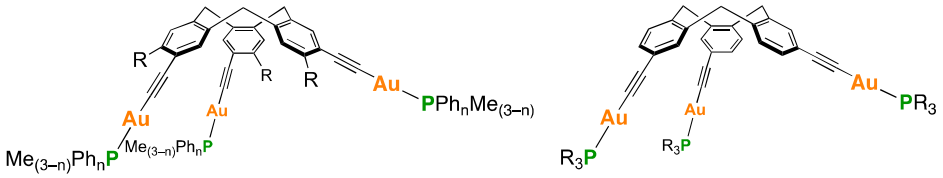
Cyclotribenzylenes (CTBs) are threefold-symmetric, concave-shaped molecules used as cryptophane precursors.[1] Two alkynyl-substituted C_3-symmetric CTBs were synthesized in racemic and enantiomerically pure forms, and eight trinuclear gold(I) acetylide complexes with phosphine auxiliary ligands (**1 - 8**) were characterized, in particular by NMR spectroscopy, electronic circular dichroism (ECD), and electrospray ionization mass spectrometry (ESI-MS).[2] Their ECD patterns depended on the substitution of the starting CTBs and were shifted bathochromically by comparison with the latter. ESI-MS in the presence of HCO_2H allowed us to detect the complexes as proton adducts. The intensities of the signals were stronger when the phosphine was more electron-rich. All the gold acetylide phosphine complexes exhibited a long-lived blue phosphorescence and a weak UV fluorescence in $CHCl_3$. In MeOH/$CHCl_3$ mixtures of > 1:1 volume ratio, **1 - 7** exhibited a new emission band at *ca* 540 nm that developed at the expense of the UV emission. DLS studies demonstrated the presence of molecular aggregates of Ø 30 - 80 nm. The green emission observed in MeOH-rich solvent mixtures was therefore induced by aggregation, and could originate from Au···Au interactions. The AIE spectrum of **8** was observed only in solutions containing 99% of MeOH, and correlated with its solid state emission. The AIE profiles of the enantiomers of **1** differed from that of *rac*-**1**, suggesting that the latter is a true racemate.[3]



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Photon Piling in Upconverting Lanthanide Clusters

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Upconversion (UC) is a photophysical phenomenon wherein multiple low-energy photons are absorbed and subsequently re-emitted as a single higher-energy photon.[1] This process typically manifests as an anti-Stokes emission, offering significant advantages due to its minimal background interference from auto-fluorescence and light scattering, thus enhancing sensitivity. UC materials generally present ladder-like energy levels that facilitate a stepwise energy ascent towards the emitting state and possess long-lived intermediate excited states, which help prevent premature decay to the ground state. Lanthanide ions, with their favorable energy level structures and long excited state lifetimes,[2] are particularly well-suited for the design of UC materials.

Although the phenomenon of UC has being known since the 1960s,[3] its observation has been predominantly confined to solid-state materials and, more recently, nanoparticles. Molecular scale UC was first reported in 2011 by Piguet's group, who demonstrated trinuclear [Er2Cr] triple helicates exhibiting UC in organic solvents at low temperatures (30 K).[4] Despite this initial breakthrough, ensuing developments in new molecular UC devices have been sparse. With a notable advancement including our group's achievement of UC at the molecular scale in water at room temperature.[5]

This project aims to develop new supramolecular heteropolynuclear lanthanide-based clusters with enhanced UC efficiencies. Our focus being mainly the design of novel ligands to form discrete molecular entities with lanthanide ions, while thoroughly characterizing the cluster assembly processes to understand their kinetic and thermodynamic parameters, and optimizing the UC properties through strategic selection of lanthanide elements and optimization of ligands.

By improving the efficiency and control of UC at the molecular scale, this research aims to create innovative tools with potential applications across various fields, including bio-labeling, microscopy, photodynamic therapy, and NIR-to-visible conversion for photovoltaic cells.

Acknowledgements: *French Agence National de la Recherche (Grant no ANR-22-CE29-0005)*

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Amino Acid-Based Cages as Bioinspired Ligands for Minimalistic models of carbonic anhydrase

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Nature gives us inspiration to develop artificial bioinspired catalysts by emulating the structural and functional complexity of natural metalloenzymes. Metalloenzymes harness the distinctive reactivity of metal centers inside meticulously structured natural proteins to perform catalysis of complex biological reactions with high efficiency and selectivity.[1] Motivated by this, bioinspired complexes merge synthetic metal complexes with designed molecular scaffolds, seeking to emulate enzymatic function while providing enhanced stability, tunability, and application in non-biological environments.[2] By creating confined environments decorated with non-covalent interactions, supramolecular systems can improve substrate identification, stabilization of reactive intermediates, and facilitation of selected transformations.

Inspired by carbonic anhydrase,[3] a metalloenzyme that effectively catalyzes CO_2 hydration using a zinc active site positioned in a hydrophobic cavity, our research merges bioinspired catalysis with supramolecular chemistry to create amino acid-based cage complexes for CO_2 valorization. These minimalist catalysts contain zinc centers within an amino acid-modified cavity, wherein hydrogen bonding, hydrophobic interactions, and steric hindrance could promote substrate activation and product release. By leveraging supramolecular control over reactivity, we aim to develop highly selective and efficient catalysts for CO_2 valorization, providing novel methods for carbon capture and usage.

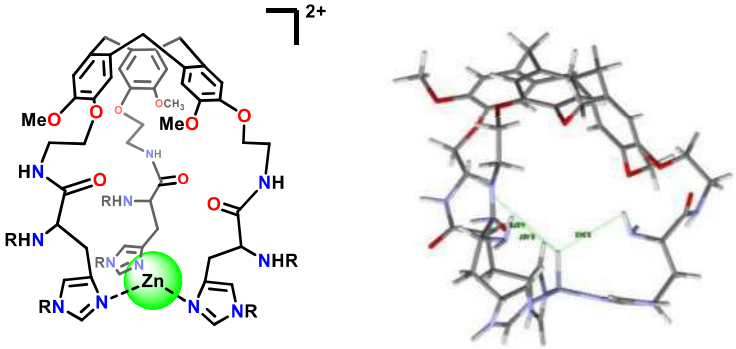

Figure: Artificial carbonic anhydrase model (Spartan 14, MMFF).

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Journées de Chimie Supramoléculaire
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Tailor-made cavitands: stitching porphyrins to calix[4]resorcinarenes

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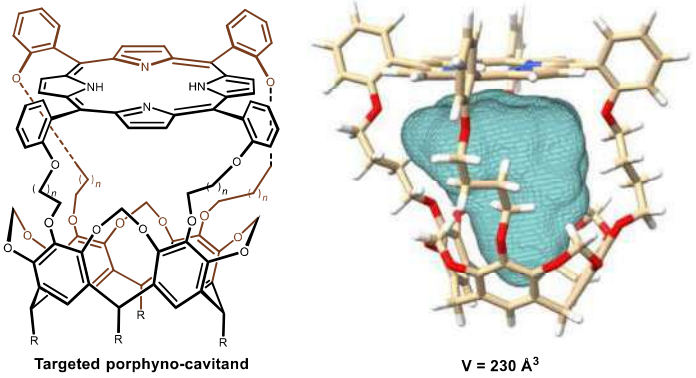
Inspired by Nature's ability to perform specific and selective reactions using enzymes, chemists have sought to confine catalytic centers in artificial pockets. One strategy aims at using covalent molecular cages. To this end, catalytic centers have been successfully confined in cyclodextrins, calixarenes, cyclophanes and many others.[1] Among them, calix[4]resorcinarene-based cavitands have been studied for decades, mainly for their host-guest properties.[2] These cages can be functionalized, creating deeper cavities suitable for confined catalysis.[2] For this project, we decided to decorate the cavitand with porphyrins which are well known for their catalytic abilities.[3] While the usual synthesis involves the poor-yielded formation of the porphyrin on a functionalized cavitand we decided to explore other pathways to get more versatility and a broad scope of confined catalysts.[4] Tuning the linker's length between the cavitand and the porphyrin will allow the tailor-made obtention of confined catalytic pockets with precise desired cavity volumes.



Structure of targeted porphyno-cavitand (left) and optimized structure of a porphyno-cavitand (n = 3, R = H) (UFF) with rendered cavity volume using the MoloVol software (right).[5]

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Synthetic Strategy for the Preparation of a Tribenzotriquinacene-Containing Small Cryptophane by Irreversible Bond Formation

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Among the different strategies used for anion binding, supramolecular enantioselective complexation of chiral anions defined as the ability of a host to selectively bind one enantiomer of a guest over the other has been the subject of intensive studies in recent years. The design and study of artificial receptors for chiral anion recognition serve two main purposes: (*i*) they contribute to understanding enantioselective anion recognition in complex biological systems, and (*ii*) they provide a powerful tool for chiral anion detection and separation based on the complexation properties of the receptor.[1] In this context, our project focuses on the multi-step synthesis and host-guest properties of a novel family of chiral receptors for chiral anion binding. These hosts are C_3-symmetric structural analogs of cryptophanes, which have been widely used as efficient container-shaped receptors for host-guest complexation studies. Cryptophanes consist of two cyclotribenzylene (CTB) units connected by three bridging chains.[2] Our distinctive approach involves replacing one CTB moiety with a tribenzotriquinacene (TBTQ) unit to facilitate the synthesis of new enantiopure covalent cages.[3] Herein, we describe the synthesis, chiral resolution, and characterization of a new artificial host (Figure 1). Strategies will be implemented to enhance their water solubility and evaluate their host-guest properties in chiral anion complexation.

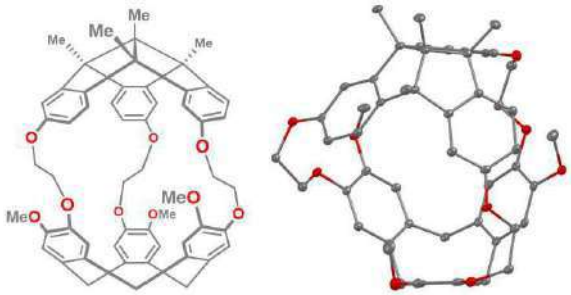

Figure 1: Molecular and X-ray structure of a new molecular cage (only one single enantiomer is shown).

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Functionalization via copper-free click chemistry: towards the design of stimuli-responsive liposomes

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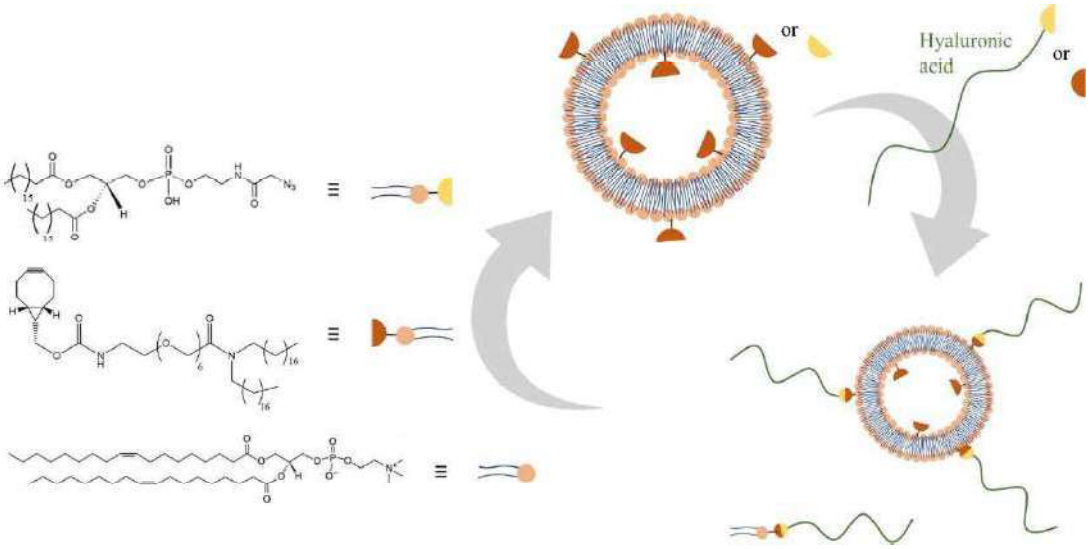
Over the last decades, liposomes have been successfully used in many biomedical applications including drug delivery, gene therapy and imaging. Their ability to encapsulate and release cargos has been extensively studied; however, some applications remain limited due to low stability and control over the release. For that, coupling liposomes with polymers brings higher colloidal stability, stimuli-responsive features, and stealth properties. Although click chemistry has previously been investigated for liposome functionalization with polymers, little is still known on the versatility of strain-promoted alkyne azide cycloaddition (SPAAC) between liposomes and polymers of different nature [1]. Here, we established a systematic study using quartz crystal balance with dissipation monitoring (QCM-D) to evaluate the click efficiency and mechanism through the use of well-defined and tunable model surfaces based on supported lipid bilayers (SLB) and self-assembled monolayers (SAM) [2]. Their functionalization via bicyclononyne (BCN) or azide and subsequent click reaction was studied using hyaluronic acid (HA) and thermo-responsive N-isopropylacrylamide (NIPAM) polymers.



Liposome functionalization via copper-free SPAAC.

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Programmable Construction of Supramolecular Polymers

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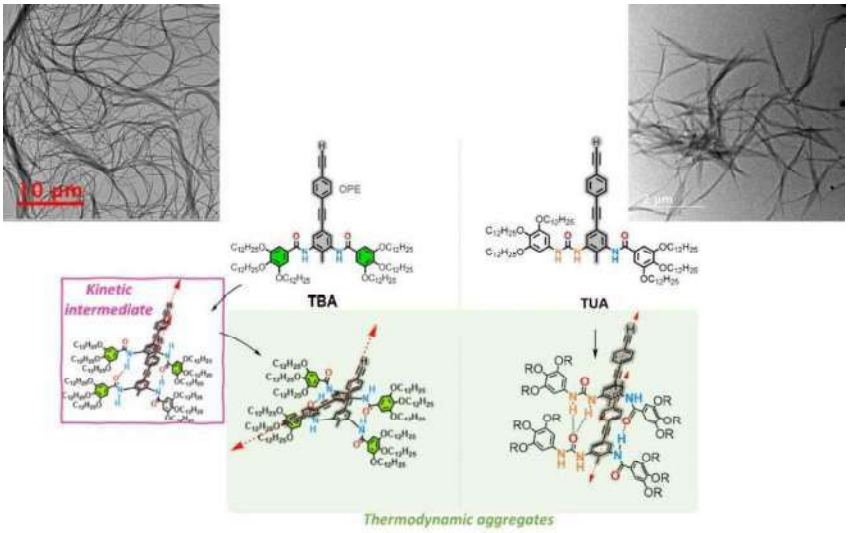
Supramolecular polymers (SP) have become ubiquitous objects as they play central roles in living organisms and have found many applications in artificial systems.[1] SP are defined as 1D materials resulting from the self-assembly of small molecules, the monomers, through a combination of weak non-covalent interactions such as, Hydrogen bonding, Halogen bonding, dispersive interactions etc… Originally thought to be under thermodynamic control, recent discoveries in the field highlighted the possibility to grow aggregates with shape and size differing from the thermodynamic state.[2] In this presentation, I will depict our recent efforts[3] to create and stabilize such kinetic aggregate using the Toluene Bis-Amide (TBA) monomers. I will also show how minute changes of the monomeric scaffold (Toluene Urea – Amide, TUA) dramatically impact the supramolecular polymerization event and how spectroscopy can be helpful to decipher supramolecular packings.[4]



Structures of the two monomers **TBA** and **TUA** and their respective supramolecular aggregation.

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Development of tetrazine-based supramolecular polymers exhibiting donor-acceptor-type interactions

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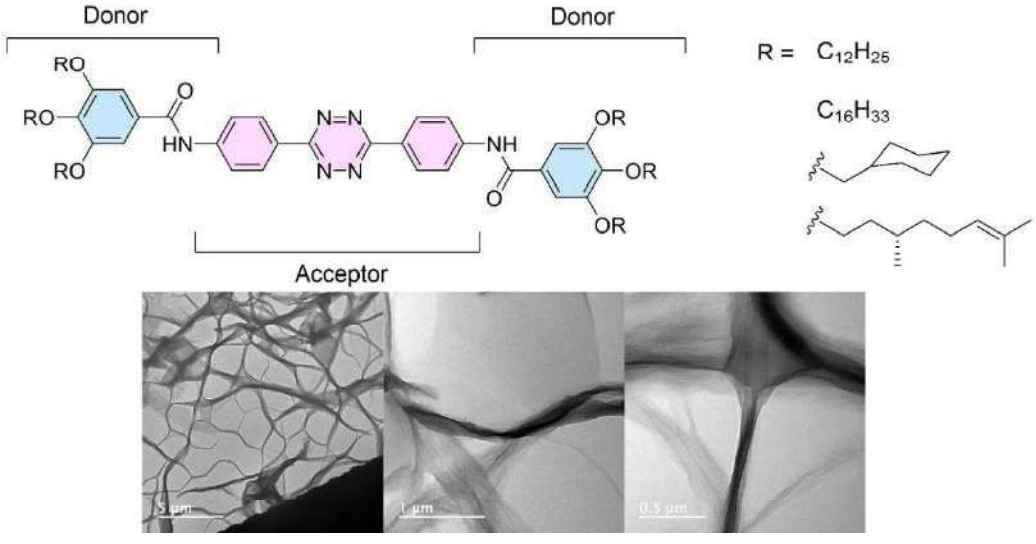
Supramolecular polymers can be defined as polymers based on monomeric units held together by highly directional and reversible secondary interactions, resulting in dynamic species that combine the characteristics of conventional macromolecules with the novel properties deriving from noncovalent interactions (e.g., self-healing functions, responsiveness towards external stimuli).[1] Initially, supramolecular polymerization was regarded as a process entirely driven by thermodynamics. Progressively, numerous cases have been reported where kinetic contributions play a significant role in the outcome of the aggregation, and multiple pathways can be in competition for the monomer. The modulation of experimental conditions (e.g., temperature or solvent modulation) can influence the self-assembly.[2] Among these, donor-acceptor interactions have also emerged as impactful factors on the polymerization.[3]

In this work, the development of a new family of supramolecular polymers is presented, featuring a central tetrazine core and different aliphatic side chains, resulting in donor-acceptor-donor structures. The aim of the project is to establish structure-property relationships among the aggregates, and, in the future, to employ these species for the development of n-type organic semiconductor materials thanks to the electron properties (e.g., available reduction potentials, electron deficiency) exhibited by tetrazine.[4]



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Supramolecular polymerization through rotation of light-driven molecular motors

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Light-activated molecular motors can have a mechanical action on their environment thanks to their ability to convert light energy into unidirectional rotation. Such molecules have been successfully integrated into soft materials to amplify the work produced at long range.[1] While Langmuir monolayers have already been prepared using photoswitchable compounds, no example has been described with molecular motors until now.[2,3] Such a study would be critical to reveal the effect of rotation on the assembling properties in a constrained environment. Here, we show that amphiphilic molecular motors can self-assemble into compressible monolayers at the air-water interface.[4] Under UV activation, the surface pressure-area isotherm is shifted towards smaller molecular areas, which was attributed to a rotation-induced supramolecular polymerization process. Effects of various parameters on the obtained monolayers were explored after being transferred onto solid substrates and characterized using cutting-edge techniques (AFM, CD, X-Ray Reflectivity, GIXD). The mechanism behind their formation was investigated and compared to a theoretical model. To our knowledge, this is the first example of supramolecular polymerization of molecular motors triggered by motion-induced processes.

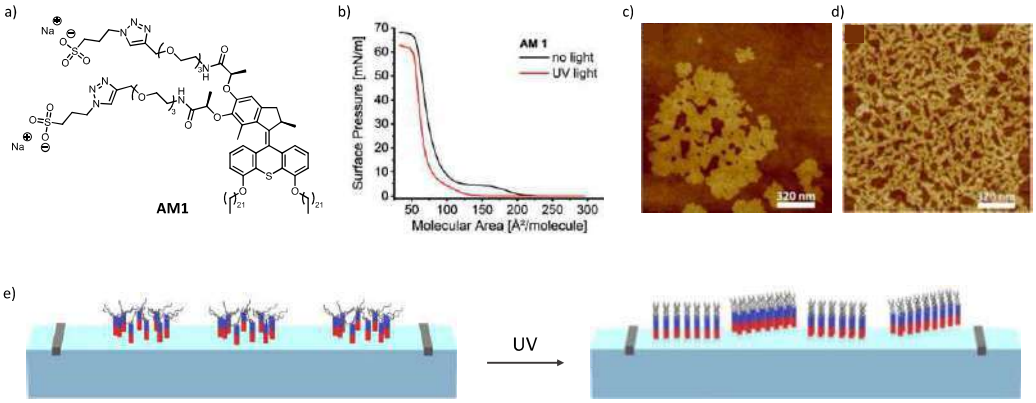

Figure 1: a) Structure of the amphiphilic motor **AM1**, b) Langmuir isotherms of **AM1** in the dark (black) and under UV light (red), c) AFM image of the monolayer obtained in the dark at 2 mN/m, d) AFM image of the monolayer obtained under UV at 2 mN/m, and e) schematic representation of **AM1** at the air/water interface

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Chiral luminescent Cu(I) complexes as metalloligands and their self-assembly into chiral luminescent architectures

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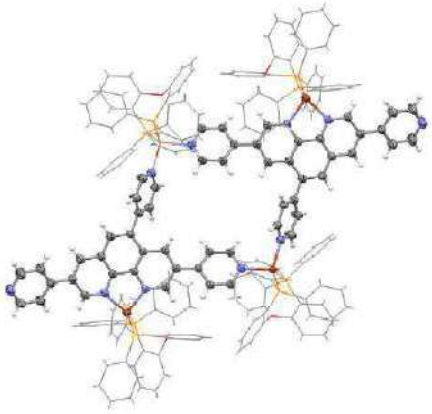
For over 30 years, self-assembled metal-organic cages (MOCs), have sparked the interest of chemists to utilize their host-guest properties for the encapsulation of small molecules as well as the enhancement of catalytic properties by preorientation of the substrates in the cage.[1,2,3] Recent developments have shown the potential of chiral MOCs in enantioselective catalysis, or the enhancement of photoluminescent properties by cooperative effects.[4,5,6] However, these materials employ high cost and low abundant metals such as ruthenium, europium or iridium which limits their expandability for large-scale use. Therefore, we are currently working on new luminescent copper(I) complexes for their use as photoactive metalloligands and their self-assembly into homometallic luminescent cages. We aim to amplify the luminescent properties through rigidification of the system and diminishing non-radiative decay. In parallel, we are developing new chiral Cu(I) complexes that show circularly polarized luminescence. These complexes will serve as precursors to form self-assembled chiral luminescent copper-based cages with enhanced chiroptical properties through cooperative effects. Herein, we will detail the synthesis of new phenanthroline ligands and their self-assembly in the presence of Cu(I) and diphosphine ligands.



X-ray structure of copper-based self-assembled structure

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Switchable porphyrin cages: allosteric encapsulation of guests and controlled motion in [2]rotaxanes

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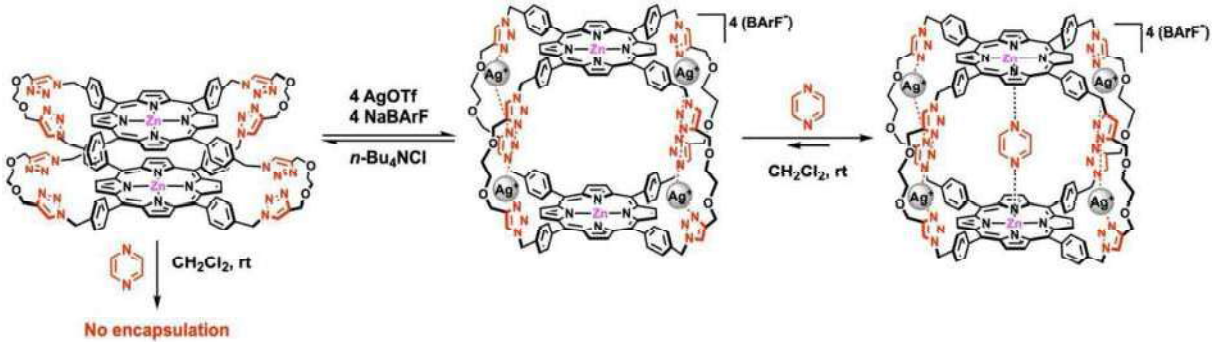
Molecular cages are hollow structures with a well-defined three-dimensional cavity that can encapsulate guest molecules or perform reactions in their cavity.[1] Metalloporphyrins are attractive constituents of cages thanks to their various properties and catalytic activities.[2]

Flexible covalent cages, endowed with two zinc(II) porphyrins and eight peripheral 1,2,3-triazolyl ligands were prepared.[3] Coordination of four silver(I) ions to the peripheral ligands switched the cage from a flattened to an open and locked conformation, allowing the allosteric control of encapsulation of neutral guest molecules, such as pyrazine (Figure).[4]

The receptor properties of our covalent cages can be leveraged for the assembly of [2]semirotaxanes[4b] and allosteric-driven motion in [2]rotaxanes, since such control of the threading step or macrocycle translation by effector binding to additional sites has rarely been reported.[5]



Acknowledgements.

Financial support from the ANR (project "Switchables cages" ANR 14-CE06-0010), The Ministry of Education and Research, LabEx-CSC and the GDR MAPYRO (macrocycles pyrroliques) are gratefully acknowledged.

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Self-complementary Dimers Based on Zwitterionic Halogen Bond Donors

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In the last years, halogen bonding (XB) has gained a lot of attention as an interesting alternative to hydrogen bonding (HB) in supramolecular chemistry. This non-covalent interaction was routinely used in the fields of organocatalysis[1], molecular recognition[2] and crystal engineering.[3] In contrast, multipoint interactions based on XBs are still quite rare – in particular self-complementary systems which are containing both XB donating and accepting moieties.[4] We aimed to synthesize zwitterionic compounds with a cyclic five-membered diaryliodonium (iodolium) core acting as Lewis acid (LA) and sulfonate or carboxylate groups acting as Lewis base (LB), that are expected to form dimers according to density functional theory (DFT) calculations (Figure 1a). Zwitterion **1** with a carboxylate group as LB showed very poor solubility which was assumed to be caused by too strong coordination (Figure 1a). So, further experiments were performed especially with zwitterionic compounds with a less basic sulfonate group as LB.[5] Modifications in the backbone lead to the first zwitterionic homodimer based on halogen bonding (**2**, Figure 1a). This zwitterion forms strongly bound dimers with XB distances of 2.73 Å in solid state (Figure 1b).[5b] This kind of building blocks can form the basis of future halogen-bonding-based linkers.

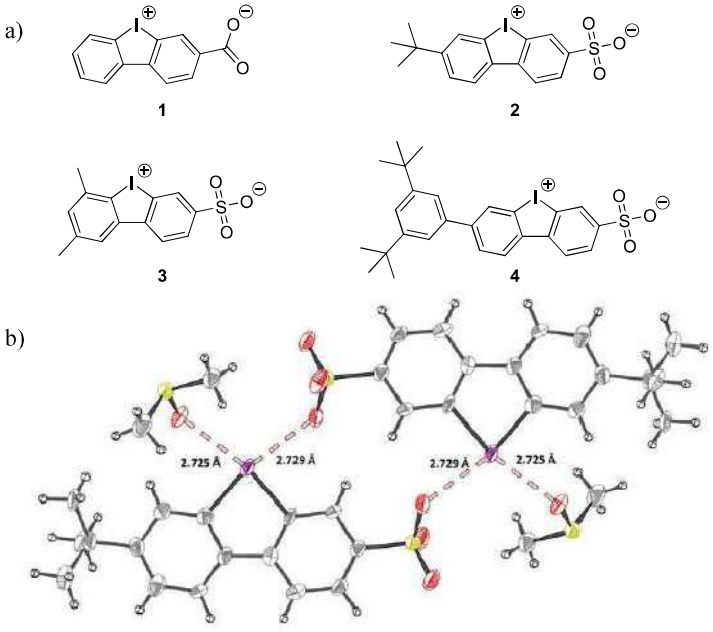

Figure 1: a) Different zwitterionic compounds that were synthesized and investigated during the study.[5] b) crystal structure of the dimer of iodolium **2**.[5b]

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Expending the Viridium Radical Family

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The acridinium core is known for its physico-chemical properties since it was exploited in photochemical reactions as photocatalyst.[1] However, its intrinsic photochemistry is less encountered. When functionalized with a 2-pyridyl moiety at their 9- position, an atypical intramolecular photocyclo-dehydrogenation reaction occurs under mild, clean, and efficient light-mediated conditions to afford a thermodynamically stable viridium radical.[2] This radical cation exhibits uncommon amphoteric redox and π-dimerization properties.

In the present work, the extension of the family of viridium cores is targeted in order to afford new building blocks in supramolecular chemistry. Therefore, the chemical space of the reaction (9- and N- positions) was explored by modification of the 9-(2-pyridyl) motif and N-substituents in order to reach new optical and redox properties.

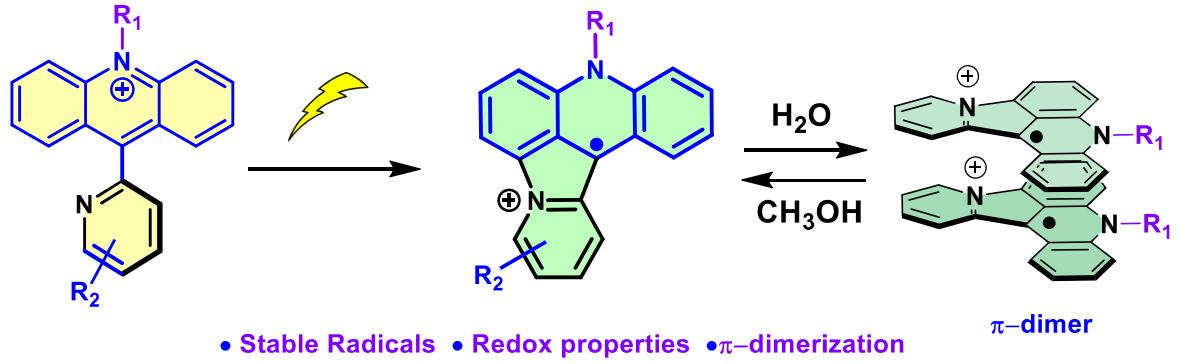

Figure 1. Photochemical reaction leading to stable viridium radicals and their π-dimerization equilibrium

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Synthesis and Study of π-Expanded Dibenzo[*a*,*e*]pentalenes Doped with Heteroatoms

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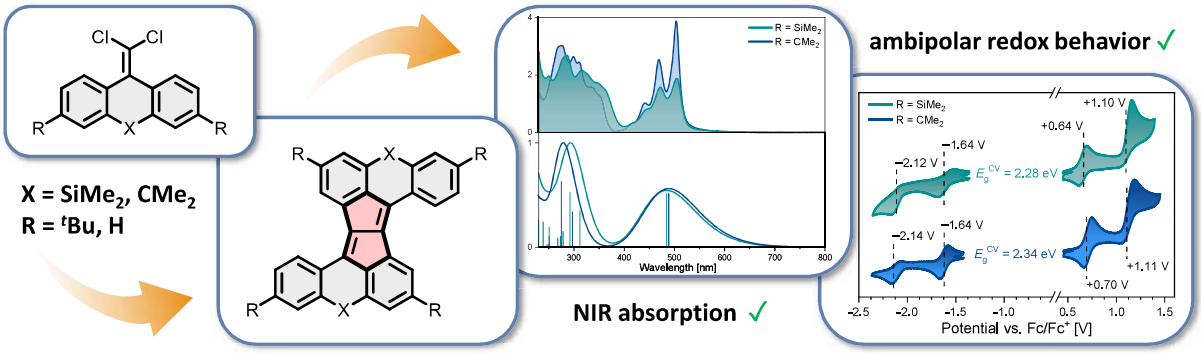
Pentalene, an antiaromatic 8π electron system, which consists of two fused, unsaturated five-membered rings is a highly unstable compound and readily dimerizes if not substituted with bulky, sterically demanding or kinetically stabilizing groups.[1] Further stabilization of parent pentalene compounds is achieved by π-annulation of aromatic benzene units, for example in dibenzo[*a*,*e*]pentalene.[2] Pentalene structures exhibit ambipolar redox character resulting in a 6- or 10π aromatic system upon chemical oxidation or reduction, respectively, which make them particularly interesting candidates for the application as organic semiconductors.[3]

Herein, we present the synthesis of a silicon-bridged dibenzo[*a*,*e*]pentalene from the corresponding *gem*-dihaloolefin.[4] Starting from the respective carbonyl-functionalized precursor, a Corey-Fuchs-Ramirez olefination was carried out towards the desired *gem*-dihaloolefin. In a palladium-mediated reaction, the desired silicon-bridged pentalene was obtained in one step. Using a similar approach, a dimethylmethylene-bridged congener was obtained as well. The obtained pentalene compounds exhibit a high stability and solubility in common organic solvents, as well as a strong absorption in the near-infrared (NIR) region. Both compounds show ambipolar redox behavior with two reversible oxidation- and reduction steps. The anionic species obtained by reduction with alkali metals were isolated and characterized by X-ray crystallography.



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Fluorescent Artificial Receptor for Dopamine based on Molecular Recognition-driven Dynamic Covalent Chemistry in a Lipid Nanoreactor

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Biologically inspired receptors may yield next generation of biosensors for fundamental research and medical diagnostics. In our work, we aim to develop a universal biosensing system for detection of the important neurotransmitter dopamine using fluorescence spectroscopy. Inspired by previous results in the lab,[1,2] we propose to combine molecular recognition and signal transmission (dye) components inside a nanoreactor - lipid nanodroplets, which already found multiple applications in the fields of bioimaging and nanomedicine.[3] In our nanosensor, we designed and synthesized a fluorescent dye bearing an aldehyde moiety, which can change its emission color on the formation of a dynamic covalent bond with dopamine. The dye was loaded into a lipid core of the droplets together with a recognition ligand specific for the dopamine side group. We found that specific recognition of dopamine by the ligand inside the lipid nanoreactor triggered the formation of an imine bond with the dyes, leading to a fluorescence response to dopamine.[4] This enabled neurotransmitter detection in the micromolar range as well as single-particle receptor imaging for visualization of dopamine concentration gradients. Selectivity of the system to dopamine was demonstrated in the mixture of competing biogenic primary amines and in the presence of complex biological media – blood serum, plasma, urine and cell lysate. Thus, we propose a concept of fluorescent supramolecular biosensors that combines specific molecular recognition with dynamic covalent chemistry inside lipid nanodroplets.

Acknowledgements. *USIAS (University of Strasbourg Institute for Advanced Study), the Fondation Jean-Marie Lehn, the Interdisciplinary Thematic Institute SysChem, the CSC Graduate School, as well as Agence Nationale de la Recherche (ANR) are acknowledged for financial support.*

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Synthesis of a Metallacage Through Self-Assembly of a Poly-NHC Perylenebisimide Based Ligand

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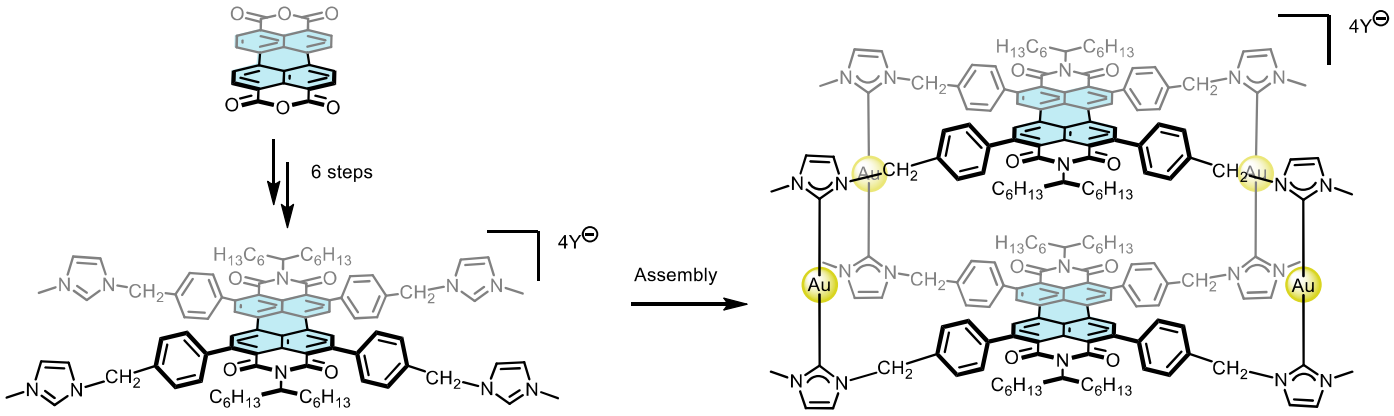
Organometallic metallacages (OMCs) based on N-Heterocyclic carbene ligands (NHC) possess strong metal-carbon bonds enabling chemical and thermal stability. However, the confined nanospaces offered by the exsisting NHC-based OMCs neither allow relevant molecular recognition nor catalytic activity.[1] To tackle this bottleneck, our group aims at the synthesis of a unique family of NHC-self-assembled OMCs featuring electrodefficient perylenebisimide (PBI) allowing for larger confined nanospaces. To increase the shape complementarity during the recognition process with electron rich aromatics, the PBI must be regioselectively functionalized on the ortho position to prevent any core distortion. This functionalization was achieved through borylation[2] which allows for a subsequent Suzuki cross-coupling with an imidazole bearing linker. A final alkylation permitted the synthesis of the desired tetra-imidazolium ligand that was engage in a narcissistic self-assembly reaction in an attempt to form the desired OMC.



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Chalcogen bonding interactions of telluronium salts and crown ethers

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Chalcogen bonding (ChB) results from an attractive interaction between electropositive regions of a chalcogen atom, known as sigma holes, with a donor of electron density (e. g., Lewis bases)[1]. Geometrically speaking, these sigma holes are located at the opposite end of the Ch-R sigma bonds, allowing for highly directional interactions (Figure 1, A). The study of ChBs has revealed several potential applications in various fields such as noncovalent catalysis[2], crystal engineering[3] and analytical chemistry[4]. As previously described by our groups, trivalent telluronium cations bearing electron-withdrawing substituents exhibit an enhanced capacity to form three ChBs with various Lewis bases, such as phosphine oxides.[5] In order to extend our studies to polydentate ligands with telluronium cations, we focused on their interactions with crown ethers, potentially capable of simultaneously occupying several sigma holes. Therefore, we explored the formation of telluronium-crown ether adducts both in solution and in the solid state. In this study, the crystallization of 1:1 adducts between a tri-aryl telluronium salt $TeAr_3^+ * BArF_{24}^-$ (Figure 1B, red) and a series of 5 crown ethers of variable size and structure was performed. A crystallographic study of such structures was coupled with a thermodynamic characterization of the interactions in solution by isothermal titration calorimetry (ITC).

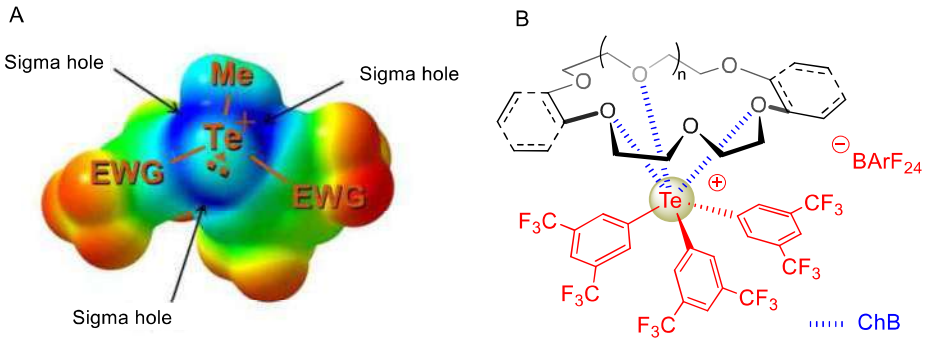

Figure 1: Electrostatic potential isosurfaces in a telluronium cation and the corresponding sigma holes (A). Representation of a chalcogen bond (ChB) interaction between the $TeAr_3^+$ telluronium and a crown ether (B).

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Controlling crystallization inside lipid-Membranized complex coacervates

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Crystallization is a crucial process in many chemical and biochemical applications, such as the determination of the three-dimensional structure of proteins or self-assembled supramolecular structures[1]. However, this process is not always simple to optimize to get crystals that are large and pure enough for X-Ray diffraction. In this context, we propose a new method of controlling crystallization inside lipid-coated complex coacervates. Membrane-coated coacervates have only recently been described, mainly as protocells or models of membraneless organelles[2,3]. Their properties are especially interesting, as they combine the ability of coacervates to compartmentalize solutes with the colloidal stability and semi-permeability of lipid bilayer membranes. This combination allows for a chemical system that is stable yet responsive to external stimuli (pH, temperature, osmotic pressure and salt concentration)[4]. Here, we plan to use these structures as new platforms to control crystallization processes. The proposed mechanism will take place as summarized in Figure 1: First, the chosen solute will be concentrated using the ability of coacervates to solubilize substrates at high concentration. Next, the lipid membrane will be added to the system, blocking the solute from diffusing out of the coacervate. Finally, the salt concentration of the system will be increased, destabilizing the coacervate phase and decreasing the solubility of the solute. This will led to a supersaturated solution inside the membrane, which will be prone to crystallization.

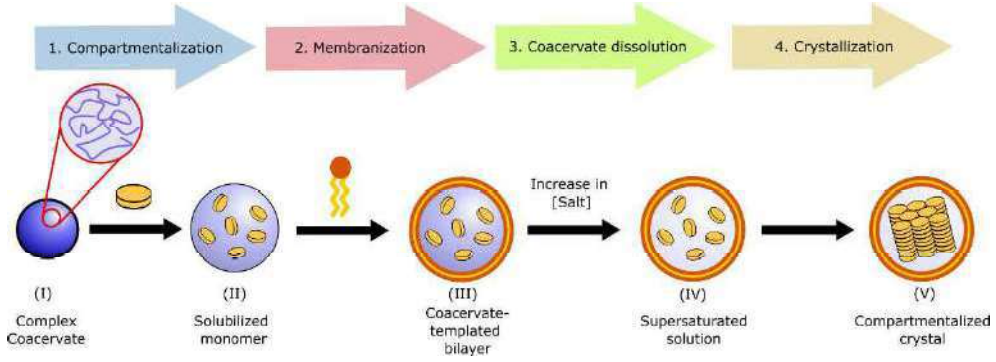

Figure 1: Schematic representation of crystallization mechanism inside a lipid-membrane coacervate.

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Understanding the Splitting Mechanism of Coacervates Under an Electric Field

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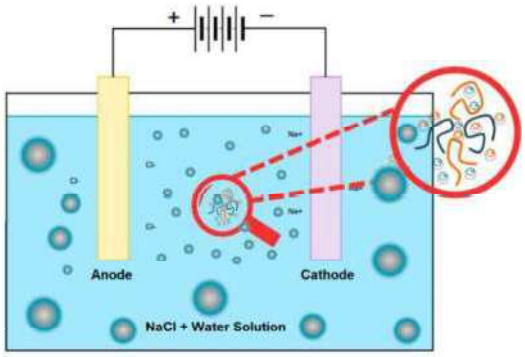
Complex coacervates are droplets spontaneously formed via liquid-liquid phase-separation when oppositely charged polyelectrolytes interact in water.[1] These droplets, rich in polymers yet immiscible with their surrounding aqueous environment, enable membranelles compartmentalization.[2] Their unique properties make them ideal for applications such as drug delivery and protocell models.[3] However, the applications of coacervate emulsions / droplets are limited by their fast coalescence, due to low surface tension.[4] Recently, we have discovered that coacervates can split in weak electric fields, leading to coacervate emulsions that are stable against coalescence. However, the mechanism of this splitting remains undetermined.

In this project, we systematically study different factors that influence the splitting: such as the ionic strength of the system, the chemical nature and molecular weight of the polyelectrolytes, and the strength of the electric field. By studying the effect of such parameters in the splitting, we can uncover new mechanistic information about this new behavior, as well as predicting and controlling it. This allows for novel approaches towards spatial control over coacervate materials. Moreover, understanding the mechanisms of coacervate splitting leads to better understanding of such complex systems.



Scheme 1: Splitting of the coacervates in the electric field between two electrodes.

Acknowledgements. *Thanks to the CSC Graduate School funded by the French National Research Agency (CSC-IGSANR-17-EURE-0016) for a Master fellowship.*

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Optical probes for the measurement of viscosity in complex coacervates

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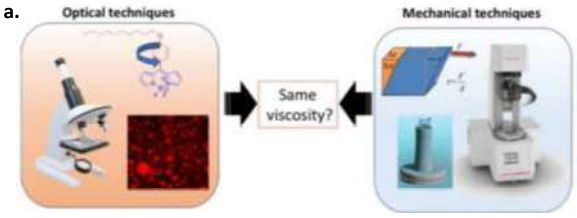
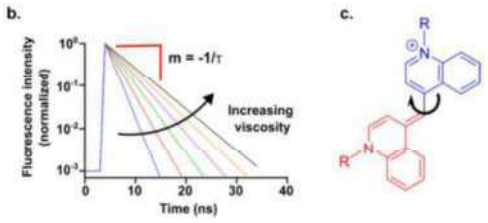
Biomolecular condensates are micrometer-sized droplets formed in the cytosol through liquid-liquid phase separation (LLPS), driven by interactions between biomolecules. Their viscosity plays a crucial role in cellular functions, but their small size makes standard mechanical characterization challenging.[1] Fluorescent probes, such as molecular rotors, offer a promising alternative for measuring viscosity at the microscale. These rotors release energy either through fluorescence or non-radiative rotation, with fluorescence becoming dominant in viscous environments where rotation is hindered.[2] Using Fluorescence Lifetime Imaging Microscopy (FLIM), we can measure fluorescence lifetime to estimate viscosity within complex coacervates, which serve as model systems for biomolecular condensates.[3] To validate this approach, viscosity measurements obtained via FLIM will be compared to bulk rheology data. In our work, we have already explored the affinity of different rotors with various coacervates, measured their fluorescence lifetimes, and studied the effects of salt concentration and type on coacervate properties. By correlating optical and rheological methods, we aim to establish fluorescence-based techniques as reliable tools for studying the mechanical properties of condensates in biological contexts.



Objective of this study



Molecular rotor representation

Acknowledgements. *We acknowledge the Imaging Center PIQ-QuESt (https://piq.unistra.fr/), member of the national infrastructure France-BioImaging supported by the French National Research Agency (ANR-24-INBS-0005 FBI BIOGEN). The authors acknowledge Ludovic Richert for the assistance with FLIM measurements.*

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Selective release and rewriting of information stored in biohybrid digital supramolecules by toehold-mediated strand displacement reactions

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Manipulation of data stored in macromolecules is a compelling yet complex challenge. While data storage on DNA and digital synthetic polymers has been well demonstrated,[1] efficient strategies for dynamic information processing remain underexplored.[2] Recently we have shown that toehold-mediated strand displacement (TMSD) can be used as a tool to process information in synthetic digital polymers.[3] This was possible due to conjugation of sequence-defined synthetic poly(phosphodiester)s (PPDEs), used to store information through a binary code (0 and 1), to single-stranded DNA domains, which facilitated the exchange of synthetic strands. In this study, we extend this concept by designing a supramolecular system that enables targeted strand displacement reactions within larger biohybrid assemblies. Monodisperse DNA-polymer bioconjugates were first synthesized through automated phosphoramidite chemistry and characterized. Afterwards, these precursors were used to prepare a linear supramacromolecule via programmed DNA self-assembly. The resulting biohybrid suprastructure contained two accessible toeholds, enabling to manipulate information selectively via TMSD. As it was verified by polyacrylamide gel electrophoresis (PAGE), by introducing one or two selected input strands we achieved either to release or to rewrite information stored in the digitally encoded synthetic segments (Figure 1). The described methodology provides a framework to develop more complex information-containing biohybrid architectures capable of multiple, programmable editing processes.

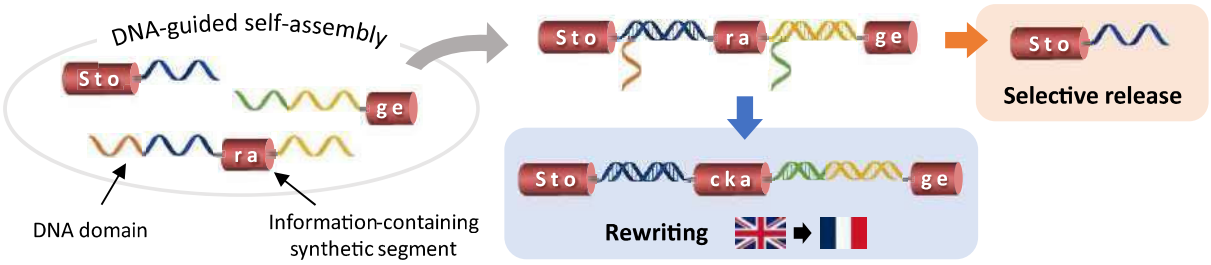

Figure 1. Concept studied herein for selective release and rewriting of digital assemblies.

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

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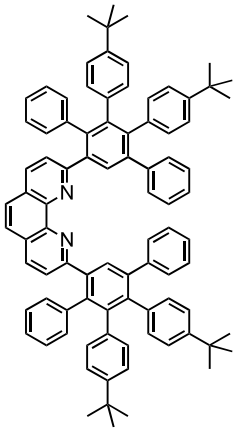
The coordination of diimine aromatic ligands with copper(I) has been widely used for the construction of fascinating metallo-supramolecular nanostructures. Classical examples include helicates, cages and molecular grids. In these particular cases, the kinetic instability of the copper(I) complexes leading 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 and rotaxanes from this particular ligand will be presented.



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Mechanochemical Synthesis of Pillar[5]arene-based [*c*2]Daisy Chain Rotaxanes

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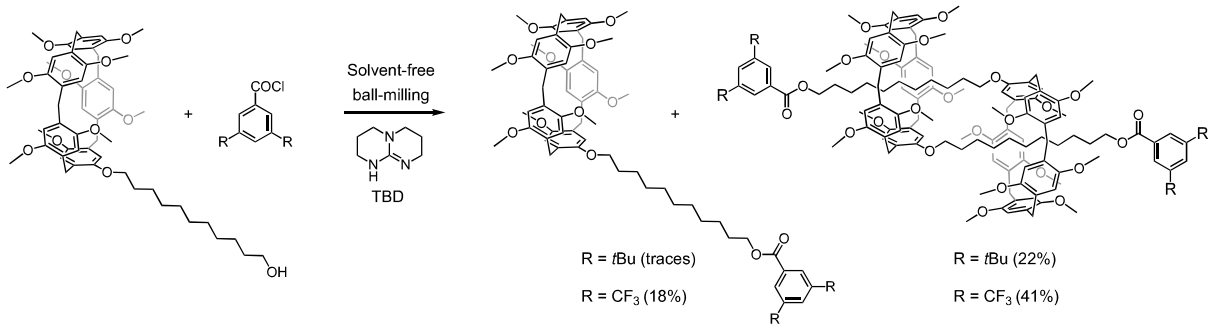
Unlike traditional chemical methods, which often rely on solvents and high temperatures, solid-state mechanochemistry is using mechanical energy to drive chemical reactions. The most common mechanochemical techniques include manual grinding with a mortar and a pestle, and ball milling using a shaker or a planetary mill. Mechanochemical solvent-free synthesis, which minimizes the need for hazardous solvents, is gaining more and more attention and a wide range of organic and inorganic reactions can be carried out under such conditions. While applications in the field of supramolecular chemistry are by far less common, solvent-free conditions have been found well-suited for the preparation of rotaxanes.[1] As part of this research, we have recently used mechanochemical conditions for the introduction of stoppers onto pillar[5]arene-based [*c*2]daisy chain derivatives.[2] Specifically, the solvent-free mechanochemical acylation of a pillar[5]arene-based daisy chain monomer bearing an alcohol function has been investigated (Scheme 1). This chemical transformation has been also carried out in solution for comparison purposes. Interestingly, stoppered [*c*2]daisy chain derivatives could be only obtained from the alcohol monomer under mechanochemical conditions. Indeed, the daisy chain monomer aggregates poorly in solution and acylation reactions performed in $CHCl_3$ only provided the corresponding acylated monomer. In this particular case, concentration effects are clearly beneficial when the reactions are performed under solvent-free conditions as daisy chain assemblies are effectively present in the solid state despite the very weak affinity of the alcohol alkyl chain for the pillar[5]arene.



Scheme 1. Acylation of a daisy chain monomer bearing an alcohol function under solvent-free mechanochemical conditions.

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pH-Controlled gliding motions in pillar[5]arene-containing molecular shuttles

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Pillar[5]arene-based molecular shuttles incorporating an axle component with two stations, namely a $-(CH_2)_{10}-$ chain and a protonable triazole subunit, have been prepared.[1] Detailed spectroscopic investigations supported by DFT calculations revealed that gliding motions of the pillar[5]arene occur over the full length of the molecular axle in the protonated state while such molecular motions are limited over the decyl station in the neutral state (Figure 1). On the other hand, electrochemical investigations revealed that the oxidation of the pillar[5]arene moiety of the protonated rotaxane also triggers conformational changes and the oxidized macrocycle is only located over the decyl station.

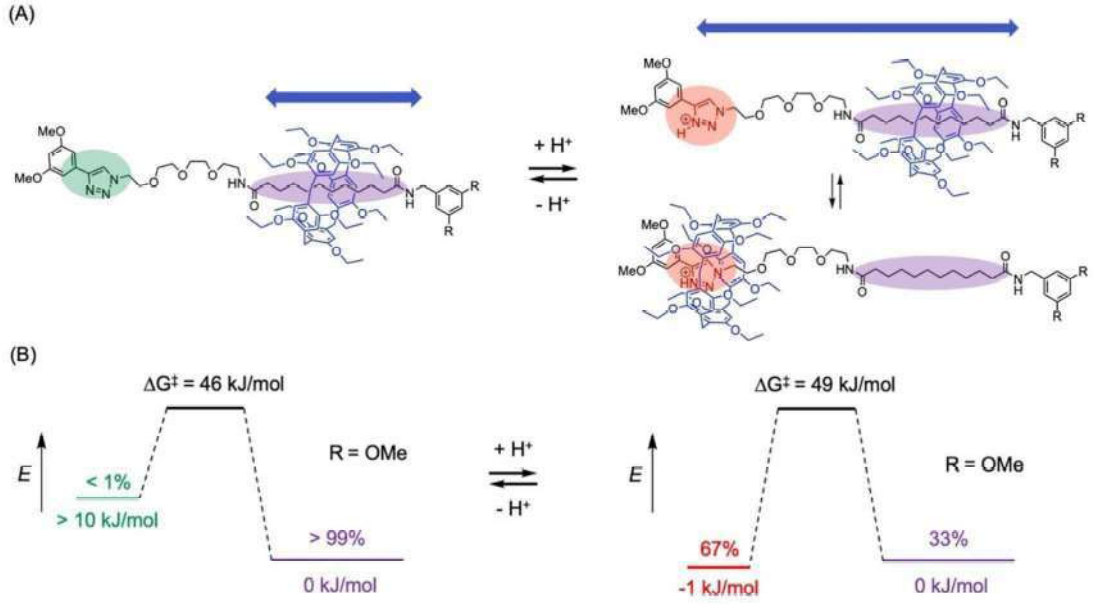

Figure 1. (A) As indicated by the blue arrows, gliding motions of the pillar[5]arene moiety occur over the full length of the molecular axle in the protonated state while such molecular motions are limited over the decyl station in the neutral state. (B) Potential energy diagrams in both the neutral and the protonated states deduced from variable temperature ^{1}H NMR studies.

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Analysis of kinetic asymmetry in a multi-cycle reaction network establishes the principles for autonomous compartmentalized molecular ratchets

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Non-equilibrium systems form the foundation of life and offer exciting prospects for developing systems with enhanced functionalities. Kinetic asymmetry[1–3] serves as a crucial parameter describing how chemical reaction networks evolve under non-equilibrium conditions, playing a fundamental role in molecular machines[3], self-assembling structures[4], and energy transduction processes.[2]

However, the evaluation of kinetic asymmetry is so far limited to networks that comprise a single reaction cycle.

In this communication, we present the expression of kinetic asymmetry in multi-cycle networks. We apply it to gain insights on a recently reported experimental system characterized by compartmentalization and kept away from equilibrium electrochemically.[5] Insightful information about directionality is predicted by investigating key parameters such as state stabilities, diffusion coefficients, and redox potentials. Additional insights are offered by kinetic simulations, which are used to explore kinetic effects induced by diffusion asymmetry.

Our findings demonstrate that compartmentalization can induce non-equilibrium behaviors that were previously thought to be exclusive to light-driven systems.[6] Furthermore, our approach provides a versatile framework for assessing kinetic asymmetry in multi-cycle networks. Indeed, we validated our methodology analyzing a light-driven rotaxane incorporating two optically active azobenzene moieties.[7]

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Synthesis and electrochemical characterization of multifunctional viologen threads

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High-energy supramolecular interlocked structures have attracted considerable attention in recent decades, and they might offer unconventional strategies to harvest energy from various external sources (e.g., chemical, redox, or light inputs)[1]. Fine-tuning the kinetic of a system is crucial and plays an important role in developing out-of-equilibrium systems. To this aim, pseudorotaxanes are ideal platforms because simple structural modifications can drastically modify the kinetics of their threading/dethreading processes.
Inspired by the seminal work of the Stoddart group[1,2], we investigated kinetically trapped states upon alternating redox stimuli in systems composed of a macrocyclic cyclobis(paraquat-*p*-phenylene) host and paraquat derivative guests. In particular, we used click chemistry to prepare multifunctional structures comprising either multiple guests or multiple hosts[3]. The combination of spectroelectrochemistry, differential pulse voltammetry, and tailored cyclic voltammetry analysis, revealed peculiar effects of the different systems.
Our study contributes to the development of redox-driven non-equilibrium systems.

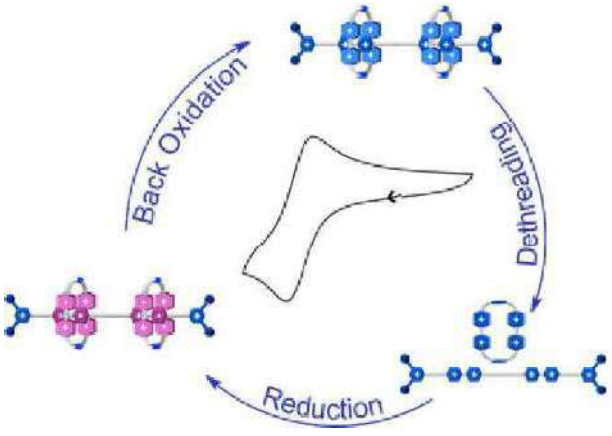

Figure 1: Schematic representation of an electrochemical reduction/oxidation cycle coupled with an assembly/disassembly of the host and guest molecules.

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Catalysis-driven active transport of small molecules across liquid membranes

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Transport across membrane is fundamental to life.[1] Among different types of transport, primary active transport is especially compelling, as living organisms transduce chemical energy into transmembrane molecular gradients.[2] For the realization of active transport, nature employs information ratchet mechanisms. These mechanisms are based on kinetic asymmetry in a fuel-to-waste reaction that results in catalysis-driven active transport.[3,4]

Here we report an artificial system capable of primary active transport driven by catalysis. We investigated the carbodiimide (fuel) promoted cyclization of maleic acid.[5] The experimental setup employed was based on a U-shaped reaction tube in which an organic solvent phase on the curved bottom acted as a liquid membrane, separating two aqueous layers. Maleic acid catalyzes the hydration of the carbodiimide fuelwhile converting into the more hydrophobic maleic anhydride. The latter enters the organic membrane but can be hydrolyzed when in contact with the aqueous phase. Kinetic asymmetry lies in the transient formation of anhydride and was established by differentiating the rates of activation and/or hydrolysis with pH or catalysts, even when equal amounts of fuel were added to both compartments.[6]

The energy transduction achieved by the catalysis-driven active transport was quantified by characterizing the non-equilibrium system through complete kinetic analysis. Feedback mechanisms were also established within this system. The final accumulation of acid in one compartment shows that chemical energy from carbodiimide hydration has been transduced and stored as energy in a chemical gradient across a macroscopic liquid membrane. The adaptation of ratchet mechanisms to macroscopic transport proved in this project provided new strategy for bioinspired nanotechnologies, reinforcing the idea that ratchet mechanisms can be used to power a variety of endergonic processes, well beyond molecular-level motion.[7]

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Azobenzene Isomerism and Kinetic Asymmetry in Chemical Reaction Network

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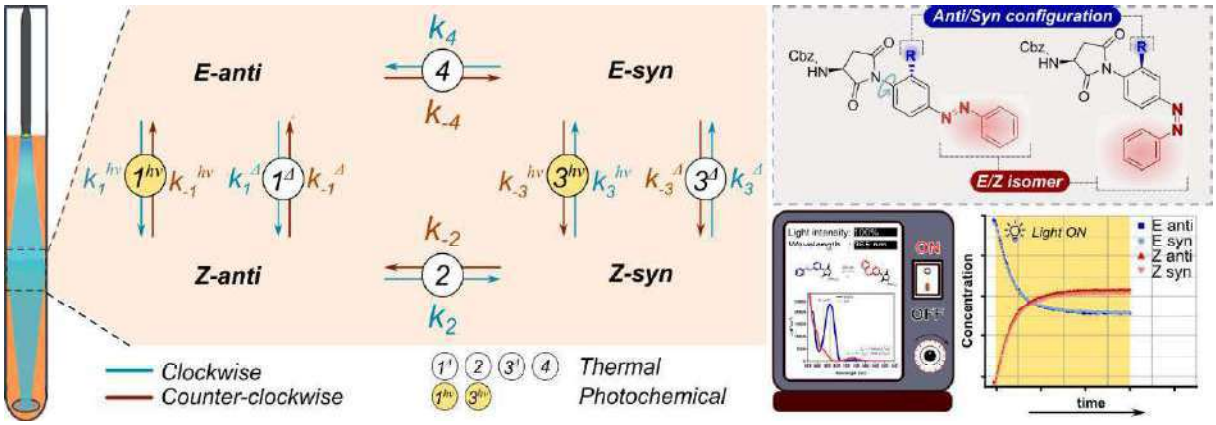
As a highly tunable, controllable, clean, and renewable energy source, light presents significant potential to power molecular motors.[1,2,3] However, the efficient operation of light-driven molecular motors remains a considerable challenge, requiring the precise integration of thermal and photoinduced reactions to achieve controlled motion. This work presents a family of axially chiral molecular rotors incorporating an azobenzene photoswitch, designed to couple photoinduced and thermal processes within a chemical reaction network. The photoisomerization of azobenzene induces kinetic asymmetry, biasing thermal interconversion between anti and syn conformations of trans and cis rotors. Using in-situ light irradiation NMR, the temporal evolution of the four species within the reaction network was tracked, providing insights into the dynamic behavior of rotor interconversion. Furthermore, kinetic asymmetry enables directional light-driven ratcheting[4,5] evolution of the chemical reaction network. This new family of molecules contributes to the development and understanding of minimal chemical reaction networks operated away from equilibrium.



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A Versatile Strategy for Light-driven Active Transport of Ions

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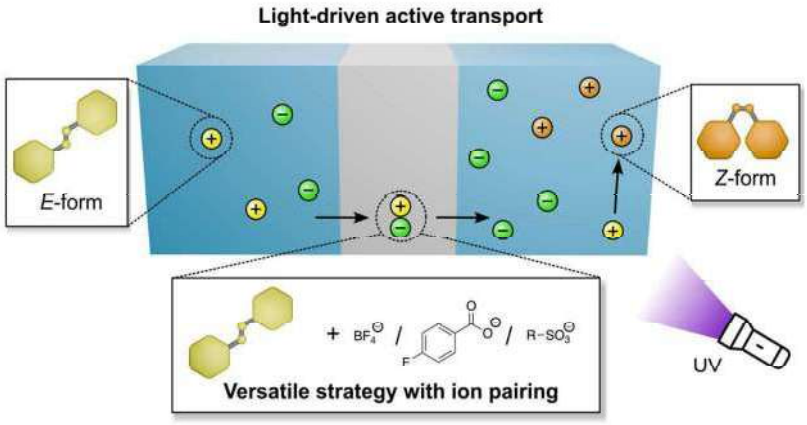
Transport across compartments is essential for biology to drive its vital processes. Chemists have developed synthetic transport systems, focusing mainly on passive transport, where cargo species move along a concentration gradient.[1,2] However, active transport—moving substances against a concentration gradient—remains a challenge. Light is a promising energy source for driving active transport due to its precise spatiotemporal control, high selectivity, and operation without waste accumulation. Yet only a few examples of light-driven active transport have been reported: these systems rely on specific host-guest interactions, which enable the transport of one particular species in each case.[3,4] Here, we present a general, robust strategy for light-driven active transport of charged cargos using charge complementarity. Positively charged azobenzene derivatives act as light-responsive carriers and their photoisomerization is coupled to transport across a liquid membrane by a molecular ratchet mechanism. Notably, their transport drives the active transport of negatively charged cargo by forming ion pairs. This system can transport various anions which are simply added as salt. It also functions in buffered solutions, making it applicable in physiological conditions. This approach utilizing charge complementarity is compatible with active transport driven by other energy sources and holds potential for biomedical applications and smart materials.



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Chemically Fueled Logic AND Gate with DoubleEncoding in the Time Domain

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Whereas real-world logic gates are fueled by electricity, so far only one report has demonstrated a molecular logic gate running on chemical fuel (1). Notably, chemical fueling allows the implementation of a time domain in ion signaling, i.e., leading to ion pulses, that resemble time-encoded ion signals in cell communication (1,2).
To increase information density and security in communication, Nature at times encodes signals in the time domain, for instance, Ca2+ ion signals (3). Double encoding in the time domain operates beyond this level of security because the data is encoded in two time-dependent output signals showing distinct periods, frequencies, and full duration half maxima. To illustrate such a protocol, a three-component ensemble consisting of a double ion-selective luminophore with two distinct receptor sites, hexacyclen, and diaza-18-crown-6 ether is demonstrated to act as a logic AND gate with Ag+ and Ca2+ ion as inputs. The gate shows an unprecedented twofold time-encoded fluorescence output at 590 and 488 nm based on metal ion pulses with distinct periods when trichloroacetic acid is applied as chemical fuel.

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May 22-23, 2025
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Substrate Selective Oxidation of Alcohols *via* Encapsulation of Neutral Ruthenium Catalyst within a Hexameric Self-Assembled Host

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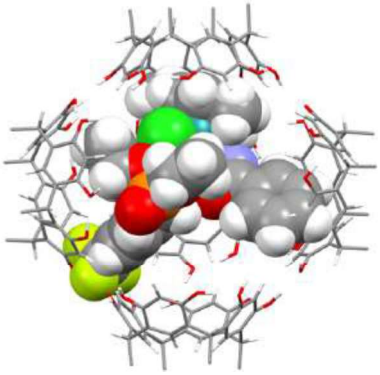
Catalysis with molecular containers is an emerging field due to its similarity to enzymes.[1] Supramolecular assemblies can provide large, confined spaces, as demonstrated by the self-assembled capsule discovered by Atwood.[2] The neutral complex dichloro-{diethyl[(5-phenyl1,3,4-oxadiazol-2-ylamino)-(4-trifluoromethyl-phenyl)methyl]phosphonate}(*p*-cymene)-ruthenium(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]



Simulation of the studied inclusion complex

Acknowledgements: This work was supported by the Agence Nationale de la Recherche (HEXCAPS Programme, ANR-24-CE07-1738).

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[2] L. R. MacGillivray, J. L. Atwood, *Nature*. **1997**, *389*, 469-472.
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Thank you for coming!