2nde JOURNEES DE CHIMIE SUPRAMOLECULAIRE

1-2 JUIN 2023

MONTPELLIER

ENSCM, Amphithéâtre Mousseron, 240 Avenue du Professeur Émile Jeanbrau
WELCOME ADDRESS

Cher(e)s collègues,

Le groupe thématique de Chimie Supramoléculaire de la Société Chimique de France organise cette 2\textsuperscript{nde} édition des Journées de Chimie Supramoléculaire (JCS) du 1er juin au 2 juin 2023 à Montpellier. Cet événement sera l’occasion pour la communauté de Chimie Supramoléculaire française de se retrouver et de partager ses résultats dans une atmosphère stimulante et conviviale. 4 conférences plénières sont prévues, ainsi que 21 créneaux pour des communications orales et 1 session de 18 présentations par posters.

Nous sommes ravis de vous accueillir à Montpellier et espérons que vous y passerez un bon moment !

Damien Bourgeois, Sébastien Ulrich

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Dear colleagues,

The Supramolecular Chemistry section of the French Chemical Society (SCF) organizes this 2\textsuperscript{nd} edition of the Supramolecular Chemistry Days from June 1 to June 2 2023 in the city of Montpellier. This event will be a great opportunity for the community of Supramolecular chemists to meet, discuss and share their results in a friendly and stimulating atmosphere. 4 plenary lectures are planned, 21 slots are allocated to oral communication, and 1 session showcasing 18 poster will be organized.

We look forward to welcoming you in the beautiful and sunny city of Montpellier, and hope you will have great time!

Damien Bourgeois, Sébastien Ulrich
RESEARCH TOPICS

SUPRAMOLECULAR CHEMISTRY

SELF-ASSEMBLY

HOST-GUEST CHEMISTRY

(BIO)MOLECULAR RECOGNITION

COORDINATION CHEMISTRY

DYNAMIC COVALENT CHEMISTRY

SUPRAMOLECULAR POLYMERS

SUPRAMOLECULAR CATALYSIS

MOLECULAR MACHINES

DYNAMIC AND RESPONSIVE MATERIALS

TRANSPORT AND DELIVERY
ORGANIZING COMMITTEE

Damien Bourgeois (48 years old): After a PhD thesis at the Ecole Polytechnique (Paris, France) on olefin metathesis applied to the synthesis of complex organic molecules and a post-doctoral fellowship at Imperial College (London, England) on nitrogen heterocycles synthesis, he joined the Rhodia Recherches Center in Lyon in 2002 and worked on applied homogeneous catalysis (butadiene hydrocyanation, Friedel-Crafts acylation) and paint & coatings formulation. He then joined the CNRS in 2007, where he has been deeply involved in chemistry related to separation of metals at ICSM during last ten years. His interest ranges from fundamental to applied studies, focusing on nuclear fuel cycle, as well as on precious metals and their use in circular economy.

Sébastien Ulrich is a CNRS research associate working at the Institut des Biomolécules Max Mousseron (IBMM) in Montpellier. He carried out his PhD with Prof. Jean-Marie Lehn at the University of Strasbourg and, subsequently, joined the groups of Prof. Harry Anderson (Oxford University, UK) as an EPSRC fellow and of Prof. Eric Kool (Stanford University, USA) as a Fulbright fellow. His current research interests focus on the generation and implementation of smart functional self-assemblies for biological applications such as nucleic acids recognition and delivery. In 2014, he was named Junior Distinguished member of the French Chemical Society, and was awarded the CNRS bronze medal in 2017.

SCIENTIFIC COMMITTEE

Damien Bourgeois (ICSM/CNRS-Université de Montpellier); Jean-Pierre Dutasta (ENS Lyon); Claire Fave (LEM/CNRS-Université de Paris); David Leboeuf (ISIS/CNRS-Université de Strasbourg); Nathan McClenaghan (ISM/CNRS-Université de Bordeaux); Jean-Francois Nierengarten (LIMA/CNRS-Université de Strasbourg); Matthieu Raynal (IPCM/CNRS-Sorbonne Université); Olivia Reinaud (LCBPT/CNRS-Université Paris Descartes); Matthieu Sologoub (IPCM-Sorbonne Université); Sébastien Ulrich (IBMM/CNRS-Université de Montpellier); Laurent Vial (ICBMS/CNRS-Université de Lyon).
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<td>nanomaterials to molecular machines and rotaxanes</td>
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<td>Marc Hennebelle, Supramolecular Nano-Clustering In Water-Lean Solvents:</td>
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<td>Clara Testard, Turning regioselectivity to pseudo-enantiomery:</td>
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<td>Rajaa Benchouaia, Toward new cryptophane analogs: synthesis and</td>
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<td>Mickael Menand, Solid state porous hierarchical assemblies</td>
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<td>Gyorgy Szaloki, Transition metal reactivity in confined spaces</td>
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<td>Yann Ferrand, From Molecular Recognition to Catalysis: Designing an</td>
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<td>David Canevet, Photochemically- and thermally-controlled chirality of</td>
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<td>Stephanie Durot, Multi-site bis(zn(ii)-porphyrin) cages: allosteric</td>
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<td>Stephane Le Gac, Moebius Zn(II) hexaphyrins with a chiral coordinating</td>
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PLENARY LECTURES

ABSTRACTS
INFLUENCE OF SUPRAMOLECULAR INTERACTIONS ON THE CATALYTIC, MATERIAL, AND BIOLOGICAL PROPERTIES OF PHOSPHORUS DENDRIMERS

Anne-Marie Caminade

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Abstract
Dendrimers are hyperbranched macromolecules, synthesized radially from a central core, and possessing a large number of functions, depending on the generation (the number of layers). These functions located on the surface are easily accessible, and can be modified at will to fulfil the desired properties. Various types of dendrimers are known, but we will consider especially those built with a phosphorus atom at each branching point [1]. These dendrimers, and the corresponding dendrons, which are dendritic wedges, possess a large number of properties, as shown below, many of them being related to supramolecular interactions. Typical examples of such supramolecular interactions in catalysis [2], materials [3], and biology [4] will be presented.

Figure 1. Schematization of dendrimers and dendrons and their properties, as well as some front pages.

Acknowledgements
I warmly thank all my present and past team members, the CNRS, and the SCF.

References
Controlling self-assembly by chemical fuels and light

Thomas M. Hermans

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Abstract
Looking at nature, we see that living materials with biological functionality, such as the actin or microtubule (MT) cytoskeletal network, achieve dynamics as well as supramolecular structures with the same protein building blocks. In other words, the components can assemble, but also react (i.e., tubulin is also an enzyme that hydrolyses guanosine triphosphate GTP), which in turn affects the assemblies. In this way, living systems use chemical fuels (e.g., GTP) and self-assembly to create a built-in chemomechanical interaction. Moreover, such networks operate in sustained out-of-equilibrium states at the onset of oscillations, which results in rapid response and adaptivity. Here, we present our recent reaction cycles in solution and gels, where interesting new behaviors were found, such as supramolecular size oscillations, traveling polymerization, or transient disassembly. We hope such reaction cycles form the basis of new life-like materials where material properties are fuel (and waste) dependent.

References
ARTIFICIAL WATER CHANNELS-TOWARD BIOMIMETIC MEMBRANES FOR DESALINATION

Mihail Barboiu

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Abstract
This lecture discusses the incipient development of the first artificial water channels systems. We include only systems that integrate synthetic elements in their water selective translocation unit. Therefore, we exclude peptide channels because their sequences derive from the proteins in natural channels. We review many of the natural systems involved in water and related proton transport processes. We describe how these systems can fit within our primary goal of maintaining natural function within bio-assisted artificial systems. In the last part, we present several inspiring breakthroughs from the last decade in the field of biomimetic artificial water channels. All these examples demonstrate how the novel interactive water-channels can parallel biomolecular systems. At the same time these simpler artificial water channels offer a means of understanding water structures useful to understanding many biological scenarios. Moreover, they can be used for the preparation of highly selective membranes for desalination.

References
ADAPTIVE CHEMISTRY: IF ORDER CAN BE, ORDER WILL BE!

Jean-Marie LEHN

ISIS, Université de Strasbourg, France.

Abstract
Supramolecular chemistry is intrinsically a dynamic chemistry in view of the lability of the non-covalent interactions connecting the molecular components of a supramolecular entity and its resulting ability to exchange components. Similarly, dynamic covalent chemistry concerns molecular entities containing covalent bonds that may form and break reversibly, so as to allow for a continuous modification in constitution by reorganization and exchange of building blocks. These features define a Constitutional Dynamic Chemistry (CDC) on both the molecular and supramolecular levels. Because of the intrinsic ability of the constituents to exchange and rearrange their components, they may in principle select them in response to physical stimuli or chemical effectors. They thus behave as adaptive chemical entities, leading to the development of an Adaptive Chemistry of both molecular or supramolecular nature.

Of special significance is the fact that the possibility of a constitutional dynamic system to achieve a state of higher level of organization (such as the transition from a Sol to a Gel) drives the amplification of those constituents that lead to that very state in a sort of autocatalysis of organization.

Dynamic and adaptive features introduce a paradigm shift in Soft Matter Chemistry, opening wide perspectives towards adaptive soft matter science and in a broader view towards higher levels of (self)organization and complexity.

References
ORAL COMMUNICATIONS

ABSTRACTS
PILLAR[5]ARENE SCAFFOLDS: FROM MULTIFUNCTIONAL NANOMATERIALS TO MOLECULAR MACHINES AND ROTAXANES

Iwona Nierengarten, Jean-François Nierengarten

Laboratoire de Chimie des Matériaux Moléculaires, Université de Strasbourg et CNRS, (LIMA – UMR 7042), Ecole Européenne de Chimie, Polymères et Matériaux (ECPM), 25 rue Becquerel, 67087 Strasbourg Cedex 2 (France).
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With their ten peripheral substituents, pillar[5]arene derivatives are attractive compact nanoscaffolds for the construction of multifunctional compounds with specific properties. The copper catalysed alkyne-azide cycloaddition (CuAAC) reaction has been particularly useful for the ten-fold post-functionalization of pillar[5]arene building blocks bearing ten peripheral azide or terminal alkyne functions. A wide range of advanced materials and bioactive compounds build on a pillar[5]arene scaffold have been thus prepared in recent years. Examples include efficient hole transporting materials for perovskite solar cells, redox-driven molecular machines, and multivalent glyoclusters targeting bacterial lectines. On the other hand, the pillar[5]arene moiety is also a supramolecular receptor offering additional features to the multifunctional materials. This has been for example used to modulate the liquid crystalline properties of pillar[5]arene columnar assemblies and to develop photo- and electro-active rotaxanes. Our latest advances in this particular field will be presented.

References
SERGEANTS-AND-SOLDIER-TYPE SUPRAMOLECULAR HELICAL CATALYSTS EFFICIENT UNDER DILUTED CONDITION

Antonio Valverde-González,1 Huanjun Kong,1 Laurent Bouteiller,1 Matthieu Raynal1
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“Sergeants-and-soldiers” effect [1] refers to the ability of a small amount of chiral monomers (the “sergeants”) to fully control the main chain helicity of polymers mainly composed of achiral monomers (the “soldiers”). This phenomenon is widely known for non-functionalized supramolecular polymers and may occur under diluted conditions [3] as long as the coassembly process is sufficiently strong. In our group, the “sergeants-and-soldiers” effect has been widely applied in supramolecular catalysis with helical assemblies of benzene-1,3,5-tricarboxamide (BTA) monomers.[2] More precisely, an achiral BTA monomer appended with a PPh2 unit (the “soldier”) is mixed with an enantiopure monomer derived from an amino ester (the “sergeant”). The enantioselectivity in the catalytic reaction of the reference, the copper-catalyzed hydrosilylation of 4-nitroacetophenone greatly depends on the nature of the sergeant. The “sergeant” derived from the dodecyl ester of Leucine (1) efficiently intercalates into the stacks of the BTA ligand (3), leading to good level of enantioselectivity. However, the selectivity drops off upon dilution. We demonstrate herein that a suble change in the molecular structure of the sergeant, i.e. replacing the ester by an ether function (2), allows to maintain a good selectivity under diluted conditions as a probable consequence of the stabilization of the coassemblies.

Figure 1. General synthetic scheme for BTAs coassemblies’ preparation.

Acknowledgements
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References
Supramolecular Nano-Clustering In Water-Lean Solvents: A Game-Changing Approach to CO₂ Capture

Hennebelle Marc,1 David J. Heldebrant,2 Leclaire Julien1

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Abstract
Capturing CO₂ from industrial processes is crucial for reducing greenhouse gas emissions.[1] In this study, we present a game-changing approach to CO₂ capture using a single-component water-lean solvent, EEMPA (N-(2-ethoxyethyl)-3-morpholinopropan-1-amine) E (fig. 1a). E is a promising absorbent for post-combustion CO₂ capture, providing the highest solvent energy efficiency and lowest costs of capture[2] compared to other capture solutions such as aqueous amines.[3] Through a combination of experimental and modeling approaches, we discovered that CO₂ capture is accompanied by the supramolecular nano-clustering of reverse micelle-like tetrameric structures in solution (fig 1b). These structures display highly contrasted kinetic and thermodynamic features due to stepwise cooperative capture phenomena. The H-bonded internal core of these supramolecular architectures allows for the formation of novel CO₂-containing molecular species such as carbamic acid and carbonic anhydride (with CO₂ molecules bound successively on the same nitrogen site, fig 1c).

Our results extend the scope of adducts and mechanisms observed during capture and open the way to new materials with a higher CO₂ storage capacity or a means to oligomerize or polymerize CO₂ in future efforts.

Figure 1. Covalent E/CO₂ adducts (a), structure and schematic representation of the tetrameric clusters generated upon CO₂ capture (b) and of the stabilized new intermediates and products (c).

References
TURNING REGIOSELECTIVITY TO PSEUDO-ENANTIOMERY: ASYMMETRIC SHAPING OF CYCLODEXTRIN CAVITIES

Clara Testard, Floriane Heis, Yongmin Zhang, Mathieu Sollogou

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Abstract
Building only from a pool of L-amino acids, Nature makes proteins capable of great enantio-discrimination. Following a precise folding scheme, the asymmetric shape of the active site is dictated by the 3D-positioning of amino-acids relative to one another. As organic chemists, can we build a similar system using only D-sugars such as cycloextrins (CDs) and achieve shape-directed enantio-discrimination (Figure 1A)?

Our group developed NHC-bridged CDs that complex transition metals inside their cavity. These complexes are active in catalysis, with interesting chemo-, regio-, and stereoselectivities. We found that 2-point bridging of a CD induces a helicoidal distortion of its cavity, that accounts for the observed selectivities. However, only the distortion into an M-helix is accessible from 2-point bridging, and no control over the catalysis stereoselectivity was possible. Pushing the concept forward, we want to gain control over the distortion of the cavity and access pseudo-enantiomeric shaped cavities from 3-point bridging.

We now propose the synthesis of 2 regioisomers with mirror-image anchoring patterns using tripodal moieties such as tren groups (Figure 1B). Delightfully, we found that corresponding Cu(II) complexes behave like enantiomers, as observed from circular dichroism spectra. Future goals include to further characterize metal-complexes of tren-bridged CDs and assess their stereoselectivity towards the recognition of chiral guests. Additionally, crystallizable and water-soluble permethylated analogues have been obtained for structural determination as well as chiral recognition in water.

Figure 1. [A] Left: Protein 3D structure. Right: 3D structure of NHC-bridged CD metal complex. [B] Left: Schematic representation of tren-bridged CD regioisomers. Right: opposite circular dichroism spectra of the corresponding copper acetate complexes.

References
MOLECULAR TWEEZERS FOR MULTIFUNCTIONAL COMMUNICATING SYSTEMS

Maksym Dekhtiarenko, 1 Guillaume Vives, 1

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

We have recently developed switchable molecular tweezers that can be controlled by metal coordination. Our system is based on a terpyridine ligand functionalised by metal salphen complexes. The open tweezers adopt “W” shaped conformation that can be switched to a closed “U” conformation, bridging the two functional salphen complexes into proximity. 2 We aim to combine such versatile mechanical machine with other orthogonal switches to achieve dynamic smart systems. 3

We report herein the multicomponent switching cascades based on terpyridine molecular tweezers and stimuli-responsive organic acids designed to switch the tweezers with photochemical or temporal control. This multicomponent system allows in situ remote control over the conformation and thus the interaction between the tweezer functional units. Such concept can be beneficial for molecular recognition leading to applications in catalysis or controlled delivery.

References
Synthesis of supramolecular polymeric materials – the interplay between covalent and non-covalent bonds

Ghislaine Vantomme

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Abstract
Ever since the seminal work of Staudinger, controlling the structures of macromolecules is a topic of great interest. Copolymerizing different monomers offers vast possibilities to tune the properties of covalent copolymers. In the field of supramolecular copolymers, in contrast to their covalent counterparts, fundamental knowledge still needs to be gained, and predictive rules to be developed to forecast the sequence, composition and length of multi-component mixtures. The dynamic nature of the non-covalent interactions makes multifunctional supramolecular copolymers versatile systems, which results in a high potential for adaptive materials, in organic electronics, and as bio-mimetic systems. However, constructing hierarchical multi-component co-assemblies is particularly challenging as it requires a balanced choice between structure and chemical reactivity.\textsuperscript{1,2} The presentation will focus on our recent findings on supramolecular copolymerization in multi-component systems, and the influence of chemical reactions on the structures obtained.\textsuperscript{3}

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**Figure.** A paradigm shift to noncovalent synthetic chemistry. Supramolecular chemistry must follow the same trajectory as organic chemistry to make complex structures that mimic those found in nature.\textsuperscript{1}

**References**

Dynamic Covalent Polymers for mRNA complexation and delivery

José García Coll, Elena M. Rodríguez Maqueda, Yannick Bessin, Nadir Bettache, Javier Montenegro, Sébastien Ulrich.

Institut des Biomolécules Max Mousseron (IBMM - UMR 5247), CNRS, Université de Montpellier, Montpellier, France; Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS), Universidad de Santiago de Compostela, Santiago de Compostela, Spain
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Abstract
Dynamic Covalent Polymers (DCPs) are emerging as promising vectors for gene delivery. In previous works, we showed that a dynamic library of complementary cationic peptides can undergo a siRNA-templated polymerization through acylhydrazone and oxime ligations leading to the formation of a glycosylated DCP which in turn trigger cell-selective uptake and siRNA delivery. Given its ever-growing therapeutic potential, we set out on implementing our approach to mRNA complexation and delivery. We report in this communication the design and synthesis of a new family of modified peptide bishydrazides having a free N-terminal position in which new functional groups have been placed. mRNA complexation studies were carried out by gel electrophoresis and confirm that these polyacylhydrazone DCPs do form by mRNA templated polymerization after only 30 min incubation. Finally, our first efforts to assess the potential of this new generation of DCPs for the delivery of mRNA in live cells will be presented.

Figure 1. mRNA complexation and delivery by dynamic covalent polymers.

Acknowledgements
ANR-SACSI, DARTER Cost Action.

References
CATALYSIS FOR CHEMICALLY FUELED SYSTEMS

Adrien Quintard, 1

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Abstract
Chemically fueled systems such as molecular machines and smart materials have the potential to considerably impact our society. However, as a main drawback, use of chemical fuels is most of the time associated with formation of undesired accumulating waste upon fuel consumption, detrimental for the systems. Taking advantage of different catalytic approaches applied with success in the context of greener organic synthesis, our group developed chemically fueled systems using catalytic transformations as alternatives avoiding waste accumulation. For example, organocatalytic decarboxylation of activated acids such as trichloroacetic acid was applied to fuel different smart materials, reversibly evolving from solution to gel.1 In a complementary approach, iridium catalyzed reversible (de)-hydrogenation could be used to trigger rotation in a rotating switch.2 In all these systems, generation of volatile compounds upon waste consumption avoided any deactivation of the molecular machinery.

Figure. Overview of our recently developed chemically fueled systems

References
NEW SUPRAMOLECULAR MULTIVALENT ANTI-ADHESIVE AGENTS AGAINST SARS-CoV-2

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In 2020, during a CRYO-EM experiment, we unexpectedly observed a SARS-CoV-2 particle near self-assembled cyclodextrins fibers. We thus wondered if we could bring specific interactions between them and trigger this assembly on purpose. Indeed, our team previously showed that it was possible to form fibers from small oligomers of DNA and cyclodextrins functionalized by an adamantane and ammonium. The hydrophobic effect between cyclodextrins and adamantanes allows the formation of small supramolecular polymers by self-assembly (1st step). Then, through multivalent electrostatic interactions between the monomers and DNA, the co-assembly becomes a lot bigger (2nd step).[1] The surprising observation encouraged us to explore the ability of cyclodextrins assemblies to cooperatively interact with SARS-CoV-2 particles and use them as anti-adhesive agents to potentially inhibit cell infection by this virus. We therefore changed non-specific electrostatic interactions into more specific ones, using sugar-based ligands allowing multivalent effect. For that, we functionalized cyclodextrins with an adamantane and the targeted ligand on the side. We are now studying their self-assemblies (1st step), their multivalent ability to interact with several receptors at the surface of SARS-CoV-2 and potentially observe cooperative assembly.

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

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Investigating Toluene Bis-Amide (TBA) supramolecular polymerization

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Supramolecular polymers are defined as 1D self-assemblies of monomers through directional, non-covalent interactions.[1] Initially triggered under thermodynamical control,[2] supramolecular polymerizations comprising kinetic metastable states that delayed the spontaneous supramolecular aggregation were recently recognized as fundamental phenomena, mimicking biological processes.[3] Since then, multiple examples of kinetic effects were reported relying mostly on the formation of intramolecular hydrogen bonds that prevented the monomers from polymerizing through intermolecular hydrogen bonds. We recently reported the supramolecular self-assembly of RuIII bis-acetyldic functionalized with a Toluene Bis-Amide (TBA) moiety generating strong intermolecular hydrogen bonding interactions and leading eventually to the solvent gelation.[4] Consequently, these outcomes prompt us to investigate the supramolecular polymerization of the corresponding organic fragments (TBA-A12 and TBA-PhA12).

In this communication, we will disclose our latest results regarding their self-assembly mechanisms. We will demonstrate that TBA-A12 and TBA-PhA12 polymerize in a cooperative way. By means of temperature controlled UV-Vis spectroscopy experiments, VT-NMR, DLS, TEM we will demonstrate that the extra phenyl-acetylide moiety deeply affects the energy landscapes, introducing kinetic metastable states.

![Figure 1. TBA-A12 and TBA-PhA12.](image)

References
EFFECT OF METALLIC CATIONS ON THE BEHAVIOR OF ACYLHYDRAZONE-BASED DYNAMIC COVALENT LIBRARIES IN BIPHASIC SYSTEMS

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Abstract
Dynamic covalent chemistry (DCC) investigates the formation, evolution and behavior of dynamic systems based on the generation of self-assemblies through reversible covalent bonds. DCC has experienced significant growth due to its adaptive properties to external stimuli. However, the behavior of this type of system in biphasic media has not been intensively investigated so far [1-3]. Palladium is a strategic metal with a well-defined coordination chemistry (square planar geometry). The response of a 2x2 acylhydrazone-based DCL to Pd(II) was studied in biphasic systems (water/chloroform). This DCL was designed so that the hydrazide moiety influences the hydrophobicity whereas the aldehyde moiety modulates the complexation properties. The behavior of such systems is driven by the affinity between metal and constituents as well as the affinity for each phase of all the species in the system, whether organic molecules or complexes. (1) The dynamic of the DCL was studied to determine partition coefficients as well as the distribution of constituents. (2) Constituents/Pd(II) complexes were characterized. (3) Pd(II) was introduced with the DCL into the biphasic system. The presence of Pd(II) induces the strong amplification of A1B2 in the organic phase by the formation of a lipophilic Pd(II) complex (Figure 1). (4) The use of Pd(II)/Cu(II) mixture as chemical effectors is in progress and will be further discussed.

References
Family of bis-Acradinium Receptors

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Abstract

In Nature, the high degree of organization allows the formation of sophisticated assemblies (double helical structure of DNA, G-quadruplex secondary structures, etc.) able to perform advanced functions (modulation of reactivity, movement, etc.). In such complex mixtures, the organization is governed by selective molecular recognition and self-assembly processes1 relying on weak interactions (hydrophobic, hydrogen-bonding, van der Waals, and π-π stacking interactions). Consequently, a growing interest in elaborating self-assembling systems has emerged in order to prepare functional synthetic systems in a simple and reliable manner.

We recently reported bis-acridinium receptors able to bind guest molecules.2 Based on molecular tweezers and their cyclophane analogues, two acridinium recognition units linked by a semi-rigid spacer are pre-organized to bind a variety of aromatic guests. The acridinium recognition units are unique multi-responsive building blocks (electrochemically and chemically switchable) able to interact with electron rich guests.3 Surprisingly, this class of bis-acridinium receptors exhibit i) self-complementary behaviors leading to the formation of entwined dimers,2a ii) narcissistic self-sorting as well2b as iii) π-donor/π-acceptor host-guest behaviors.3 In addition, the multi-switching properties of these bis-acridinium receptors were investigated to alter the recognition events and were also studied as selective phase transfer agents of perylene in perfluorocarbons.

Acknowledgements

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References

Toward new cryptophane analogs: synthesis and encapsulation properties of an amphoteric azacryptophane

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Abstract
Cryptophanes[1] are cage-like host molecules and composed of two cyclotribenzylene (CTB) units usually connected by alkylene-dioxy linkers. Since the first synthesis of cryptophane-A in 1981 by A. Collet et al.,[2] considerable progress has been made in designing cryptophanes that exhibit selective encapsulation properties toward organic and inorganic guests.[3] Indeed, cryptophane-A and its congeners, which have a small cavity size, remain the most studied host derivatives with xenon. Cryptophanes can vary widely in their form and properties, depending on stereochemistry, the nature of the linker unit. These molecular cages represent an important class of hollow molecules with remarkable binding properties. For instance, it has been shown that these host molecules have a very high affinity for xenon[4] and they constitute, among other host systems, excellent candidates for biosensing applications.[5] Nevertheless, only few examples of binding properties in aqueous media are described.[6] In this context, we aim to explore new chiral cages (Scheme 1), cryptophane derivatives. Some preliminary results showed decorated CTB with aromatic amines entail a drastic modification of their supramolecular properties. In our lab, we aim to develop a new family of hydrophilic cryptophanes analogs.[7] The amphoteric cage, shown here, presents three aniline functions and three phenol functions, which can be protonated and deprotonated, at low pH and high pH values respectively. Such compounds demonstrate remarkable binding properties with xenon and cations in basic media.

Scheme 1. Guest encapsulation by the amphoteric cryptophane in aqueous media.

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Solid state porous hierarchical assemblies of di-functionalized cyclodextrins

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Abstract
Singly functionalized cyclodextrins are known to form supramolecular polymers in the solid state through the iterative inclusion of the hydrophobic function into the cavity of the next cyclodextrin. While this behavior is well documented in the literature,¹² the effect of a second function on the assembly outcome is less predictable and remains to be explored. In this context, we have showed that the regioselective di-functionalization of an α-cyclodextrin with two azido groups not only allows the formation of the expected supramolecular polymer but also provides additional interactions that strengthen the polymer (azido-azido interactions) and brings cohesion between the polymer strands through lateral azido-groove interactions.³ To continue in this direction, we have recently described the solid state of a bridged cyclodextrin bearing two phenyl groups.⁴ Again, one of the phenyl rings ensures the polymer formation while the other one forms hydrophobic domains in a controlled manner. This controlled orientation ultimately gives access to an original hierarchical spanning over three levels and governed by synergistic host-guest inclusions, directed hydrophobic effect and hydrogen bonding. This combination of interactions precisely positioned in space through regioselective functionalization of a cyclodextrin creates a porous organic architecture.

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References
TRANSITION METAL REACTIVITY IN CONFINED SPACES

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Abstract

Enzymes are extremely powerful catalysts: they alter the rate and selectivity of biological reactions, through confinement of reactive intermediates within their cavities (enzyme pocket). For a long time, chemists have sought to reproduce such activities in abiotic cavities: it has been shown that the principle of confinement is transposable from biological systems to artificially designed hosts (e.g. supramolecular cage).[1] Nevertheless, their efficiency lags far behind that of the natural analogues and new confinement strategies are highly desired.

Figure 1. The main concept of our work.

Given the spectacular progress witnessed by gold chemistry in the past 20 years, it is not surprising that the confinement of gold complexes has been envisioned, but such studies remain very scarce. The proof-of-concept of altering the reactivity of a model gold complex, using a small anionic supramolecular cage has been recently demonstrated,[2] however, the lack of large cages prevents developing this concept further. Based on the strong background of our group in the field of gold chemistry, we have tackled this challenge.[3] In the framework of the JCS 2023, we would like to present our latest results.

References
Aromatic oligoamides present all the required features to act as efficient scaffolds for the molecular recognition of chiral polar guests. Their oligomeric nature offers unmatched modularity in that each and every monomer may be varied in order to tune the structure, the dynamics and host-guest properties. Helices with variable inner diameters can be used as capsules that can totally isolate a substrate from the external medium (Fig. 1, left). While catalysis using foldamers is a rapidly developing area, there has been no account on catalysis within foldamer containers making use of their recognition properties.

Recent efforts in our group have focused on the design of capsule shaped catalysts for the decarboxylations of perfluorosuccinic acid (Fig. 1). The functionalization of a capsule with electron donating morpholine moieties allowed the deprotonation of the dicarboxylic acid guest and its subsequent double decarboxylations. Surprisingly, the CO$_2$ molecules generated during the reaction could be trapped in the foldamer cavity and the resulting gas-foldamer complex could be characterized in solution and in the solid state. Alternatively, heating of the capsule in the presence of an excess of diacid allows for catalysis to proceed.

**Figure 1.** Schematic representation of the host/guest complex formation followed by two consecutive decarboxylation reactions of a diacid guest.

**References**


PHOTOCHEMICALLY- AND THERMALLY-CONTROLLED CHIRALITY OF HELICAL FOLDAMERS

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Multi-stranded helical structures such as DNA¹ and proteins² are ubiquitous in nature and play a fundamental role in biological processes. To mimic their behavior, much effort has been devoted to the synthesis and modifications of oligomers that fold in a both compact and highly organized manner, called foldamers. Among various examples, helical foldamers have found interest in various research fields, such as HIV treatment,³ catalysis,⁴ or stimuli-responsive molecules and materials.⁵,⁶ To obtain enantiopure or enantio-enriched helical foldamers, two strategies have been considered so far: the introduction of stereogenic centers of known configuration on the foldamer backbone and the interaction between the helical structure and a chiral guest through non-covalent bonds. The former strategy implies the synthesis of both enantiomers, which may require much synthetic effort, while the efficiency of the latter one strongly depends on the strength of the host-guest interaction. This is the reason why being able to switch the chirality of foldamers in a reversible manner constitutes both a challenging and exciting objective.

In this context, grafting the unidirectional rotary motors developed by Feringa and coworkers appeared relevant, since their helical chirality can be controlled thanks to photochemical and thermal stimulations.⁷ On this basis, this communication will focus on our recent efforts to prepare a ‘foldamer-molecular motor’ conjugate and show how the chirality of helical foldamers can be photochemically and thermally switched in a successful manner (Figure 1).⁸

![Figure 1. Left. Schematic representation of the explored concept.](image-url)

References

Low molecular weight supramolecular hydrogels are formed by the self-assembly of small, non-polymer molecules in supramolecular fibers which entraps water. These hydrogels are often mechanically fragile and as such, they are not often considered for cell culture applications and 3D printing. To tackle with applications requiring large quantities of gel, we developed a family of gelators of simple structures, based on long chain amides coupled with sugar polyols. The synthesis is short and gives molecules of high purity suitable for cell culture. On the hydrogels, the cell culture of neural or mesenchymal stem cells, fibroblasts or neural cell lines provides small 3D cell clusters linked together by cell extensions guided by the supramolecular fibers (b). Specific methods are implemented to observe the 3D cell organization in these fragile hydrogels.

We are also developing different gelation methods and notably wet spinning or 3D printing. Because the hydrogels are not shear-thinning nor thixotropic, direct injection of the gels is not possible. So we developed a method in which the gelation is triggered by liquid-liquid exchange. The very fast self-assembly of the gelator provides well-resolved 3D printed patterns and well-shaped gel noodles (c). Also, by changing slightly the structure of molecular gelator, we got either sacrificial or persistent gels which can be imbricated by 3D printing. The spontaneous dissolution of the sacrificial gel gives supramolecular gel architectures with channels.

The gelation mechanism at the liquid-liquid interface has been analyzed by the introduction of fluorescent dyes or colored indicators. In addition, at the microscopic level, in some conditions, the supramolecular fibers are radially organized highlighting diffusion and/or mixing phenomenon at the liquid-liquid interface (a).

Cucurbituril switches: toward advanced molecular machines in water

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Abstract

The construction of molecular machines remains a high scientific challenge especially in water.1 In this context, we found that macrocycles resembling pumpkins (cucurbiturils) are well-suited to prepare molecular switches in water activated by pH2 or silver coordination.3 The presence of H+ or Ag+ cations enables to switch the position of the macrocycle between two stations of a linear axle composed of three stations: viologen–phenylene–imidazole (VPI, Figure 1). Extension of the track with a small hydrophobic group changed the molecular switch into a molecular shuttle, making the cucurbit[7]uril (CB[7]) ring navigating autonomously between two stations.4 Finally, functionalizing the viologen with two benzoic acid groups enabled to control the exchange of guest molecules following one particular direction under pH/redox activation, thanks to a partial energy ratchet in water.5

![Figure 1](image)

Figure 1. Translocation of CB[7] between the V and P stations by silver cations.

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References

MULTI-SITE BIS(ZN(II)-PORPHYRIN) CAGES: 
ALLOSTERIC RECEPTORS 
AND ACTIVE COMPONENTS OF [2]ROTAXANES

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Abstract
Mechanically interlocked molecules (MIM), used in a large variety of applications, are supramolecular assemblies in which at least two covalent subcomponents are held together not through a conventional covalent bond but through a mechanical one. The assembly of [2]pseudorotaxanes or [2]rotaxanes by threading a molecular axis through a ring, by slipping the ring over a stopper, by clipping the ring precursor around a dumbbell, or by using a template to gather the ring and the string components requires specific interaction sites on both precursors. Allosteric control of the threading step by the binding of effectors to additional sites has seldom been reported. To this purpose, a flexible covalent cage, endowed with two zinc(II) porphyrins and eight peripheral 1,2,3-triazolyl ligands, is of particular interest, since it provides increased preorganization for a higher stabilization of the threaded species compared to simple macrocycles. The principle of this allosterically driven assembly of semirotaxanes is given in Figure 1. This step can be followed by the addition of the second stopper to form the corresponding [2]rotaxane.

Figure 1. Principle of the allosteric control of half-dumbbell threading through a molecular cage receptor.

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References
Möbius Zn(II) hexaphyrins with a chiral coordinating arm: an appealing adaptative system for tunable chirality induction

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Among the various types of chirality (central, axial, helical, planar…), that inherent to Möbius topology remains almost unexplored, partly due to the difficult access to Möbius compounds.[1] Considering the paramount importance of chirality in biological processes, drug design, material sciences and many other fields, scrutinizing Möbius chirality could benefit to a large community of researchers. Currently, the asymmetric preparation of Möbius compounds remains challenging, the main strategy relying on stereochemically stable Möbius ring.[2] Focusing on the Möbius [28]hexaphyrin scaffold, our group has investigated a different approach for chirality induction taking advantage of the dynamic character of the twisted π system.[3] Indeed, this scaffold is conformationally flexible and undergoes rapid $P \leftrightarrow M$ equilibrium in solution, thus exhibiting a dynamic Möbius chirality. This feature enables a transfer of chirality from an exogenous stereogenic source under thermodynamic control, useful to build up adaptative systems. Möbius Zn(II) metallo-receptors exhibiting a strong interplay between aromaticity, guest recognition, and chirality transfer have been revealed, opening a new playground. Recently, we have extended our dynamic approach to a different situation, where a source of fix chirality is part of a covalently attached coordinating arm, leading to the following main findings: (i) both Möbius configurations are reached in-situ by simple addition of suitable achiral effectors tuning the way a fix stereogenic source interacts with the ring. Impressive stereoselectivities (diast. excess > 95%) highlight the most efficient transfer of chirality to a Möbius ring reported so far; (ii) these achiral effectors generate distinct chiroptical states featuring electronic circular dichroism spectra with bisignate Cotton effect of opposite signs. Switching between these two states owing to ligand exchange was successfully achieved with high robustness using a chemical trigger (10 cycles).[3f]

Figure 1. Working principle of a Möbius-type chiroptical switch.

References
POSTER PRESENTATIONS

ABSTRACTS
SELF-ASSEMBLY OF ELECTRON POOR *ORTHO*-EXTENDED BISAZACORONENEDIIMIDES NANOGRAFENES

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Abstract
Organic electronics are on the rise and the synthetic efforts to produce semiconducting carbon-based molecules are considerably growing[1] affording original structures exhibiting unique properties. Large nanographenes, conjugated polymers, curved, twisted or macrocyclic architectures all display different features making them suitable for applications in organic electronics. Understanding the self-assembly processes of such compounds is crucial for the development of organic electronic devices since the molecular packing of the compounds has a direct impact[2] on the devices’ performances. Although the investigation and the diversity of electron-rich/holes-conducting (p-type) scaffolds has seen a continuous increase, their n-type equivalents, electron-poor/electron-conducting, are lagging behind. Being as essential as their p-type equivalents, the need to develop new synthetic methodologies yielding original organic n-type materials as well as the exploration of their supramolecular chemistry are of key importance.

Herein, we report the synthesis of large electro-deficient nanographenes obtained in two steps: a light-mediated benzannulation[3] and diverse ortho C–H activations. This synthetic strategy allows us to created various (hetero)cycles from simple amine-functionalized perylene diimide derivatives. The preliminary results of their optoelectronic and supramolecular properties will be presented.

Acknowledgements
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References
Understanding the Self-Assembly of Precision Catalytic Oligomers through Molecular Dynamics Simulations

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Abstract
Sequence-defined macromolecules, inspired by the control over the monomer sequence in biopolymers such as proteins and DNA, are now accessible through various synthetic pathways.[1] Previous studies by our group and collaborators have shown the paramount importance of the sequence in short catalytic oligomers.[2,3] In view of combining control over monomer sequence and supramolecular interactions, a new system, requiring the self-assembly of two chains to be catalytically active, was designed (Figure 1). The precision macromolecules, oligomer A (Oₐ) and oligomer B (O₈), are able to bind through complementary nucleobase derivatives pairs G-C and T-D (see colored units in Figure 1). The formation of the di(oligomeric) Oₐ/O₈ complex brings all five necessary catalytic subunits (M, 2 P, I, I’) close to each other, a mandatory step to enable catalytic activity. The model reaction studied here is the aerobic oxidation of benzyl alcohol into benzaldehyde.

Molecular dynamics (MD) simulations are a powerful tool to decipher the mechanisms of assembly at the atomistic level. The Oₐ/O₈ duplex being identified as the most catalytically active species by experiments, an assembly of the two oligomers was simulated. Overall, our analyses of simulations, including original representations in network and modules, showed the formation of a very flexible, compact and globular duplex, in which the interactions between the complementary nucleobase derivatives play an important role but are not the only contribution to the binding.

Figure 1. Chemical structure of the Oₐ/O₈ self-assembled catalytic system.

Acknowledgements
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References
Stereodivergent catalysis achieved by means of an achiral ligand embedded into switchable supramolecular helices

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Abstract
Developing general and practical strategies for obtaining all possible stereoisomers of an organic compound with multiple stereogenic centers is of great importance, especially in the drug discovery and development process. Stereodivergent catalysis is the most efficient strategy to tackle this challenge but requires the use of enantiomeric catalysts to access all stereoisomers. Herein, we developed a general and predictable method for stereodivergent catalysis by means of an achiral ligand integrated in properly designed supramolecular helices (Scheme 1). Switching the enantiomeric state of a single catalyst in between sequential transformations could provide access to any stereoisomers in stereoselective cascade reactions without purification of the reaction intermediate. It can be achieved by constructing supramolecular helices composed of three types of monomers: two ligand-free enantiopure co-monomers of opposite configurations and one phosphine-functionalized achiral monomer (for copper coordination). Thanks to dynamic properties and chirality amplification effects, dual stereocontrol of the asymmetric reaction could be achieved in situ by addition of a small amount of the enantiopure co-monomers to invert the handedness of the supramolecular helices. The fast and predictable stereochemical switch plays a key role in the precise stereocontrol of the catalytic reaction in real-time, which cannot be reached by conventional catalysts.

Scheme 1. Copper-catalyzed stereodivergent syntheses of all the possible stereoisomers by an achiral ligand embedded into switchable helices.

References
ORGANOPlatinum-BRIGDED CyclicTriBenzylene Dimers

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Cyclotribenzylenes (CTBs) are bowl-shaped compounds, generally of $C_3$ symmetry. They are useful building blocks for making cryptophanes and hemicryptophanes. Originally constructed from covalent bonds, cryptophanes can also be obtained by transition metal-directed self-assembly. CTBs in which the substituent of one phenyl ring differs from those of the two other phenyl rings are $C_1$-symmetric. Representatives, which combine carbonitrile (-CN) and alkynyl (-C≡H) substituents, were synthesized as racemic mixtures and resolved by HPLC on chiral stationary phases. Two of these compounds were used to prepare platinum-bridged CTB dimers, in which Pt(II) is bound to the CTBs via Pt-alkynyl bonds in cis configuration. The organometallic complexes were examined by mass spectrometry and NMR spectroscopy, which indicated that they were obtained as mixtures of diastereoisomers (a meso or syn form and a pair of chiral or anti forms) when racemic CTBs were used. Enantiomerically pure complexes were prepared from resolved CTBs, which allowed us to distinguish the NMR signals of the chiral and meso forms in the diastereomeric mixtures. In certain conditions, the platinum complexes played the role of a pincer $\pi$-alkynyl ligand for Cu(I) coming from the copper iodide used as an auxiliary in their preparation. The Cu sites could be easily removed by treatment with NaCN, affording the mononuclear bis-cyclotribenzylene complexes.

In earlier work, we had investigated the self-assembly of metallo-cryptophanes from $C_3$-symmetric carbonitrile-functionalized CTBs and [M(dppp)]$^{2+}$ complex subunits ($M = Pd, Pt; dppp = 1,3-bis(diphenylphosphino)propane)$.[6] We envisioned that the current platinum-bridged CTB dimers could be used as direct precursors for the preparation of metallo-cryptophanes containing an organometallic bridge. The results of our investigations in this direction will be presented and discussed.

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References
Chiral triggers for induction of homochirality in supramolecular helical catalysts

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Abstract

Supramolecular polymers constituted of non-covalent monomeric units has emerged in the last decades in the field of science materials engineering for various applications.1] Introducing stereochemical information in these systems is leading to the formation of homochiral helices, mostly through the use of enantiopure monomers embedding a stereochemical center in their side chain.2]3] Our group demonstrated that achiral anions can be used to modulate the length and thus the selectivity of supramolecular helical catalysts based on benzene-1,3,5-tricarboxamide (BTA) monomers.4] We are now interesting in probing the possibility to use chiral ions as triggers of the formation of supramolecular helices by means of several strategies: i) using chiral triggers mainly composed of ammonium halides capable of interacting with (thio)urea function appended to a BTA backbone (Scheme 1a), ii) using ions as chiral chain stoppers (Scheme 1b).

Scheme 1. a) Chiral induction by interaction of chiral triggers with (thio)urea-containing BTA b) Amplification of chirality and length modulation controlled by the chain stopper

References

Probing achiral benzene-1,3,5-tricarboxamide monomers as inducers of homochirality in supramolecular helical catalysts

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Abstract: Adding a complementary achiral monomer, an additive, to macromolecules embedding a mixture of enantiopure monomers (the “sergeants”) and achiral monomers (the “soldiers”) is expected to decrease the optical purity of the polymer main chain because of the dilution of the “sergeant” in the generated terpolymer.[1] Herein, we report the influence of different achiral benzene-1,3,5-tricarboxamide (BTA) additives on the structural, chiroptical and catalytic properties of sergeants-and-soldiers type (S&S) mixtures composed of an achiral BTA ligand coordinated to copper and of an enantiopure BTA monomer derived from cyclohexylalanine. Whilst N,N’,N”-tris(octyl)benzene-1,3,5-tricarboxamide (BTA C8) shows no significant improvement in term of enantioselectivity (e.e.) of the catalytic reaction of reference, achiral BTA monomers derived from α,α’-disubstituted amino esters all led to an increase in the selectivity at low sergeant ratio. Both BTA C8 and the BTA derived from the ester of 1-aminocyclohexane carboxylic acid (BTA Achc), the best-performing additive,[2] were found to efficiently intercalate with the ligand and the sergeant leading to the formation of single helices. However, only the terpolymer embedding BTA Achc exhibits a cooperative assembly behavior that leads to long, stable, and homochiral coassemblies, accounting for the good e.e. even with only 0.25% of “sergeants” present in the supramolecular terpolymers.[3]

Figure 1. Achiral BTA additives led to an enhancement of the enantioselectivity of a catalytic reaction as result of their ability to induce homochirality (g values) in the supramolecular helical assemblies.

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References
**Abstract**

Polymersomes are self-assemblies of amphiphilic polymer molecules, organised in a spherical architecture, which can be employed for the incorporation and the delivery of molecules of interest (MOI) such as dyes or molecules with biological activities. \[1\] Control of the release of MOI is challenging and can be accomplished through polymersomes explosion via external visible light irradiation stimuli. The mechanism involves the irradiation of a photocleavable molecule, co-incorporated in the polymersome lumen, which can be excited and undergo heterolytically covalent bond breaking. \[2\] This process generates several fragments after irradiation from the initial molecule, leading to an increase of the osmotic pressure and resulting in the burst of the polymersome structure. Here we focus on the syntheses of dyes integrating alkylated-pyridinium electron acceptors as potential polymersome explosion initiators, by harnessing a mechanism based on a photo-induced electron transfer (PET) from the excited dye to the pyridinium motif. Subsequent fragmentation of the irradiated material induces an osmotic shock, destabilising the capsule and releasing MOI. \[3\] One advantage of such system is the use of longer wavelength light where the number of side reactions can be reduced. Relevant pyridinium-functionalised dyes can be activated by the absorption of blue (~460 nm), green (~550 nm) and red (~700 nm) light.

![Figure 1](image-url)  
*Figure 1.* Principle of polymersome explosion via PET and synthetized visible-light absorbing dyes.

**Acknowledgement**

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**References**

QUADRUPOLAR AND OCTUPOLAR CARBO-BENZENIC MESOGENS

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Abstract
Carbo-benzene derivatives, having a C18 macrocycle formally obtained by expansion of the C6 benzene ring by insertion of C2 units into its six carbon-carbon bonds, were shown to exhibit remarkable properties.[1] In the context of an international collaboration, the design, synthesis and study of a family of discotic mesogens based on the carbo-benzene core, called carbo-mesogens, was envisioned. The carbo-benzene macrocycle can indeed be considered as a modulable hexagonal platform, allowing for the introduction at its vertices of 2 to 6 dispersive groups made of lipidic pyrogallol or resorcinol ethers. A first example of quadrupolar carbo-mesogen bearing two dodecyl ether pyrogallol dispersive groups was shown to exhibit thermotropic liquid crystal properties, giving a rectangular columnar mesophase at 115°C, and to give 2D supramolecular assemblies.[2] The synthesis of new carbo-mesogens, both in the octupolar series with 3 dispersive groups, and in the quadrupolar series with 2 or 4 dispersive groups, was then envisaged with the aim of studying the influence on the mesogenic properties of the nature, the number, and the position of the dispersive groups on the C18 carbo-benzene ring.

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References
Towards a better control of the ligand coordination sphere(s) in supramolecular helical catalysts

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Abstract

Non-covalent interactions have recently been harnessed for the construction of ligands enabling more diverse structures for potentially efficient asymmetric catalysis. Our group is particularly interested in benzene-1,3,5-tricarboxamides (BTAs) and their derivatives, which are disk-like molecules decorated with hydrogen bonding moieties. These molecules are unique in their ability to form robust threefold hydrogen-bonded helical assemblies in apolar solvents. Co-assembly between an achiral BTA-phosphine monomer (“soldier”) and a chiral co-monomer (“sergeant”) yield homochiral supramolecular helical catalysts (S&S-mixtures) (Fig.1). This work looked at tuning supramolecular helices by varying the connecting units (linker) between the helices and the catalyst in order to gain a better control of the coordination sphere(s) of the metal. New supramolecular achiral BTA ligands para-BTA, meta-BTA, benzylic type (Bz) ligands (para-Bz-BTA and meta-Bz-BTA), and tropos achiral ligand (bpp-BTA) were evaluated in the copper-catalyzed asymmetric hydrosilylation reaction of a prochiral ketone (NPnone) yielding promising and divergent enantioselectivities.

Figure 1. S&S-mixtures in Hydrosilation of NPnone

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References

SWITCHABLE MOLECULAR TWEEZERS FOR STIMULI-RESPONSIVE ORGANOGEELS

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Abstract

In recent years, molecular machines[1] have attracted increasing interest for their ability to control motion at the molecular level. However, artificial systems are far from approaching the complexity of natural systems and exploiting their inherent properties to perform useful functions remains a major challenge. We are interested in harnessing the mechanical motion of molecular switches as an innovative approach to control physical or chemical properties at the molecular level.

We have developed a versatile family of switchable molecular tweezers based on a terpyridine ligand functionalized by metal-salen complexes. By switching the conformation of the terpyridine moiety using a coordination stimulus, the distance between the two functional salen complexes can be controlled. Drastic modulation of luminescence,[2] magnetic[3] or even catalytic[4] properties has been achieved using Pt(II), Cu(II) and Zn(II) salen moieties, respectively. A remarkable six-level system was also achieved by combining the ion-triggered mechanical motion with the redox activity of Ni(II)-salen complexes.[5] Our current work focuses on utilizing the mechanical motion of tweezers functionalized with alkyl chains as gelling groups for the development of multi-functional switchable organogels. The large structural reorganization driven by the mechanical motion results in reversible sol-gel transitions. The synthesis and characterization of the reversible gelation will be highlighted.

Acknowledgements

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References

Dissymmetric molecular tweezers for multifunctional systems

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

We aim to go a step further in the elaboration of multi-state multifunctional systems. As a proof of concept, we have shown that a six-level system can be achieved with the combination of three orthogonal stimuli for homonuclear tweezers.[5] To reach more advanced multi-state systems, dissymmetric molecular tweezers, based on a terpyridine switchable unit substituted by two different metal-salphen complexes, are being developed. Herein we wish to modulate the luminescence properties of heteronuclear tweezers by controlling Förster Resonance Energy Transfer between the two metal-salphen units. Zn-salphen and Pt-salphen were selected due to the overlap between the emission of Zn and the absorption of the Pt moiety. Due to the large intramolecular distance in the open form, we expect independent luminescence properties. However, the spatial proximity of the closed state should allow for strong transfer energy from the Zn to the Pt-salphen. The synthesis and studies of the heterometallic tweezers will be presented.

Figure 1 FRET properties obtained in the closed form of the dissymmetric tweezers.

References
Self-assembled Triazatruxene-based cages: structural and electronic properties

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Abstract
The coordination driven self-assembly methodology is of great interest as it provides access to discrete three-dimensional structures often unreachable by traditional covalent chemistry. Their synthesis is thermodynamically favored and geometrically predictable thanks to the reversibility and the high directionality of the coordination bond. Most of these polyhedra exhibit a cavity that can be used for host-guest binding, with possible applications in catalysis, remediation and drug delivery. In this context, our team has developed molecular hosts which are able to trigger the guest release thanks to a redox stimulation. Similarly to the case of macrocycles which allow the construction of 2-catenanes, the 3D cavity of coordination cages allows access to interpenetrated species, namely interlocked cages, the latter being characterized by a high compactness.

In this context, we have been interested in controlling the self-assembly process of an electron rich triazatruxene-based ligand (TaT) “L” with an electro-deficient bis-rhodium complex (Rhtpphz) “M”. This association leads, depending on the experimental conditions, to the selective formation of: i) a cage (M₃L₂), ii) two interlocked cages (M₆L₄) or iii) a host-guest complex (M₃L₄) (Figure 1) where the relative location of donating and accepting units is perfectly controlled. Details of their formation, their structure as well as their electronic properties will be presented.

Figure 1. The three structures which are obtained upon self-assembling ligand TaT (L) and complex Rhtpphz (M).

References
LIGHT-INDUCED CONFORMATIONAL CHANGE OF A LUMINESCENT HELICAL FOLDAMER

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Abstract

Over the last decades, supramolecular chemistry has allowed major breakthroughs in miscellaneous research and applied fields. In this context, and inspired by naturally-occurring molecules, chemists have dedicated much effort to design oligomers that fold into well-defined conformations and are named foldamers[1]. In particular, helical foldamers have shown their interest in the fields of catalysis[2], selective host-guest encapsulation[3] or more recently stimuli responsive materials[4]. Among the diversity of foldamer skeletons, some are able to hybridize and form multiple helices[5]. The latter present different geometrical features and hence, new physicochemical properties, which could be of interest to develop original materials with singular optoelectronic properties.

To this end, luminescent helical foldamers grafted with tetraphenylethylene units were designed and synthesized. Since this luminophore is well-known for its aggregation-induced fluorescence, we initially anticipated that the formation of the double helices would lead to a decreased conformational freedom and thus, to an increased quantum yield of emission in solution. Surprisingly, the first spectroscopic measurements have allowed to highlight an unexpected behaviour, which has sparked our curiosity. The presented results will show which photochemical reaction takes place upon irradiation and its impact over the conformation of the foldamer backbone.

References

CU(I)-ASSISTED FORMATION OF A STERICALLY CONGESTED ROTAXANE

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Abstract
In the literature, two main strategies have been reported for the selective synthesis of stable heteroleptic bis-phenanthroline copper(I) complexes. The first is based on topological constraints and was introduced by Sauvage et al. [1] and has been largely exploited for the preparation of rotaxanes, catenanes and molecular machines [2]. The second approach was mainly developed by Schmittel et al. and is based on steric constraints [3] and has been used for the construction of multi-component supramolecular architectures like for instance nanoboxes, rectangles, or tweezers [4]. The aim of the present research project was the preparation of heteroleptic copper(I) complexes via the steric control concept. Correspondingly, a phenanthroline ligand carrying very bulky polyaromatic substituents at the 2,9-positions has been synthesized. After having proven that the homoleptic complex cannot be formed, a series of heteroleptic complexes has been successfully prepared with four different NN-type ligands [5]. Likewise, starting from a macrocyclic phenanthroline ligand, we succeeded in the preparation of a rotaxane (Fig. 1), which will be presented herein. This is the first example of a copper(I) complex combining both topological and steric constraints.

Figure 1. Calculated structure of the Cu(I)-centered rotaxane.

References
Dy[n]arenes: their new supramolecular architectures and applications

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Abstract

Dy[n]arenes are macrocyclic cavitands product by the combination of thiol-containing building-blocks when exposed to O2.[1] Their synthesis by using Dynamic Combinatorial Chemistry (DCC) present the advantage to be able to obtain different sizes of macrocycles with the same building-block only by changing the stimulus applied to the system.[2] Different strategies have been tried in order to amplify and enantioenriched the Dynamic Combinatorial Library (DCL).[3] One of them consist in the formation of a supramolecular “totem”, with a metallic centre crowned by a cyclodextrin.[4] In addition of being versatile objects of study,[1][3][5] dy[n]arenes present the capacity to be useful for a broad range of applications,[6] such as the capture of CO2, as interesting as complex to elucidate.

Once upon a time in the CO2

Starring:

The Hunt of the DAJtons

Starring:

References

Cyclodextrin enhanced synthesis of chiral cobalt complexes
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Abstract
Asymmetric induction, which consists in transferring chirality, is one of the biggest challenge in chemistry. It was awarded a Nobel prize in 2021, through the topic of organocatalysis[1]. In this case, chiral induction is generally performed by covalent means, with sterically hindered enantiopure catalysts[2].

Herein, we explore the possibility of inducing chirality on well-known and described cobalt (III) complexes, through the use of supramolecular interactions. In the present case, the chiral inductor is α-cyclodextrin, a readily available macrocyclic oligosaccharide. Previous example showed the added value of α-cyclodextrin in the enantio-enrichment of organometallic complexed upon repeated crystallization steps[3][4]. In this study, we demonstrate that enantio-enriched complexed can be readily assembled from achiral ligands in the presence of chiral inductors in water.

We herein present the first results obtained, i.e. the studies performed which allowed us to identify the conditions affording new enantio-enriched complexes whose structure was elucidated. The long term goal of this project consist in relaying chirality transfer on long range through the sequential self-assembling of interacting architectures, leading to a supramolecular chiral totem.

References
Foldamers constitute a new family of oligomers that adopt well-defined architectures stabilized by non-covalent interactions. They are mostly inspired by the complexity and the amazing variety of functions in biomacromolecules. The latter find numerous applications related to biology, molecular recognition, catalysis, or more recently, stimuli responsive materials. Among the wide diversity of building blocks allowing for the construction of foldamers, some of these structures fold into helical form and hybridize to form double and multiple helices. The corresponding dynamics proved to be affected by parameters, such as temperature, concentration and solvent. However, controlling this equilibrium in a reversible manner remained largely unexplored until recently. In this context, we explored the possibility to tune the homoduplex formation through redox stimulations (Fig.1). This challenge was first tackled with tetrathiafulvalene-based foldamers endowed with five-pyridyl rings. Herein, we focus on the generalization of this strategy to longer oligomers and on our recent efforts to extend this concept to double helices made up of two complementary strands and called heteroduplexes (Fig.1).

Figure 1. Schematic representation of the redox-controlled hybridization of foldamers into homoduplexes and heteroduplex formation through donor-acceptor interactions.

References

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Calix[4]arenes are bowl-shaped macrocyclic molecules that have attracted great interest in supramolecular chemistry because they are synthesized from accessible and cheap starting materials and because of the possibility for decoration of the calix[4]arene structure with different functional groups, at both wide (upper) and narrow (lower) rims.1,2 Properly designed molecules can possess useful properties for application in biomedicine, nanoscience, sensor development or catalysis. Among numerous functionalised calix[4]arenes, chiral derivatives are of particular interest but have been much less used in asymmetric catalysis than in other fields.

Recently, we started to test chiral calixarenes in asymmetric catalysis.3 We now want to report a simple and efficient method for preparation of two types of inherently chiral calix[4]arene phosphoric acids (ABHH and ABCH) with programmed disposition of H-bond donor functional groups on the narrow rim in high yields and the first tests of this Brønsted acids with inherent chirality only in organocatalyzed reactions. To the best of our knowledge, calixarenes bearing phosphorylhydroxy groups have not yet been explored in asymmetric organocatalysis to the best of our knowledge while chiral phosphoric acids have been so successfully used as organocatalysts.4

References
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