Société Chimique de France
Le réseau des chimistes

N° 02
Avril 2023

La SupInfo

Les infos du Groupe de Chimie Supramoléculaire

SOMMAIRE

LE MOT DU PRÉSIDENT

Cher.ère.s sociétaires,

Notre bureau est très heureux de vous proposer le deuxième numéro de notre gazette semestrielle, *La SupInfo*.

Si ce n’est pas déjà fait, nous vous invitons à découvrir dans nos « Actualités récentes » le premier épisode de Pod’Chem, une nouvelle série d'émissions de discussion scientifique autour de la chimie diffusée sur YouTube.

Vous trouverez aussi dans ce numéro deux nouvelles rubriques : « Un point sur… » qui propose la présentation accessible d’un concept fort en chimie supramoléculaire, et « À la rencontre de… » qui propose de connaitre un peu mieux l’une ou l’un des membres remarquables de notre groupe thématique.

Nous espérons également vous voir nombreux début juin à Montpellier pour la 2ème édition des Journées de Chimie Supramoléculaire qui sont une occasion unique pour notre communauté de se retrouver chaque année. Tous les détails sur cette manifestation sont à retrouver dans la rubrique « À vos agendas ».

Finalement, ne manquez pas « Notre sélection d’articles » publiés au cours des 6 derniers mois par nos sociètaires.

Au nom des membres du bureau de SupraSCF, je vous souhaite une bonne lecture.

Bien cordialement,

Laurent Vial, Président du Groupe SupraSCF

T0105-713- F: 0,00 €

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ACTUALITÉS RÉCENTES

Pod’Chem

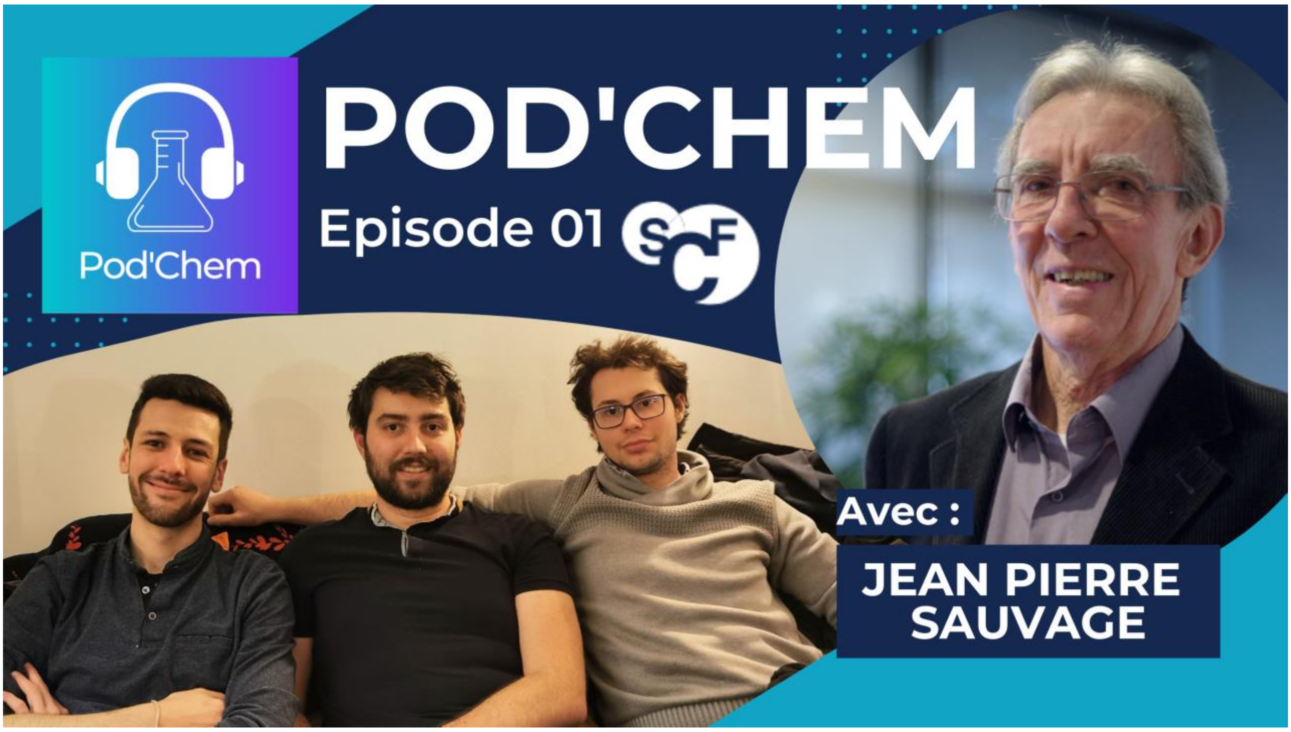
Sous le patronage du groupe SupraSCF, nous sommes très heureux de vous présenter une nouvelle série d'émissions de discussion scientifique autour de la chimie. Pod’Chem a pour ambition de proposer un nouveau moyen de communication dynamique, accessible et compréhensible du monde de la recherche en chimie.

Animée par 3 étudiants lyonnais, l’invité de marque de cette première émission est Jean-Pierre Sauvage, Prix Nobel de Chimie 2016.

Vous pouvez trouver cet épisode ici: https://www.youtube.com/watch?v=RWuyQzlgVvk

Un deuxième épisode est déjà en préparation, et nous sommes impatients de vous le proposer très prochainement sur cette nouvelle chaine YouTube !

Marc Hennebelle, Maxime Ducreux & Titouan Chetot



À VOS AGENDAS

Les Journées de Chimie Supramoléculaire 2023

Le groupe thématique de Chimie Supramoléculaire de la Société Chimique de France organisera la prochaine édition des Journées de Chimie Supramoléculaire (JCS) du 1er juin (14h) au 2 juin (12h) 2023 à Montpellier. Cette 2nde édition sera l'occasion pour la communauté de Chimie Supramoléculaire française de se retrouver et de partager leurs résultats dans une atmosphère stimulante et conviviale. 3 conférences plénières sont prévues, ainsi que 14 créneaux pour des communications orales (en anglais) et 1 session de présentations par posters.

Frais d'inscription :
Participant membre SCF : 50 €
Participant non-membre SCF : 100 €
Étudiant, doctorant et post-doctorant membre SCF : 0 €
Étudiant, doctorant et post-doctorant non-membre SCF : 50 €

Date limite d'inscription :
14 avril 2023

Pour plus d'informations et pour déposer un résumé, visitez https://jcs2023.sciencesconf.org

Au plaisir de vous retrouver à Montpellier.

Le comité d'organisation : Damien Bourgeois & Sébastien Ulrich.

SOCIÉTE CHIMIQUE DE FRANCE

GROUPE THÉMATIQUE CHIMIE SUPRAMOLÉCULAIRE

JCS2023

2nde Journée de Chimie Supramoléculaire

MONTPELLIER • 1 - 2 JUIN 2023

3 PLENARY LECTURES:

Dr. Anne-Marie CAMINADE, LCC, CNRS, Toulouse
2022 André Collet prize laureate
Supramolecular interactions of phosphorus dendrimers and their applications in catalysis, materials, and biology

Pr. Thomas HERMANS, Université de Strasbourg
2022 Christine Dietrich-Buchecker prize laureate
Controlling self-assembly by chemical fuels and light

Dr. Mihail D. BARBOIU, IEM, CNRS, Université de Montpellier
Artificial Water Channels-toward Biomimetic Membranes for Desalination

+ 14 ORAL COMMUNICATIONS + 1 POSTER SESSION + 4 PRIZES FOR BEST COMMUNICATION

Deadline for abstract submission: 14 April 2023
Program & Registration (deadline 5 May 2023) at: https://jcs2023.sciencesconf.org

UN POINT SUR…LA COOPÉRATIVITÉ

La coopérativité reste sans doute à ce jour l'un des Graals de la chimie supramoléculaire.[1] L'IUPAC en donne la définition suivante : *l'association d'un partenaire moléculaire (par exemple un invité) sur un premier site d'un récepteur, modifie la conformation de ce dernier tant et si bien que l'association d'un second partenaire sur un site voisin du premier est favorablement modifiée*.[2] Le concept peut s'appréhender grossièrement par le biais d''analogies renvoyant au macroscopique et notamment à la vie humaine : imaginons qu'un hôte reçoive autour d'une grande tablée. La motivation des derniers invités à rejoindre leur place (et le temps qu'il passeront in fine à table ou à dissiper leur énergie sur la piste de danse) est souvent dépendante de la qualité des interactions qu'ils développeront avec celles et ceux qui occupent les places voisines ! On comprend dès lors qu'il peut ou pas y avoir coopérativité et que celle-ci peut être soit positive, soit négative.

La coopérativité concerne notamment les systèmes moléculaires qui comprennent au moins une architecture multivalente (la tablée), i.e. équipés de plusieurs sites géographiquement distincts, chacun d'entre eux pouvant développer son propre jeu d'interactions non covalentes avec un partenaire, qui peut être distinct ou bien lui-même (dans ce cas, notre table possède des rallonges et se replie sur elle-même). Les exemples les plus emblématiques de systèmes coopératifs nous viennent du monde du vivant. Ce sont les biomacromolécules ubiquitaires sélectionnées par l'évolution comme les protéines fortement structurées, celles transportant de petites molécules-invitées comme l'hémoglobine ou encore la double hélicé d'ADN. La coopérativité se manifeste lors de la variation graduelle d'un paramètre physique (température, pression) ou chimique (concentration en partenaire, en agent dénaturant) par le biais d'une transition conformationnelle, d'une agrégation ou d'une association avec un/des partenaires. Le dénominateur commun est la formation/rupture concertée (en cascade) de liaisons non covalentes intra- ou intermoléculaires.

Dans le premier cas, on passe d'un état parfaitement replié à totalement désordonné, dans le second d'un taux d'occupation nul (tablée vide) a un taux d'occupation plein (tablée remplie), dans le dernier de deux simples brins à un double brin (fermeture éclair totalement ouverte ou fermée). On comprend donc au passage que la conséquence d'une coopérativité positive est le dépeuplement des états intermédiaires (partiellement replié / occupé / hybridé). Ceux-ci sont pourtant intrinsèquement favorisés entropiquement, car de nombreux micro-états correspondent souvent à chacun de ces macro-états intermédiaires (imaginons les permutations possibles des invités autour d'une table ronde à moitié pleine, selon la même séquence de voisins). Le corollaire est donc que la coopérativité est (du point de vue des solutés tout au moins) un phénomène plutôt de nature enthalpique, chaque état extrême étant non-dégénéré mais hautement favorisé du fait de l'optimisation étendue d'interactions non covalentes.[3]

Au-delà des architectures multi-sites, la coopérativité se manifeste à également au sein d'assemblées d'objets simples, identiques ou différents, mais ayant la capacité de s'auto-assembler ou s'auto-agréger. Sous les événements familiers de micellisation et cristallisation se cache bien souvent la coopérativité. Au-delà d'une concentration critique, les interactions entre ces briques moléculaires, bien qu'individuellement faibles, induisent une auto-association spontanée vers des états remarquablement organisés. La coopérativité est donc l'exception au dogme qui affirme que des constructions solides ne peuvent être bâties qu'à partir d'interactions individuellement fortes. Cette leçon de vie, l'humain l'a expérimenté au cours de son histoire mais elle mérite souvent de lui être rappelée. D'un regroupement d'individus peuvent émerger des phénomènes collectifs qui transcendent les contributions individuelles, soit dans le positif (la performance sportive d'une équipe, l'harmonie d'une chorale ou d'un orchestre), soit dans le négatif (débordements et mouvements de foule). Chacun sait qu'il faut plus qu'une collection de talents individuels incapables de coopérer pour accomplir une grande œuvre commune. A contrario, l'histoire est ponctuée de grandes victoires remportées par des collectifs dont les apports individuels pouvaient sembler modeste sur le papier, mais qui articulées avec synergie, ont accompli des miracles.

Cet article a été rédigé par Julien Leclaire, Professeur à l'Université Claude Bernard Lyon 1
(julien.leclaire@univ-lyon1.fr)

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[1] C. A. Hunter, H. L. Anderson, *Angew. Chem. Int. Ed.* **2009**, *48*, 7488–7499.

[2] *IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). Online version (2019-) created by S. J. Chalk. ISBN 0-9678550-9-8. https://doi.org/10.1351/goldbook.*

[3] Pour un des rares exemples de coopérativité d'origine entropique, voir : D. Shimoyama, T. Haino, *Chem. Eur. J.* **2020**, *26*, 3074-3079.

À LA RENCONTRE DE…IVAN HUC

Carrière:

Depuis 2017:	Professeur, Faculté de Chimie et de Pharmacie, Université Louis et Maximilien, Munich (Allemagne)
1998-2017:	Chargé puis directeur de recherche CNRS, Institut Européen de Chimie et Biologie (Université de Bordeaux)
1995-1998:	Chargé de recherché CNRS, Université de Strasbourg
1994-1995:	Post-Doc, Université de Strasbourg

Formation:

1994	Doctorat en Chimie de l'Université Paris VI pour des recherches effectuées à l'ENS (Paris) et au MIT (Cambridge, USA)
1991	Maîtrise et DEA en chimie organique, ENS, Paris

Ma première expérience en laboratoire a été si passionnante que j'ai arrêté d'aller en cours pour y passer plus de temps, ce qui a ensuite causé quelques difficultés…

Les jeunes devraient s'intéresser à la chimie supramoléculaire car elle est omniprésente, de la physique de la matière molle à la biologie moléculaire, en passant par les matériaux, l'état solide, et la conception de médicaments.

La chose la plus excitante dans mes recherches, et en recherche en général, est l'absence de limite du champ à explorer. Alors que notre planète entière apparait dorénavant petite et se trouve sous la contrainte de l'activité humaine, le champ du savoir offrira toujours de l'espace aux explorateurs de demain.

Ma devise (au laboratoire) est que les molécules ont davantage d'imagination que nous et que l'on doit s'attendre à être surpris. Comme a dit Pasteur : la chance ne sourit qu'aux esprits bien préparés.

Ce que je préfère (et que je cultive) dans mon groupe de recherche est la diversité des façons de bien faire et de penser.

Si je n'avais pas fait carrière dans la chimie, je serais géologue. Les chimistes n'ont guère l'occasion d'être sur le terrain. Et donc :

Mon endroit préféré pour passer des vacances est sur un sentier de haute montagne.

Intérêts de recherche : ingénierie de la forme des molécules

Les foldamères aromatiques : des molécules de synthèse adoptant des conformations repliées bien définies ; leurs applications en reconnaissance moléculaire, en catalyse, dans des machines moléculaires et des matériaux organiques ; la chimie supramoléculaire biomimétique ; l'inhibition des interactions protéine-protéine et protéine-acides nucléiques ; l'élucidation cristallographique de structures moléculaires par diffraction des rayons X.

Page web: https://huc.cup.uni-muenchen.de/

Quelques prix et distinctions : lauréat national des olympiades de la chimie (au lycée), médaille d'argent du CNRS (2012), grand prix « Mme Victor Noury » de l'Académie des Sciences (2015), Prix international « Izatt-Christensen » de chimie macrocyclique et supramoléculaire, Prix « Michel Delalande » de l'Académie Nationale de Pharmacie (2022), ERC advanced grant (2012 et 2022).

Cinq références significatives :

C. G. Pappas, P. K. Mandal, B. Liu, B. Kauffmann, X. Miao, D. Komáromy, W. Hoffmann, C. Manz, R. Chang, K. Liu, K. Pagel, I. Huc, S. Otto, Emergence of low-symmetry foldamers from single monomers, *Nat. Chem.* **2020**, *12*, 1180.

K. Ziach, C. Chollet, V. Parissi, P. Prabhakaran, M. Marchivie, V. Corvaglia, P. P. Bose, K. Laxmi-Reddy, F. Godde, J.-M. Schmitter, S. Chaignepain, P. Pourquier, I. Huc, Single helically folded aromatic oligoamides that mimic the charge surface of double-stranded B-DNA, *Nat. Chem.* **2018**, *10*, 511.

S. De, B. Chi, T. Granier, T. Qi, V. Maurizot, I. Huc, Designing cooperatively folded abiotic uni- and multimolecular helix bundles, *Nat. Chem.* **2018**, *10*, 51.

N. Chandramouli, Y. Ferrand, G. Lautrette, B. Kauffmann, C. D.Mackereth, M. Laguerre, D. Dubreuil, I. Huc, Iterative design of a helically folded aromatic oligoamide sequence for the selective encapsulation of fructose, *Nat. Chem.* **2015**, *7*, 334.

Q. Gan, Y. Ferrand, C. Bao, B. Kauffmann, A. Grélard, H. Jiang, I. Huc, Helix-rod host-guest complexes with shuttling rates much faster than disassembly, *Science* **2011**, *331*, 1172.

NOTRE SÉLECTION D'ARTICLES

Le bureau du Groupe SupraSCF met en avant chaque semestre une sélection d'articles dont les auteur.rice.s sont membres de notre groupe thématique.
Vous trouverez ici un choix d'articles publiés sur la période Nov. 2022 - Mars 2023 dans les journaux suivants :
- *J. Am. Chem. Soc.*
- *Nat. Chem.*
- *Chem. Sci.*
- *Angew. Chem. Int. Ed.*
- *Chem. Comm.*
- *Chem. Eur. J.*

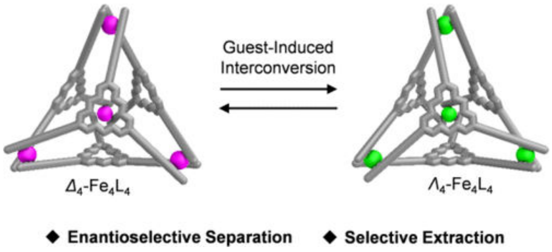
Cette sélection est évidemment subjective. N'hésitez pas à nous soumettre des propositions de travaux à mettre en avant.

Subtle Stereochemical Effects Influence Binding and Purification Abilities of an FeII4L4 Cage

W. Xue, L. Pesce, A. Bellamkonda, T. K. Ronson, K. Wu, D. Zhang, N. Vanthuyne, T. Brotin, A. Martinez, G. M. Pavan, J. R. Nitschke

J. Am. Chem. Soc. **2023**, 145, 5570–5577

DOI: 10.1021/jacs.3c00294



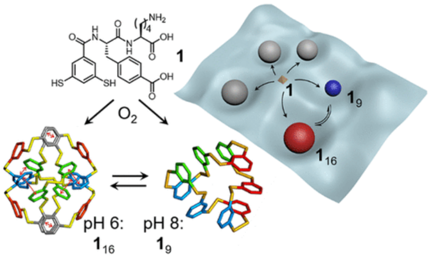
Abstract: A tetrahedral Fe$^{II}_4$L$_4$ cage assembled from the coordination of triangular chiral, face-capping ligands to iron(II). This cage exists as two diastereomers in solution, which differ in the stereochemistry of their metal vertices, but share the same point chirality of the ligand. The equilibrium between these cage diastereomers was subtly perturbed by guest binding. This perturbation from equilibrium correlated with the size and shape fit of the guest within the host; insight as to the interplay between stereochemistry and fit was provided by atomistic well-tempered metadynamics simulations. The understanding thus gained as to the stereochemical impact on guest binding enabled the design of a straightforward process for the resolution of the enantiomers of a racemic guest.

(Re-)Directing Oligomerization of a Single Building Block into Two Specific Dynamic Covalent Foldamers through pH

Y. Jin, P. K. Mandal, J. Wu, N. Böcher, I. Huc, S. Otto

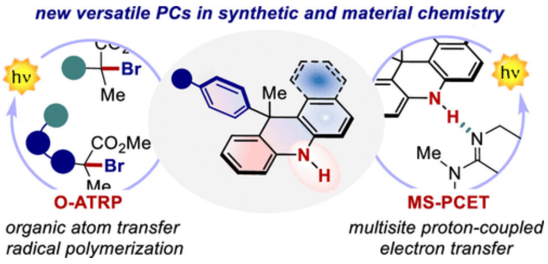
J. Am. Chem. Soc. **2023**, *145*, 2822–2829

DOI: 10.1021/jacs.2c09325



Abstract: Dynamic foldamers are synthetic folded molecules which can change their conformation in response to an external stimulus and are currently at the forefront of foldamer chemistry. However, constitutionally dynamic foldamers, which can change not only their conformation but also their molecular constitution in response to their environment, are without precedent. We now report a size- and shape-switching small dynamic covalent foldamer network which responds to changes in pH. Specifically, acidic conditions direct the oligomerization of a dipeptide-based building block into a 16-subunit macrocycle with well-defined conformation and with high selectivity. At higher pH the same building block yields another cyclic foldamer with a smaller ring size (9mer). The two foldamers readily and repeatedly interconvert upon adjustment of the pH of the solution. We have previously shown that addition of a template can direct oligomerization of the same building block to yet other rings sizes (including a 12mer and a 13mer, accompanied by a minor amount of 14mer). This brings the total number of discrete foldamers that can be accessed from a single building block to five. For a single building block system to exhibit such highly diverse structure space is unique and sets this system of foldamers apart from proteins. Furthermore, the emergence of constitutional dynamicity opens up new avenues to foldamers with adaptive behavior.

The Rational Design of Reducing Organophotoredox Catalysts Unlocks Proton-Coupled Electron-Transfer and Atom Transfer Radical Polymerization Mechanisms



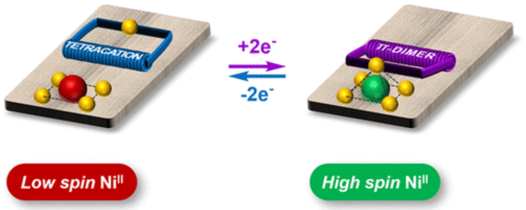
T. Bortolato, G. Simionato, M. Vayer, C. Rosso, L. Paoloni, E. M. Benetti, A. Sartorel, D. Lebœuf, L. Dell'Amico

J. Am. Chem. Soc. **2023**, *145*, 1835–1846

DOI: 10.1021/jacs.2c11364

Abstract: Photocatalysis has become a prominent tool in the arsenal of organic chemists to develop and (re)imagine transformations. However, only a handful of versatile organic photocatalysts (PCs) are available, hampering the discovery of new reactivities. Here, we report the design and complete physicochemical characterization of 9-aryl dihydroacridines (9ADA) and 12-aryl dihydrobenzoacridines (12ADBA) as strong reducing organic PCs. Punctual structural variations modulate their molecular orbital distributions and unlock locally or charge-transfer (CT) excited states. The PCs presenting a locally excited state showed better performances in photoredox defunctionalization processes (yields up to 92%), whereas the PCs featuring a CT excited state produced promising results in atom transfer radical polymerization under visible light (up to 1.21 *Đ*, and 98% I*). Unlike all the PC classes reported so far, 9ADA and 12ADBA feature a free NH group that enables a catalytic multisite proton-coupled electron transfer (MS-PCET) mechanism. This manifold allows the reduction of redox-inert substrates including aryl, alkyl halides, azides, phosphate and ammonium salts (E_{red} up to −2.83 vs SCE) under single-photon excitation. We anticipate that these new PCs will open new mechanistic manifolds in the field of photocatalysis by allowing access to previously inaccessible radical intermediates under one-photon excitation.

Ni-Centered Coordination-Induced Spin-State Switching Triggered by Electrical Stimulation



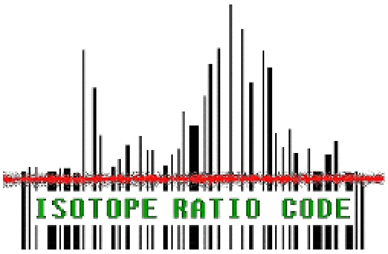
S. Al Shehimy, O. Baydoun, S. Denis-Quanquin, J.-C. Mulatier, L. Khrouz, D. Frath, E. Dumont, M. Murugesu, F. Chevallier, C. Bucher

J. Am. Chem. Soc. **2022**, *144*, 17955–17965

DOI: 10.1021/jacs.2c07196

Abstract: We herein report the synthesis and magnetic properties of a Ni(II)-porphyrin tethered to an imidazole ligand through a flexible electron-responsive mechanical hinge. The latter is capable of undergoing a large amplitude and fully reversible folding motion under the effect of electrical stimulation. This redox-triggered movement is exploited to force the axial coordination of the appended imidazole ligand onto the square-planar Ni(II) center, resulting in a change in its spin state from low spin ($S = 0$) to high spin ($S = 1$) proceeding with an 80% switching efficiency. The driving force of this reversible folding motion is the π-dimerization between two electrogenerated viologen cation radicals. The folding motion and the associated spin state switching are demonstrated on the grounds of NMR, (spectro)electrochemical, and magnetic data supported by quantum calculations.

Isotope Ratio Encoding of Sequence-Defined Oligomers



M. Zwillinger, L.Fischer, G. Sályi, S. Szabó, M. Csékei, I. Huc, A. Kotschy

J. Am. Chem. Soc. **2022**, *144*, 19078–19088

DOI: 10.1021/jacs.2c08135

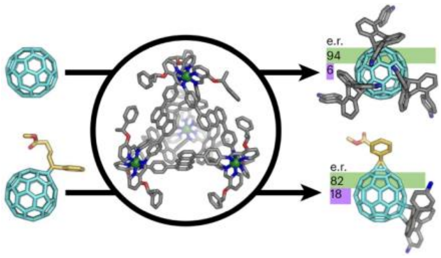
Abstract: Information storage at the molecular level commonly entails encoding in the form of ordered sequences of different monomers and subsequent fragmentation and tandem mass spectrometry analysis to read this information. Recent approaches also include the use of mixtures of distinct molecules noncovalently bonded to one another. Here, we present an alternate isotope ratio encoding approach utilizing deuterium-labeled monomers to produce hundreds of oligomers endowed with unique isotope distribution patterns. Mass spectrometric recognition of these patterns then allowed us to directly readout encoded information with high fidelity. Specifically, we show that all 256 tetramers composed of four different monomers of identical constitution can be distinguished by their mass fingerprint using mono-, di-, tri-, and tetradeuterated building blocks. The method is robust to experimental errors and does not require the most sophisticated mass spectrometry instrumentation. Such isotope ratio-encoded oligomers may serve as tags that carry information, but the method mainly opens up the capability to write information, for example, about molecular identity, directly into a pure compound via its isotopologue distribution obviating the need for additional tagging and avoiding the use of mixtures of different molecules.

Enantioselective fullerene functionalization through stereochemical information transfer from a self-assembled cage

Z. Lu, T. K. Ronson, A. W. Heard, S. Feldmann, N. Vanthuyne, A. Martinez, J. R. Nitschke

Nat. Chem. **2023**, *15*, 405–412

DOI: 10.1038/s41557-022-01103-y



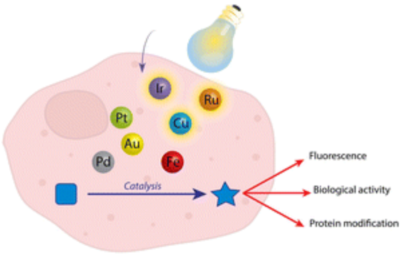
Abstract: The regioselective functionalization of C_{60} remains challenging, while the enantioselective functionalization of C_{60} is difficult to explore due to the need for complex chiral tethers or arduous chromatography. Metal–organic cages have served as masks to effect the regioselective functionalization of C_{60}. However, it is difficult to control the stereochemistry of the resulting fullerene adducts through this method. Here we report a means of defining up to six stereocentres on C_{60}, achieving enantioselective fullerene functionalization. This method involves the use of a metal–organic cage built from a chiral formylpyridine. Fullerenes hosted within the cavity of the cage can be converted into a series of C_{60} adducts through chemo-, regio- and stereo-selective Diels–Alder reactions with the edges of the cage. The chiral formylpyridine ultimately dictates the stereochemistry of these chiral fullerene adducts without being incorporated into them. Such chiral fullerene adducts may become useful in devices requiring circularly polarized light manipulation.

Metal complexes for catalytic and photocatalytic reactions in living cells and organisms

H. Madec, F. Figueiredo, K. Cariou, S. Roland, M. Sollogoub, G. Gasser

Chem. Sci, **2023**, *14*, 409-442

DOI: 10.1039/D2SC05672K



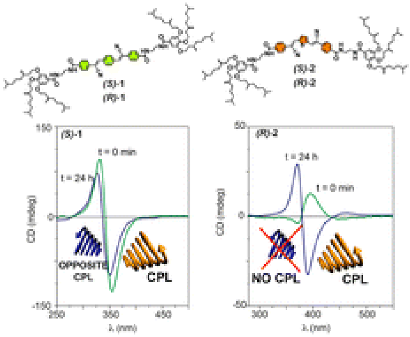
Abstract: The development of organometallic catalysis has greatly expanded the synthetic chemist toolbox compared to only exploiting "classical" organic chemistry. Although more widely used in organic solvents, metal-based catalysts have also emerged as efficient tools for developing organic transformations in water, thus paving the way for further development of bio-compatible reactions. However, performing metal-catalysed reactions within living cells or organisms induces additional constraints to the design of reactions and catalysts. In particular, metal complexes must exhibit good efficiency in complex aqueous media at low concentrations, good cell specificity, good cellular uptake and low toxicity. In this review, we focus on the presentation of discrete metal complexes that catalyse or photocatalyse reactions within living cells or living organisms. We describe the different reaction designs that have proved to be successful under these conditions, which involve very few metals (Ir, Pd, Ru, Pt, Cu, Au, and Fe) and range from *in cellulo* deprotection/decaging/activation of fluorophores, drugs, proteins and DNA to *in cellulo* synthesis of active molecules, and protein and organelle labelling. We also present developments in bio-compatible photo-activatable catalysts, which represent a very recent emerging area of research and some prospects in the field.

Stereomutation and chiroptical bias in the kinetically controlled supramolecular polymerization of cyano-luminogens

L. López-Gandul, C. Naranjo, C. Sánchez, R. Rodríguez, R. Gómez, J. Crassous, L. Sánchez

Chem. Sci. **2022**, *13*, 11577-11584

DOI: 10.1039/D2SC03449B



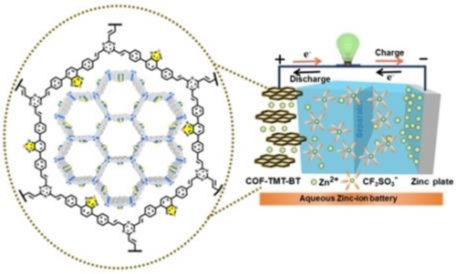
Abstract: The synthesis of two pairs of enantiomeric cyano-luminogens **1** and **2**, in which the central chromophore is a *p*-phenylene or a 2,5-dithienylbenzene moiety, respectively, is described and their supramolecular polymerization under kinetic and thermodynamic control investigated. Compounds **1** and **2** form supramolecular polymers by quadruple H-bonding arrays between the amide groups and the π-stacking of the central aromatic moieties. In addition, the peripheral benzamide units are able to form intramolecularly H-bonded pseudocycles that behave as metastable monomer **M*** thus affording kinetically and thermodynamically controlled aggregated species AggI and AggII. The chiroptical and emissive features of compounds **1** and **2** strongly depend on the aggregation state and the nature of the central aromatic unit. Compounds **1** exhibit a bisignated dichroic response of different intensity but with similar sign for both AggI$_1$ and AggII$_1$ species, which suggests the formation of helical aggregates. In fact, these helical supramolecular polymers can be visualized by AFM imaging. Furthermore, both AggI and AggII species formed by the self-assembly of compounds **1** show CPL (circularly polarized light) activity of opposite sign depending on the aggregation state. Thienyl-derivatives **2** display dissimilar chiroptical, morphological and emissive characteristics for the corresponding kinetically and thermodynamically controlled aggregated species AggI and AggII in comparison to those registered for compounds **1**. Thus, a stereomutation phenomenon is observed in the AggI$_2$ → AggII$_2$ conversion. In addition, AggI$_2$ is arranged into nanoparticles that evolve to helical aggregates to afford AggII$_2$. The dissimilar chiroptical and morphological features of AggI$_2$ and AggII$_2$ are also appreciated in the emissive properties. Thus, whilst AggI$_2$ experiences a clear AIE (aggregation induced emission) process and CPL activity, the thermodynamically controlled AggII$_2$ undergoes an ACQ (aggregation caused quenching) process in which the CPL activity is cancelled.

Supramolecular Engineering of Cathode Materials for Aqueous Zinc-ion Energy Storage Devices: Novel Benzothiadiazole Functionalized Two-Dimensional Olefin-Linked COFs

H. Peng, S. Huang, V. Montes-García, D. Pakulski, H. Guo, F. Richard, X. Zhuang, P. Samorì, A. Ciesielski

Angew Chem. Int. Ed. **2023**, *62*, e202216136

DOI: 10.1002/anie.202216136



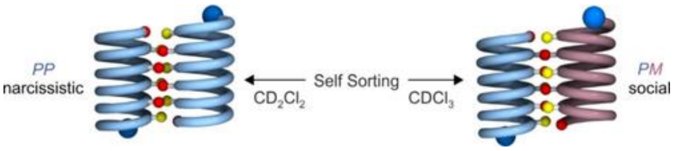
Abstract: We report a novel and structurally robust olefin-linked covalent organic frameworks (COFs), where benzothiadiazole units are explored as novel electrochemically-active groups. Our COFs exhibit an outstanding Zn^{2+} storage capability, delivering a state-of-the-art capacity of 283.5 mAh g^{-1} at 0.1 A g^{-1}. We shed light onto the charge-storage mechanism through the benzothiadiazole units in the COFs electrodes via computational and experimental analyses.

Homochiral versus Heterochiral Dimeric Helical Foldamer Bundles: Chlorinated-Solvent-Dependent Self-Sorting

F. S. Menke, B. Wicher, V. Maurizot, Ivan Huc

Angew Chem. Int. Ed. **2023**, *62*, e202217325

DOI: 10.1002/anie.202217325



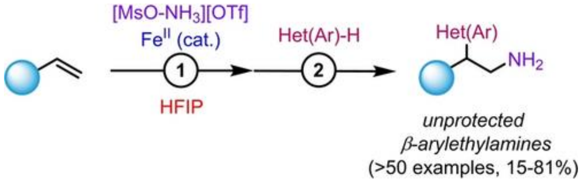
Abstract: Aromatic oligoamide sequences programmed to fold into stable helical conformations were designed to display a linear array of hydrogen-bond donors and acceptors at their surface. Sequences were prepared by solid-phase synthesis. Solution ^1H NMR spectroscopic studies and solid-state crystallographic structures demonstrated the formation of stable hydrogen-bond-mediated dimeric helix bundles that could be either heterochiral (with a *P* and an *M* helix) or homochiral (with two *P* or two *M* helices). Formation of the hetero- or homochiral dimers could be driven quantitatively using different chlorinated solvents—exemplifying a remarkable case of either social or narcissistic chiral self-sorting or upon imposing absolute handedness to the helices to forbid *PM* species.

Synthesis of Unprotected β-Arylethylamines by Iron(II)-Catalyzed 1,2-Aminoarylation of Alkenes in Hexafluoroisopropanol

V. Pozhydaiev, M. Vayer, C. Fave, J. Moran, D. Lebœuf

Angew Chem. Int. Ed. **2023**, *62*, e202215257

DOI: 10.1002/anie.202215257



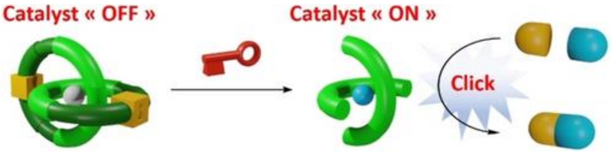
Abstract: β-Arylethylamines are prevalent structural motifs in molecules exhibiting biological activity. Here we report a sequential one-pot protocol for the 1,2-aminoarylation of alkenes with hydroxylammonium triflate salts and (hetero)arenes. Unlike existing methods, this reaction provides a direct entry to unprotected β-arylethylamines with remarkable functional group tolerance, allowing key drug-oriented functional groups to be installed in a two-step process. The use of hexafluoroisopropanol as a solvent in combination with an iron(II) catalyst proved essential to reaching high-value nitrogen-containing molecules.

Stimuli-Responsive Catenane-Based Catalysts

A. Bessaguet, Q. Blancart-Remaury, P. Poinot, I. Opalinski, S. Papot.

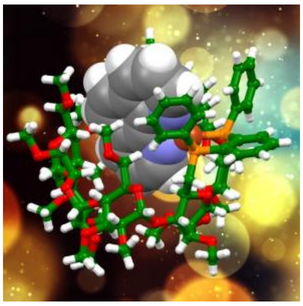
Angew Chem. Int. Ed. **2023**, *62*, e202216787

DOI: 10.1002/anie.202216787



Abstract: Rotaxanes and molecular knots exhibit particular properties resulting from the presence of a mechanical bond within their structure that maintains the molecular components interlocked in a permanent manner. On the other hand, the disassembly of the interlocked architecture through the breakdown of the mechanical bond can activate properties which are masked in the parent compound. Herein, we present the development of stimuli-responsive Cu^I-complexed [2]catenanes as OFF/ON catalysts for the copper-catalyzed alkyne-azide cycloaddition (CuAAC) reaction. The encapsulation of the Cu^I ion inside the [2]catenanes inhibits its ability to catalyze the formation of triazoles. In contrast, the controlled opening of the two macrocycles induces the breaking of the mechanical bond, thereby restoring the catalytic activity of the Cu^I ion for the CuAAC reaction. Such OFF/ON catalysts can be involved in signal amplification processes with various potential applications.

Stable Luminescent [Cu(NN)(PP)]$^+$ Complexes Incorporating a β-Cyclodextrin-Based Diphosphane Ligand with Metal-Confining Properties



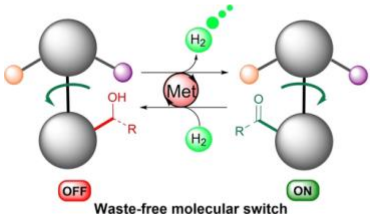
T.-A. Phan, N. Armaroli, A. Saavedra Moncada, E. Bandini, B. Delavaux-Nicot, J.-F. Nierengarten, D. Armspach

Angew Chem. Int. Ed. **2023**, *62*, e202214638

DOI: 10.1002/anie.202214638

Abstract: A β-cyclodextrin-based diphosphane with metal-confining properties was efficiently synthesized thanks to an unprecedented Smiles-like rearrangement of diphenyl-(2-phosphanylphenyl)phosphane in the presence of excess *n*-BuLi. The *cis*-chelating bidentate ligand is capable of forming very stable heteroleptic [Cu(NN)(PP)]$^+$ complexes in which a metal-bound diimine ligand (bpy, phen, or mmp) is located within the cyclodextrin cavity. As a result of ligand encapsulation, flattening of the metal tetrahedral geometry in the excited state is disfavored, thereby resulting in enhanced luminescent properties.

Catalytic Reversible (De)hydrogenation To Rotate a Chemically Fueled Molecular Switch



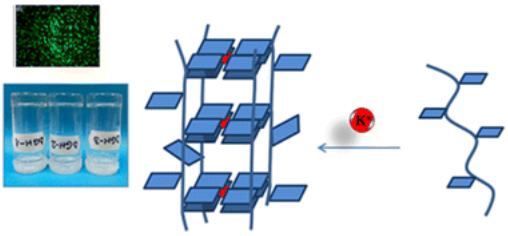
E. Olivieri, N. Shao, R. Rosas, J.-V. Naubron, A. Quintard

Angew Chem. Int. Ed. **2022**, *61*, e202214763

DOI: 10.1002/anie.202214763

Abstract: We report here the development of a rotating molecular switch based on metal-catalyzed reversible (de)-hydrogenation. Under an argon atmosphere, acceptorless dehydrogenation induces a switch from an alcohol to a ketone, while reversing to a hydrogen pressure switches back the system to the alcohol. Based on a tolane scaffold, such reversible (de)-hydrogenation enables 180° rotation. The absence of waste accumulation in a switch relying on chemical stimuli is of great significance and could potentially be applied to the design of efficient complex molecular machines.

Dynameric G-quadruplex–dextran hydrogels for cell growth applications



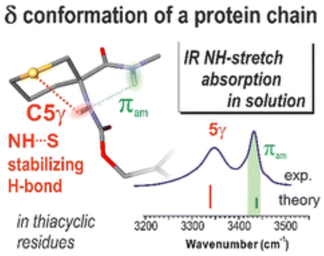
M.-C. Sardaru, S. Morariu, O.-E. Carp, E.-L. Ursu, A. Rotaru, M. Barboiu

Chem. Comm. **2023**, *59*, 3134-3137

DOI: 10.1039/D2CC06881H

Abstract: Hybrid dextran–G-quartet produces tunable biocompatible three-dimensional thixotropic hydrogels, able to support cell growth.

Non-covalent interactions reveal the protein chain *δ* conformation in a flexible single-residue model



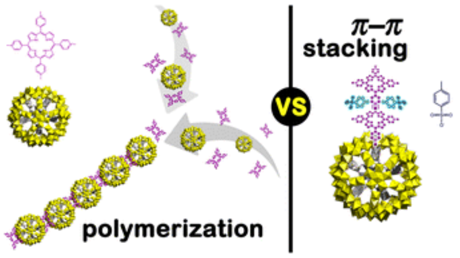
Z. Imani, V. Rao Mundlapati, V. Brenner, E. Gloaguen, K. Le Barbu-Debus, A. Zehnacker-Rentien, S. Robin, D. J. Aitken, M. Mons

Chem. Comm. **2023**, *59*, 1161-1164

DOI: 10.1039/D2CC06658K

Abstract: The *δ* conformation is a local secondary structure in proteins that implicates a π_{amide} N–H···N interaction between a backbone N atom and the NH of the following residue. Small-molecule models thereof have been limited so far to rigid proline-type compounds. We show here that in derivatives of a cyclic amino acid with a sulphur atom in the γ-position, specific side-chain/backbone N–H···S interactions stabilize the *δ* conformation sufficiently to allow it to compete with classical C5 and C7 H-bonded conformers.

Gigantic supramolecular assemblies built from dynamic hierarchical organization between inorganic nanospheres and porphyrins



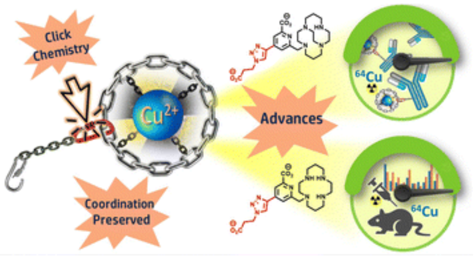
K. Grzhegorzhevskii, M. Haouas, M. Lion, A. Vashurin, A. Denikaev, Y. Marfin, G. Kim, C. Falaise, E. Cadot

Chem. Comm. **2023**, *59*, 86-89

DOI: 10.1039/D2CC05193A

Abstract: Noncovalent ionic interactions between nanosized Keplerate-type capsules {Mo_{132}} and tetra-cationic porphyrins have been investigated in aqueous solution using small-angle X-ray scattering, ^1H NMR and photophysical methods. These complementary multiscale methods reveal the formation of large hybrid oligomers built from a short-range organization in which the cationic porphyrin is glued onto the large POM surface. The local structuring appears to be strongly dependent on the dye : {Mo_{132}} ratio changing the morphology of the oligomers from linear to dense aggregates.

Highly inert Cu(ii) complexes of *C*-aryl bifunctional cyclam-picolinates with remarkable ^{64}Cu-labelling and biodistribution



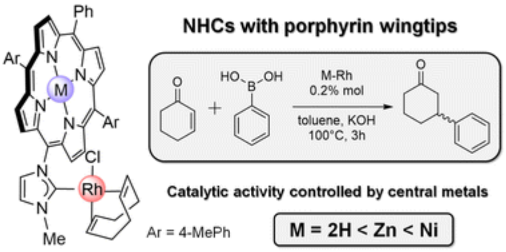
J. Pineau, L. M. P. Lima, M. M. Le Roy, S. Marionneau-Lambot, M. Cordier, P. Le Saëc, J. Rijn Zeevaart, C. H. S. Driver, A. Faivre-Chauvet, N. Le Bris, R. Tripier

Chem. Comm. **2023**, *59*, 888-891

DOI: 10.1039/D2CC06602E

Abstract: Cyclam-picolinate chelators were functionalized *via* click chemistry with an additional carboxyl group for subsequent bioconjugation to antibodies or for the modification of the overall charge of the corresponding ^{64}Cu-radiocomplexes. The *C*-aryl functionalization strategy developed here preserves the chemical properties of the radiocomplexes whilst deeply enhancing their applications within nuclear medicine.

Electronic, steric and catalytic properties of N-heterocyclic carbene rhodium(i) complexes linked to (metallo)porphyrins



L. Poyac, S. Scoditti, X. Dumail, M. Granier, S. Clément, R. Gramage-Doria, C. H. Devillers, S. Richeter

Chem. Comm. **2022**, *58*, 13270-13273

DOI: 10.1039/D2CC05547C

Abstract: Electronic and steric properties of NHC ligands functionalized with porphyrins were investigated. When porphyrins are used as NHC-wingtips, nickel(II) in the macrocyle significantly improves the catalytic activity of the neighbouring NHC-Rh(I) complex in the conjugate addition of phenylboronic acid to cyclohexen-2-one.

Extended Tripodal Hydrotris(indazol-1-yl)borate Ligands as Ruthenium-Supported Cogwheels for On-Surface Gearing Motions

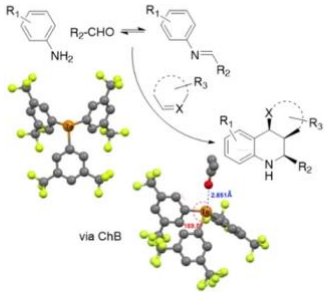
K.enichiro Omoto, M. Shi, K. Yasuhara, C. Kammerer, G. Rapenne

Chem. Eur. J. **2023**, *29*, e202203483

DOI: 10.1002/chem.202203483

Abstract: This paper reports the synthesis of ruthenium-based molecular gear prototypes composed of a brominated or non-brominated pentaphenylcyclopentadienyl ligand as an anchoring unit and a tripodal ligand with aryl-functionalized indazoles as a rotating cogwheel. Single crystal structures of the ruthenium complexes revealed that the appended aryl groups increase the apparent diameter of the cogwheel rendering them larger than the diameter of the anchoring units and consequently making them suitable for intermolecular gearing motions once the complexes will be adsorbed on a surface.

Chalcogen-Bond Catalysis: Telluronium-Catalyzed [4+2]-Cyclocondensation of (in situ Generated) Aryl Imines with Alkenes



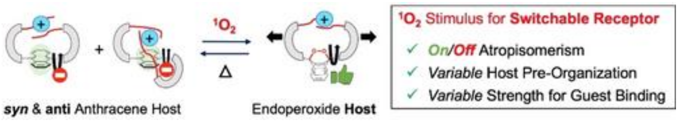
L. Groslambert, A. Padilla-Hernandez, R. Weiss, P. Pale, V. Mamane

Chem. Eur. J. **2023**, *29*, e202203372

DOI: 10.1002/chem.202203372

Abstract: In the chalcogen series, tellurium species exhibit the strongest chalcogen bonding (ChB) interaction with electron-rich atom. This property explains the renewed interested toward tellurium-based derivatives and their use in different applications, such as organocatalysis. In this context, the catalytic activity of telluronium salts in the Povarov reaction is presented herein. Different dienophiles, as well as imines of variable electronic nature, efficiently react in the presence of catalytic amount of either diarylmethyltelluronium or triaryltelluronium salts. Both catalysts could also readily perform the three-component Povarov reaction starting from aldehyde, aniline and dihydrofuran. The reactivity of telluroniums towards imines and aldehydes was confirmed in the solid state by the ability of Te atom to interact through ChB with the oxygen carbonyl of acetone, and in solution with significant shift variations of the imine proton and of the tellurium atom in ^{1}H and ^{125}Te NMR spectroscopy. For the most active telluronium catalysts bearing CF_3 groups, association constants (*K*) with *N*-phenyl phenylmethanimine in the range 22–38 M^{-1} were measured in dichloromethane.

Singlet Oxygen Responsive Molecular Receptor to Modulate Atropisomerism and Cation Binding



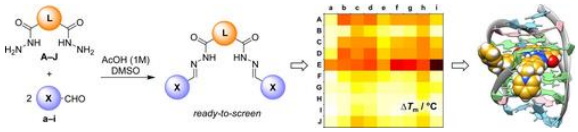
Q. Bouteille, D. Sonet, M. Hennebelle, J.-P. Desvergne, E. Morvan, A. Scalabre, E. Pouget, R. Méreau, B. Bibal

Chem. Eur. J. **2023**, *29*, e202203210

DOI: 10.1002/chem.202203210

Abstract: A combined experimental and computational study highlights the crucial role played by intermolecular non-covalent weak-interactions in the conformer selection, the solid-state organization and the photophysical properties observed in a series of phases of a $Cu^I_8Pd^{II}_2$ multimetallic assembly. Rationalization of the structure/properties relationships allows understanding their mechanical and thermal stimuli-sensitive responses.

Optimization of G-Quadruplex Ligands through a SAR Study Combining Parallel Synthesis and Screening of Cationic Bis(acylhydrazones)



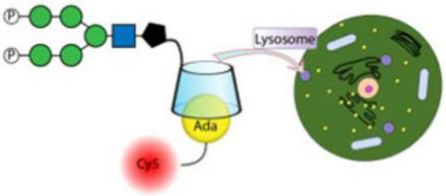
O. Reznichenko, D. Leclercq, J. Franco Pinto, L. Mouawad, V. Gabelica, A. Granzhan

Chem. Eur. J. **2023**, *29*, e202202427

DOI: 10.1002/chem.202202427

Abstract: A library of cationic bis(acylhydrazones) as putative G4-DNA ligands was prepared by a straightforward condensation of the corresponding building blocks. Screening the resulting samples (without any isolation or purification steps) by fluorescence-melting experiments identified three novel hits, whose interactions with G4-DNA targets were studied in detail by several biophysical methods and molecular modeling.

Lysosomal Targeting of β-Cyclodextrin



A. Mascherpa, N. Ishii, A. Tayagui, J. Liu, M. Sollogoub, A. Fairbanks

Chem. Eur. J. **2023**, *29*, e202203252

DOI: 10.1002/chem.202203252

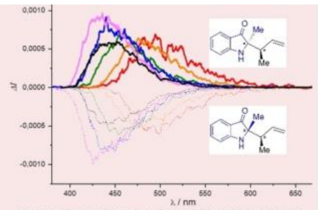
Abstract: Attachment of a bis-mannose-6-phosphate terminated glycan to β-cyclodextrin increases both cellular internalisation and transport to the lysosome, indicating potential application for improved treatments for lysosomal metabolite accumulation

Asymmetric Ruthenium Catalysis Enables Fluorophores with Point Chirality Displaying CPL Properties

Y. Sun, K. Dhbaibi, H. Lauwick, C. Lalli, G. Taupier, Y. Molard, R. Gramage-Doria, S. Dérien, J. Crassous, M. Achard

Chem. Eur. J. **2023**, *29*, e202203243

DOI: 10.1002/chem.202203243



Not enantiomers but mirror image chiroptical responses

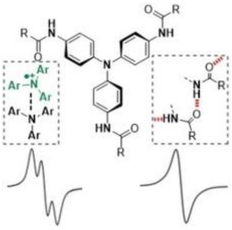
Abstract: Through the use of a well-defined enantiopure π-allylic ruthenium(IV) precatalyst, facile access to enantioenriched indolin-3-one emitters was achieved. Facile separation of diastereoisomers demonstrated mirror image chiroptical responses.

Interplay Between Hydrogen Bonding and Electron Transfer in Mixed Valence Assemblies of Triarylamine Trisamides

Q. Sallembien, P. Aoun, S. Blanchard, L. Bouteiller, M. Raynal

Chem. Eur. J. **2023**, *29*, e202203199

DOI: 10.1002/chem.202203199



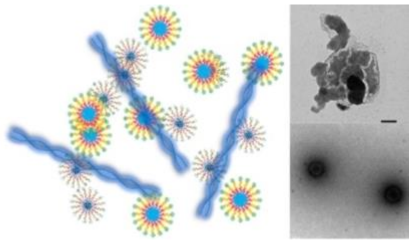
Abstract: Not only hydrogen bonds but also a specific packing arrangement are necessary to get fast electron transfer in mixed valence assemblies of triarylamine trisamides. Defects in the hydrogen bonding network are detected upon increasing the number of radical species in the mixed valence assemblies present in the film state without impeding the delocalization of the unpaired electrons.

Complexation Preferences of Dynamic Constitutional Frameworks as Adaptive Gene Vectors

D.-D. Su, V. Gervais, S. Ulrich, M. Barboiu

Chem. Eur. J. **2023**, *29*, e202203062

DOI: 10.1002/chem.202203062



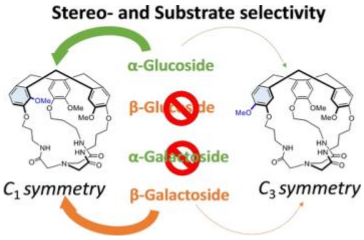
Abstract: Dynamic constitutional frameworks: 40 different amphiphilic dynamic constitutional frameworks were prepared in a stepwise covalent self-assembly process and their DNA complexation preferences revealed marked differences, not only as a function of the number and type of cationic headgroups, but also as a function of the type of DNA, yielding distinct polyplex architectures.

Probing the Importance of Host Symmetry on Carbohydrate Recognition

A.-D. Manick, C. Li, E. Antonetti, M. Albalat, Y. Cotelle, P. Nava, J.-P. Dutasta, B. Chatelet, A. Martinez

Chem. Eur. J. **2023**, *29*, e202203212

DOI: 10.1002/chem.202203212



Abstract: A simple switch from formic acid to HFIP allows the formation of the C_3 symmetrical hemicryptophane cage analogue of the previously reported C_1 symmetrical one. The cage with low symmetry exhibits higher binding constants towards carbohydrates than the C_3 analogue. The receptors showed remarkable high substrate selectivity and stereoselectivity towards *α*-glucoside and *β*-galactoside.

Bis(Vinylenedithio)-Tetrathiafulvalene-Based Coordination Networks

F. Solano, P. Auban-Senzier, I. Olejniczak, B. Barszcz, T. Runka, P. Alemany, E. Canadell, N. Avarvari, N. Zigon

Chem. Eur. J. **2023**, *29*, e202203138

DOI: 10.1002/chem.202203138

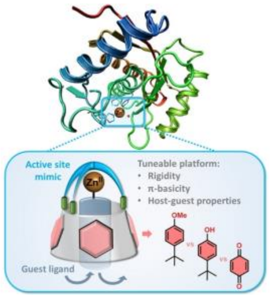
Abstract: Sulphurous lateral interactions. For electroactive coordination polymers, through space charge transport phenomenon are most often 1D. By increasing the size of the electroactive core, lateral sulphur-sulphur interaction take place and create a 2D conducting pathway. Post-synthetic oxidation is used to increase the materials conductivity.

Selective Metal-ion Complexation of a Biomimetic Calix[6]arene Funnel Cavity Functionalized with Phenol or Quinone

P. Aoun, N. Nyssen, S. Richard, F. Zhurkin, I. Jabin, B. Colasson, O. Reinaud

Chem. Eur. J. **2023**, *29*, e202202934

DOI: 10.1002/chem.202202934



Abstract: The calixarene core allows the introduction of functional groups at remote distance from the metal ion, but in the vicinity of its labile site. Introducing a phenol or quinone moiety in the calix core, in place of anisole, drastically changes not only thermodynamics but also kinetics of metal ion and guest-ligand binding, while the first coordination sphere is not affected.

A Triazolium-Anchored Self-Immolative Linker Enables Self-Assembly-Driven siRNA Binding and Esterase-Induced Releas

S. Hollstein, L. M. A. Ali, M. Coste, J. Vogel, N. Bettache, S. Ulrich, M. von Delius

Chem. Eur. J. **2023**, *29*, e202203311

DOI: 10.1002/chem.202203311

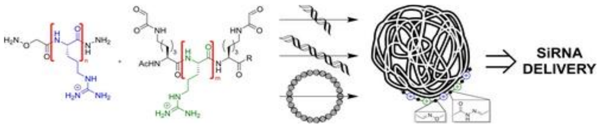
Abstract: **Self-assembled** triazolium-based amphiphiles lose the ability to bind siRNA upon addition of esterase, due to the degradation of the polar head group and conversion to a neutral triazole.

Structure-Activity Relationships in Nucleic-Acid-Templated Vectors Based on Peptidic Dynamic Covalent Polymers

D.-D. Su, L. M. A. Ali, M. Coste, N. Laroui, Y. Bessin, M. Barboiu, N. Bettache, S. Ulrich

Chem. Eur. J. **2023**, *29*, e202202921

DOI: 10.1002/chem.202202921



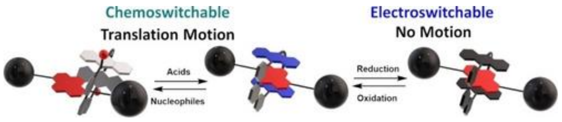
Abstract: The use of nucleic acids as templates, which can trigger the self-assembly of their own vectors represent an emerging, simple and versatile, approach toward the self-fabrication of tailored nucleic acids delivery vectors. However, the structure-activity relationships governing this complex templated self-assembly process that accompanies the complexation of nucleic acids remains poorly understood. Herein, the class of arginine-rich dynamic covalent polymers (DCPs) composed of different monomers varying the number and position of arginines were studied. The combinations that lead to nucleic acid complexation, in saline buffer, using different templates, from short siRNA to long DNA, are described. Finally, a successful peptidic DCP featuring six-arginine repeating unit that promote the safe and effective delivery of siRNA in live cancer cells was identified.

Dual-Readout of the Mechanical Response of a Bis-acridinium [2]Rotaxane

J. Hu, S. Adrouche, E. S. Gauthier, N. Le Breton, M. Cecchini, C. Gourlaouen, S. Choua, V. Heitz, H.-P. Jacquot de Rouville

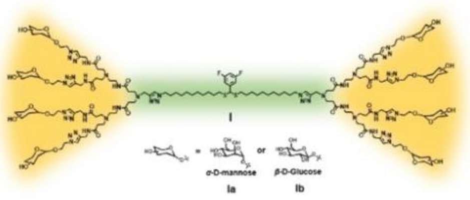
Chem. Eur. J. **2022**, *28*, e202202840

DOI: 10.1002/chem.202202840



Abstract: A [2]rotaxane built around a multi-responsive bis-acridinium macrocycle has been synthesized. Structural investigation has confirmed the interlocked nature of the molecule, and MD simulations illuminated its conformational dynamics with atomic resolution. Both halochromic and redox-switching properties were explored to shed light on the mechanical response and electronic changes that occur in the bis-acridinium [2]rotaxane. The topology of the rotaxane led to different mechanical behaviors upon addition of hydroxide ions or reduction that were easily detected by UV/Vis spectroscopy and electrochemistry.

Bola-Amphiphilic Glycodendrimers: New Carbohydrate-Mimicking Scaffolds to Target Carbohydrate-Binding Proteins



W. Zhang, D. Dhumal, X. Zhu, B. Ralahy, A. Ellert-Miklaszewska, J. Wu, E. Laurini, Y.-W. Yao, C.-L. Kao, J. L. Iovanna, S. Pricl, B. Kaminska, Y. Xia, L. Peng

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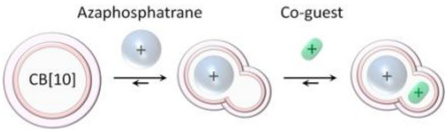
Abstract: Innovative bola-amphiphilic glycodendrimers with mannose and glucose terminals have been designed and synthesized. They demonstrated stronger binding to the carbohydrate-binding protein ConA than conventional amphiphilic glycodendrimers thanks to their unique dumbbell-like structure. In addition, these bola-dendrimers targeted mannose receptors and glucose transporters for effective cellular uptake, and thus hold great promise in carbohydrate-binding protein-targeted drug delivery.

Sequential Formation of Heteroternary Cucurbit[10]uril (CB[10]) Complexes



C. Li, A.-D. Manick, Y. Zhao, F. Liu, B. Chatelet, R. Rosas, D. Siri, D. Gigmes, V. Monnier, L. Charles, J. Broggi, S. Liu, A. Martinez, A. Kermagoret, D. Bardelang

Chem. Eur. J. **2022**, *28*, e202201656

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Abstract: An azaphosphatrane (AZAP) forms a host:guest 1 : 1 complex with the cucurbit[10]uril (CB[10]) macrocycle in water and forces CB[10] to adopt an 8-shape with AZAP occupying the majority of the cavity. The CB[10] contraction leads to a residual space which favors the co-inclusion of planar and monocationic co-guest (CG) molecules, affording heteroternary CB[10]·AZAP·CG complexes.