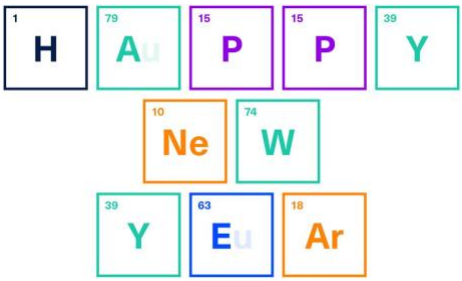
N°05
Janvier 2025

La SupInfo

Les infos du Groupe de Chimie Supramoléculaire

SOMMAIRE



LE MOT DU PRÉSIDENT

Cher·ère·s sociétaires,

Au nom de tous les membres du bureau du groupe Supr@SCF, je vous souhaite une bonne année 2025 !

Cette année commence par la triste nouvelle du décès de Sir J. Fraser Stoddart, un géant de la chimie supramoléculaire. Plusieurs de ses anciens collaborateurs français ont tenu à lui rendre ici un hommage en partageant des anecdotes marquantes de leur expérience dans son laboratoire.

Ce début d'année est aussi celle de l'élection des membres de notre bureau. N'hésitez pas à candidater (date limite de dépôt fixée au 27 janvier 2025), et à voter (vote clôturé le 11 février 2025) !

2025 verra également la tenue des *Journées de Chimie Supramoléculaire* JCS2025 à Strasbourg du 22 au 23 mai 2025, dont le programme est largement dédié à l'intervention de jeunes chercheuses et jeunes chercheurs français. Nous espérons vous y voir nombreux !

D'un commun accord, cette année sera celle du départ de notre groupe de la plateforme X (anciennement Twitter). Vous pouvez nous retrouver dès maintenant sous un ciel plus bleu : @suprascf.bsky.social.

Vous trouverez de plus dans ce numéro une de vos rubriques préférées avec le portrait de l'un des membres de notre communauté, Christophe Bucher.

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

Au nom des membres du bureau, je vous souhaite une bonne lecture !

Bien cordialement,

Laurent Vial, Président du Groupe Supr@SCF

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HOMMAGE À FRASER STODDART

C'est avec une grande tristesse que la communauté française des chimistes a appris la disparition de Sir J. Fraser Stoddart le 30 décembre dernier. Figure emblématique de la chimie moderne, la contribution la plus marquante de Fraser Stoddart réside dans ses travaux sur la chimie supramoléculaire et les machines moléculaires, pour lesquels il est co-lauréat en 2016 du Prix Nobel de Chimie avec Jean-Pierre Sauvage et Ben Feringa.
Outre son parcours scientifique hors-norme, Fraser Stoddart était reconnu pour son engagement remarquable envers la formation de centaines de jeunes chercheurs et chercheuses. En hommage à leur mentor, plusieurs chercheurs de la communauté française témoignent ici d'une anecdote marquante de leur passage dans son laboratoire :

Dominique Armspach (Alumni, Sheffield 1990-1991 then Birmingham, 1991-1994)
Fraser allait toujours de l'avant et a fait preuve d'une énergie hors du commun tout au long de sa carrière jusqu'à la veille de son décès. Il savait saisir les opportunités qui s'offraient à lui pour faire avancer sa science. Une anecdote qui m'a particulièrement marqué est l'annonce le premier jour de ma thèse à l'université de Sheffield de notre déménagement à Birmingham l'année suivante. Cette expérience, à priori déconcertante pour un thésard en première année, s'est en réalité déroulée dans de très bonnes conditions grâce à une organisation sans faille que Fraser a su mettre en place et sa capacité exceptionnelle à maintenir la cohésion du groupe. Ce n'était que le début d'un long périple qui l'a mené de son Ecosse natale à Hong-Kong, en passant par les Etats-Unis.

Arthur David (Alumni, Northwestern University, 2021-2022)
Dès mon arrivée à Northwestern University, un projet captivant était en cours : un postdoctorant nommé Liang Feng avait intégré des pompes sur un metal-organic framework (MOF) 2D, suscitant une effervescence dans le laboratoire. Après des mois de maturation, Fraser est venu avec le concept de mechanisorption pour expliquer ce phénomène, une idée qui a conduit à la publication d'un article dans Science. Je me souviens encore du jour où il a reçu la réponse d'acceptation : il est entré dans le Research Palace (RP) – mon bureau faisait face à la porte – et a exprimé toute sa joie, non pas pour lui-même, mais pour Liang Feng. À 80 ans, Fraser restait profondément engagé à mettre en avant ses collaborateurs et à célébrer leur succès.

Sébastien Vidal (Alumni, UCLA, 2000-2003)
Fraser était non seulement en mentor exceptionnel pour débuter une carrière en sciences, mais aussi comme un deuxième père pour moi. Lui et sa regrettée femme Norma étaient toujours soucieux de mon équilibre et adaptation à mon arrivée à Los Angeles. Sur l'aspect recherche, je me souviens d'une expérience où il m'a demandé si je voulais cracher dans un tube à essai pour démontrer quelque chose en compagnie d'Alexander Star. Ils avaient placé dans une solution aqueuse des nanotubes de carbone et de l'amylose qui a rendu ces nanotubes hydrosolubles. Puis il a craché dans le tube à essai et la solution est devenue trouble et les nanotubes se sont déposés au fond, insolubles. Je me souviens, non sans émotion aujourd'hui, de son rire malicieux quand il me regardait observer la solution. L'amylase contenue dans la salive avait dépolymérisé l'amylose et rendu les nanotubes insolubles. Cette découverte provenait de son côté glycochimiste et a été publiée rapidement dans Angewandte Chemie (https://doi.org/10.1002/1521-3773(20020715)41:14<2508::AID-ANIE2508>3.0.CO;2-A). C'était aussi ça travailler avec Fraser, des moments simples, complices et joyeux autour d'une idée ou d'une expérience.

Seifallah Abid (Alumni, Northwestern University, 2021-2022)
Fraser était un scientifique hors du commun qui incarnait à la perfection l'esprit collaboratif. Il n'hésitait pas à mettre en avant ses collaborations. Dès mon intégration au groupe à Northwestern University, il m'a conseillé de commencer à développer mon propre réseau. Pour lui, il était essentiel de créer des relations basées sur la confiance, de valoriser les échanges et comprendre que collaborer, c'est un moyen pour s'enrichir mutuellement et grandir ensemble. J'ai mis en pratique cette recommandation qui me restera gravée dans la mémoire.

Henri-Pierre Jacquot de Rouville (Alumni, Northwestern University, 2010-2012)
Fraser était une personne profondément humaine, généreuse et empreinte d'humour. Grace à ses qualités, il savait créer un lien particulier avec ses collaborateurs. Je me rappelle d'une fois, un des postdoctorants du groupe s'était assoupi à son bureau. Bien mis en évidence, Fraser avait placé un dessin de son petit-fils sur lequel était marqué : « *Don't wake me up, except for orange juice!* ». Tout au long de sa vie, Fraser a profondément impacté les personnes qui gravitaient autour de lui aussi bien d'un point de vue scientifique qu'humain.

À vos agendas

Journées de Chimie Supramoléculaire 2025 à Strasbourg

Le Groupe de Chimie Supramoléculaire (Supr@SCF) de la Société Chimique de France (SCF) organise les prochaines *Journées de Chimie Supramoléculaire* JCS2025 du 22 au 23 mai 2025 à Strasbourg. Au programme quatre conférences plénières. En plus, des communications orales (14) ainsi que des communications flash (12) et une session de présentation par posters.

L'inscription est gratuite pour les étudiants, doctorants et post-doctorants qui sont membres de la SCF ; pour plus d'information visitez le site https://jcs2025.sciencesconf.org

Cet événement sera l'occasion pour toutes les personnes intéressées et passionnées par la chimie supramoléculaire de se retrouver, discuter et partager leurs résultats. La chimie supramoléculaire étant un domaine de recherche hautement interdisciplinaire, nous espérons que chacun d'entre vous trouvera beaucoup d'inspiration et appréciera cet événement.

Au plaisir de vous rencontrer à Strasbourg, capitale de l'Europe.

Le comité d'organisation : Iwona, Henri-Pierre, Giulio & Aline

À LA RENCONTRE DE…CHRISTOPHE BUCHER

Carrière:

2013-	Directeur de recherche CNRS au Laboratoire de Chimie de l'ENS de Lyon-France.
2012-2013	Chargé de recherche CNRS au Laboratoire de Chimie de l'ENS de Lyon-France.
2001-2012	Chargé de recherche CNRS au Laboratoire d'Electrochimie Organique et de Photochimie Redox puis au Département de Chimie Moléculaire, Université Joseph Fourier, Grenoble-France.
1999-2001	Post-Doctorat, Université du Texas à Austin-USA (groupe du Pr. J. L. Sessler).

Formation:

1999	Doctorat de chimie physique de l'Université de Bourgogne à Dijon (LIMSAG)
1995-1996	Maitrise de chimie et D.E.A de chimie physique, Université de Bourgogne à Dijon

Un aspect important de ma personnalité est mon optimisme, c'est ce qui me permet d'avancer et d'appréhender les nombreux obstacles qui se présentent sur mon chemin dans la joie et la bonne humeur.

En regardant ma carrière, je ne regrette aucun de mes choix professionnels et je suis conscient d'avoir eu de la chance dans mon parcours. J'ai toujours travaillé dans des environnements privilégiés et extrêmement stimulants, entouré de mentors, collègues et d'étudiants brillants et motivés. J'ai également eu de nombreuses occasions de transmettre ma passion pour la chimie supramoléculaire ou pour l'électrochimie dans différents contextes, aussi bien au laboratoire que dans différents parcours d'enseignements.

Les jeunes devraient s'intéresser à la chimie supramoléculaire car c'est un domaine qui permet de développer de très nombreuses compétences et de mener des activités de recherche extrêmement variées qui laissent une grande place à la créativité.

Mon endroit préféré pour passer des vacances est la montagne. Partir pour un périple familial en autonomie avec le sac à dos et la tente. C'est pour moi le meilleur moyen de me reposer psychologiquement tout en faisant du sport.

Une chose importante que j'ai apprise de mes étudiants est qu'un contrôle excessif peut bloquer la créativité et qu'il faut être très attentif aux idées insolites et aux résultats inattendus.

J'admire particulièrement les personnes créatives aussi bien en science que dans tous les domaines artistiques.

Une de mes devises préférées est « à cœur vaillant rien d'impossible ».

Intérêts de recherche : Electrochimie Supramoléculaire

Utiliser des transferts d'électrons pour activer ou signaler des évènements se produisant à l'échelle de la molécule, des assemblages supramoléculaires ou des matériaux. Développement de systèmes (supra)moléculaires électro/photo-stimulables (rotors, pinces, Gels…). Commutation de propriétés magnétiques. Activation de petites molécules (Électrocatalyse). Électrosynthèse. (Spectro)Électrochimie moléculaire.

https://www.ens-lyon.fr/CHIMIE/recherche/Teams/Supramolecular-Chemistry-and-Chemical-Biology/Stimuli-Responsive-Molecules-and-Materials

https://orcid.org/0000-0003-1803-6733

Cinq références significatives :

S. Al Shehimy; O. Baydoun; S. Denis-Quanquin; J.-C. Mulatier; L. Khrouz; D. Frath; E. Dumont; M. Murugesu; F. Chevallier; C. Bucher. Ni-Centered Coordination-Induced Spin-State Switching Triggered by Electrical Stimulation. *J. Am. Chem. Soc.* **2022**, *144* (39), 17955.

C. Kahlfuss; T. Gibaud; S. Denis-Quanquin; S. Chowdhury; G. Royal; F. Chevallier; E. Saint-Aman; C. Bucher. Redox-Induced Molecular Metamorphism Promoting a Sol/Gel Phase Transition in a Viologen-Based Coordination Polymer. *Chem. Eur. J.* **2018**, *24* (49), 13009.

C. Kahlfuss; S. Denis-Quanquin; N. Calin; E. Dumont; M. Garavelli; G. Royal; S. Cobo; E. Saint-Aman; C. Bucher. Electron-Triggered Metamorphism in Porphyrin-Based Self-Assembled Coordination Polymers. *J. Am. Chem. Soc.* **2016**, *138*, 15234.

A. Iordache; M. Oltean; A. Milet; F. Thomas; B. Baptiste; E. Saint-Aman; C. Bucher. Redox control of rotary motions in ferrocene-based elemental ball bearings. *J. Am. Chem. Soc.* **2012**, *134*, 2653.

T.-T. Bui; A. Iordache; Z. Chen; V. V. Roznyatovskiy; E. Saint-Aman; J. M. Lim; B. S. Lee; S. Ghosh; J.-C. Moutet; J. L. Sessler; D. Kim; C. Bucher. Electrochemical Synthesis of a Thiophene-containing Cyclo[9]pyrrole. *Chem. Eur. J.* **2012**, *18*, 5853.

NOTRE SÉLECTION D'ARTICLES

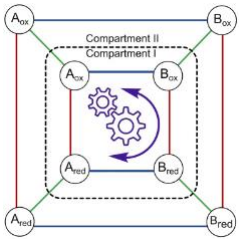
Le bureau du Groupe SupraSCF met en avant chaque semestre une sélection d'articles dont les auteur.rice.s sont membres de notre groupe thématique.
Vous trouverez ici un choix d'articles publiés sur la période juillet 2024 - Janvier 2025 dans les journaux suivants :
- *Chem*
- *J. Am. Chem. Soc.*
- *Angew. Chem. Int. Ed.*
- *Chem. Sci.*

Cette sélection est évidemment non exhaustive.

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

E. Penocchio, A. Bachir, A. Credi, R. D. Astumian, G. Ragazzon

Chem **2024**, *10*, 3644-3655

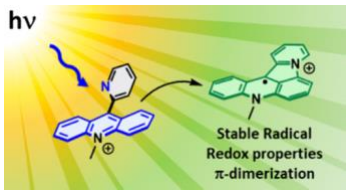


***Abstract*:** Kinetic asymmetry is a key parameter describing non-equilibrium systems: it indicates the directionality of a reaction network under steady-state conditions. So far, kinetic asymmetry has been evaluated only in networks featuring a single cycle. Here, we have investigated kinetic asymmetry in a multi-cycle system using a combined theoretical and numerical approach. First, we report the general expression of kinetic asymmetry for multi-cycle networks. Then, we specify it for a recently reported electrochemically controlled network comprising diffusion steps, which we used as a model system to reveal how key parameters influence directionality. In contrast with the current understanding, we establish that spatial separation—including compartmentalization—can enable autonomous energy ratchet mechanisms, with directionality dictated by thermodynamic features. Kinetic simulations confirm analytical findings and illustrate the interplay between diffusion, chemical, and electrochemical processes. The treatment is general, as it can be applied to other multi-cycle networks, facilitating the realization of endergonic processes across domains.

Viridium: A Stable Radical and Its π-Dimerization

H.-P. Jacquot de Rouville, C. Gourlaouen, D. Bardelang, N. Le Breton, J. S. Ward, L. Ruhlmann, J.-M. Vincent, D. Jardel, K. Rissanen, J.-L. Clément, S. Choua, V. Heitz

J. Am. Chem. Soc. **2025**, *147*, 1823–1830

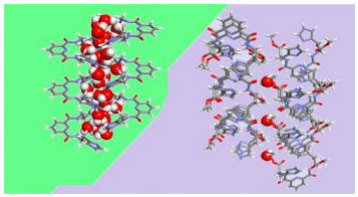


***Abstract*:** The discovery of a stable organic radical formed under mild, clean, and efficient light-mediated conditions is reported. The structure of the stable acridinium-based radical photoproduct was unambiguously established by single-crystal X-ray diffraction, mass spectrometry, and in solution by EPR, UV/vis, and NMR spectroscopies. The photochemical mechanism of its formation has been elucidated by photophysical experiments coupled with EPR experiments and theoretical investigations. This unique aromatic radical is featured by amphoteric redox behavior and π-dimerization properties. Its ability to π-dimerize has been demonstrated in water and in the less studied perfluorohexane, two solvents of opposite polarity. By a simple counterion exchange, direct comparison of π-dimer thermodynamics between both antagonist solvents allowed an elucidation of the solvophobic behavior in perfluorocarbon.

Water-Pore Flow Permeation through Multivalent H-Bonding Pyridine-2,6-dicarboxamide-histamine/Histidine Water Channels

L.-B. Huang, D.-D. Su, A. Hardiagon, I. Kocsis, A. van der Lee, F. Sterpone, M. Baaden, M. Barboiu

J. Am. Chem. Soc. **2025**, *147*, 678-686



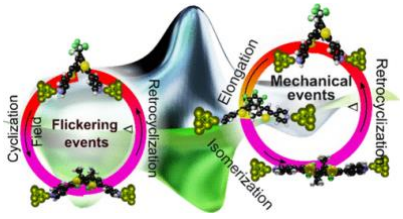
***Abstract*:** Aquaporins (AQPs) are natural proteins that can selectively transport water across cell membranes. Heterogeneous H-bonding of water with the inner wall of the pores of AQPs is of maximal importance regarding the optimal stabilization of water clusters within channels, leading to selective pore flow water transport against ions. To gain deeper insight into the water permeation mechanisms, simpler artificial water channels (AWCs) have been developed. Several H-bonding motifs (i.e., imidazole, polyhydroxy, etc.) have been reported as distinct and efficient for water-cluster stabilization within AWCs. Herein we combine two pyridine-2,6 dicarboxamide and imidazole to conceive multivalent U-shaped AWCs able to stabilize, like in AQP water clusters via different H-bonding groups. The crystal structures reveal that stable water superstructures are formed in the solid state, one with hydrophilic pores of ~9 Å diameter, accommodating water clusters, and one with sterically hindered hydrophobic channels of ~3 Å diameter, stabilizing water wires. As a result, a single-channel permeability of 1.2×10^7 H_2O/s/channel has been achieved by the

U-channels, which is only 1 order of magnitude lower than that of AQPs. Moreover, U-channels perform proton transport and completely reject anions and potentially can be applied in desalination membranes. Molecular simulation confirmed that U-channels can generate stable supramolecular porous sponges when they are decorated with hydrophobic alkyl chains featuring multivalent water H-bonding units that serve as water-cluster relays within the channel. To the best of our knowledge, this work is a rare biomimetic example of the importance of water-cluster stabilization *via* multivalent H-bonding and toward selective transport through water channels.

Mapping the Extended Ground State Reactivity Landscape of a Photoswitchable Molecule at a Single Molecular Level

U. Rashid, L. Medrano Sandonas, E. Chatir, Z. Ziani, PA Sreelakshmi, S. Cobo, R. Gutierrez, G. Cuniberti, V. Kaliginedi

J. Am. Chem. Soc. **2025**, *147*, 830–840



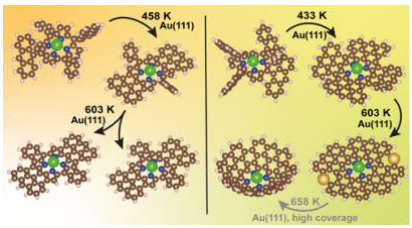
***Abstract*:** Photoswitchable molecules with structural flexibility can exhibit a complex ground state potential energy landscape due to the accessibility of multiple metastable states at merely low energy barriers. However, conventional bulk analytical techniques are limited in their ability to probe these metastable ground states and their relative energies. This is partially due to the difficulty of inducing changes in small molecules in their ground state, as they do not respond to external stimuli, such as mechanical force, unless they are incorporated into larger polymer networks. This hinders the understanding of ground-state reactivity and the associated dynamics. In this study, we leverage the "perturb-probe" capability of the single molecular break junction technique to explore the ground state 6π electrocyclization of a dithienylethene (DTE) derivative, a process traditionally achieved through electro- or photochromism. Our findings reveal that this reaction can also be triggered by mechanical force and an oriented electric field at the single-molecule level via ground state dynamics. We demonstrated that external perturbations could control the ground state reaction dynamics and steer the reaction trajectories away from constraints imposed by typical excited state dynamics. This strategy will thus offer access to a whole new dimension of single molecular electromechanical conversions and extend our knowledge of the ground state potential energy surface available to molecules under external force fields.

Planar and Curved π-Extended Porphyrins by On-Surface Cyclodehydrogenation

M. Baljozović, J. Pijeat, S. Campidelli, K.-H. Ernst

J. Am. Chem. Soc. **2024**, *146*, 34600–34608

DOI: 10.1021/jacs.3c11004



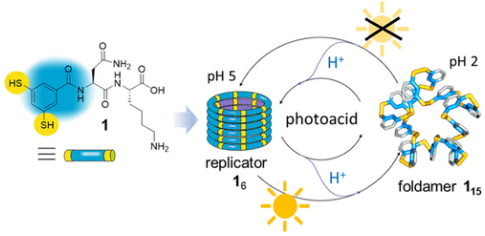
***Abstract*:** Recent advancements in on-surface synthesis have enabled the reliable and predictable preparation of atomically precise low-dimensional materials with remarkable properties, which are often unattainable through traditional wet chemistry. Among these materials, porphyrins stand out as a particularly intriguing class of molecules, extensively studied both in solution and on surfaces. Their appeal lies in the ability to fine-tune their unique chemical and physical properties through central metal exchange or peripheral functionalization. However, the synthesis of π-extended porphyrins featuring unsubstituted anthracenyl groups has remained elusive. Herein, we report an *in vacuo* temperature-controlled cyclodehydrogenation of bis- and tetraanthracenyl Zn(II) porphyrins on a gold(111) surface. By gradually increasing the temperature, sequential dehydrogenation leads to the formation of fused anthracenyl porphyrin products. Notably, at high molecular coverage, the formation of bowl-shaped porphyrins occurs, along with transmetalation of Zn with Au. These findings open the door to a variety of π-extended anthracenyl-containing porphyrin products via cyclodehydrogenation and transmetalation, offering significant potential in the fields of molecular (photo/electro)catalysis, (opto)electronics, and spintronics.

Light-Mediated Interconversion between a Foldamer and a Self-Replicator

Y. Jin, P. K. Mandal, J. Wu, A. Kiani, R. Zhao, I. Huc, S. Otto

J. Am. Chem. Soc. **2024**, 146, 33395–33402

DOI: 10.1021/jacs.3c10835

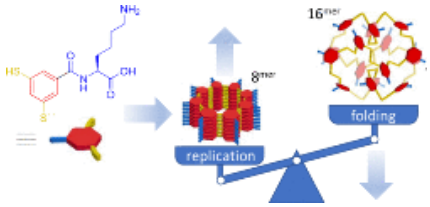


***Abstract*:** Self-replicating molecules and well-defined folded macromolecules are of great significance in the emergence and evolution of life. How they may interconnect and affect each other remains largely elusive. Here, we demonstrate an abiotic system where a single building block can oligomerize to yield either a self-replicating molecule or a foldamer. Specifically, agitation of a disulfide-based dynamic combinatorial library at moderately elevated pH channels it selectively into a self-replicating hexamer assembled into fibers, after passing through a period where a 15-subunit macrocyclic foldamer existed transiently. Without mechanoagitation or at lower pH, the formation of hexamer fiber is suppressed, resulting in the accumulation of the 15mer foldamer. Foldamer and self-replicator can be interconverted in response to external stimuli, including agitation and a change in pH. Furthermore, upon the addition of a photoacid, the pH of the medium can be controlled by irradiation, driving the switching between replicator and foldamer and allowing a dissipative out-of-equilibrium state to be accessed, using light as a source of energy.

Simultaneous Formation of a Foldamer and a Self-Replicator by Out-of-Equilibrium Dynamic Covalent Chemistry

A. Sood, P. K. Mandal, J. Ottelé, J. Wu, M. Eleveld, J. Hatai, C. G. Pappas, I. Huc, S. Otto

J. Am. Chem. Soc. **2024**, *146*, 33386–33394

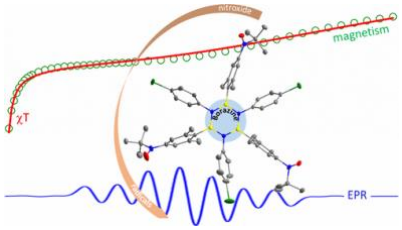


***Abstract*:** Systems chemistry has emerged as a useful paradigm to access structures and phenomena typically exhibited by living systems, including complex molecular systems such as self-replicators and foldamers. As we progress further toward the noncovalent synthesis of life-like systems, and eventually life itself, it is necessary to gain control over assembly pathways. Dissipative chemical fueling has enabled access to stable populations of (self-assembled) structures that would normally form only transiently. Here, we report a synthetic dynamic combinatorial library, made from a single structurally simple building block, from which a self-replicator and a foldamer can emerge along two distinct and competing pathways through an inter- or intramolecular assembly process, respectively. A fueled chemical reaction cycle is then set up to generate the foldamer transiently, in the presence of the self-replicator. The partitioning of the building block between the folding and self-replication pathways and the duration of the fueled reaction cycles are controlled by adjusting the amount of the chemical fuel. An out-of-equilibrium steady state involving the two assemblies could also be achieved by using a continuous stirred tank reactor with inflow and outflow of material. This work connects the domains of folding and self-replication in synthetic systems through dissipative out-of-equilibrium chemistry. It demonstrates that foldamers and self-replicators, formed from the same building block, can stably coexist if the system is continuously supplied with energy, while at equilibrium, the Gibbs phase rule prohibits such coexistence.

An Open-Shell Functionalization of Inorganic Benzene

S. Grenda, N. Claiser, A. Barbon, F. Guégan, B. Toury, D. Luneau

J. Am. Chem. Soc. **2024**, *146*, 32906–3291

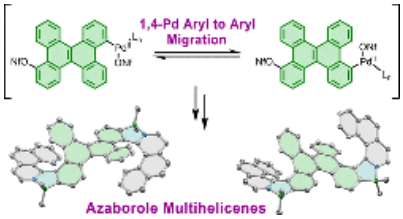


***Abstract*:** A borazine derivative functionalized by nitroxide free radicals, *N*,*N*′,*N*″-(tris(4-Bromophenyl))-*B*,*B*′,*B*″-tris((2,6-dimethyl-4-(*N*-*tert*-butyl-*N*-oxyamino)phenyl) borazine (**TriBNit**), was synthesized as a milestone of open-shell inorganic benzene. The crystal structure determined from X-ray diffraction on a single crystal ascertains the grafting of three nitroxide radicals. The temperature dependence of the magnetic susceptibility evidences weak intramolecular antiferromagnetic interactions between the radicals with strong intermolecular antiferromagnetic interactions between two nitroxide moieties of two neighboring molecules. EPR spectroscopy at 80 K on a frozen glassy solution evidences the coexistence of $S = 1/2$ and $S = 3/2$ ground-spin state species. This is ascribed to the nitroxide radicals having different orientations with respect to the borazine core giving rise either to antiferromagnetic interaction with a low ground-spin state $S = 1/2$ or to ferromagnetic interaction with a high ground-spin state $S = 3/2$ as supported by theoretical data. At room temperature, because of nitroxide mobility, the EPR spectrum is averaged to a ground-spin state $S = 1/2$.

Controllable 1,4-Palladium Aryl to Aryl Migration in Fused Systems–Application to the Synthesis of Azaborole Multihelicenes

F. Full, A. Artigas, K. Wiegand, D. Volland, K. Szkodzińska, Y. Coquerel, A. Nowak-Król

J. Am. Chem. Soc. **2024**, *146*, 29245–29254

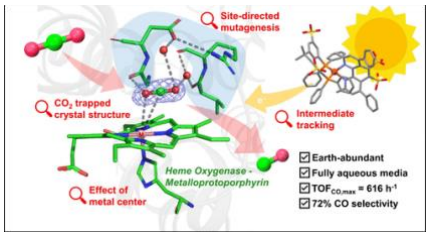


***Abstract*:** Herein, we report the first 1,4-Pd aryl to aryl migration/Miyaura borylation tandem reaction in fused systems. The Pd shift occurred in the bay region of the dibenzo[*g*,*p*]chrysene building blocks, giving rise to a thermodynamically controlled mixture of 1,8- and 1,9-borylated compounds that allowed the preparation of regioisomeric azaborole multihelicenes from the same starting material. The outcome of this synthesis can be controlled by the choice of reaction conditions, allowing the migration process to be turned off in the absence of an acetate additive and the target multiheterohelicenes to be prepared in a regioselective manner. The target compounds show bright green fluorescence in dichloromethane with emission quantum yields (Φ) of up to 0.29, $|g_{lum}|$ values up to 2.7×10^{-3}, and green or green-yellow emission in the solid state, reaching Φ of 0.22. Single crystal X-ray diffraction analyses gave insight into their molecular structures and the packing arrangement. Evaluation of aromaticity in these multihelicenes revealed a nonaromatic character of the 2*H*-1,2-azaborole constituent rings.

Light-Activated Artificial CO_2-Reductase: Structure and Activity

R. J. Labidi, B. Faivre, P. Carpentier, J. Perard, P. Gotico, Y. Li, M. Atta, M. Fontecave

J. Am. Chem. Soc. **2024**, *146*, 28296–28305



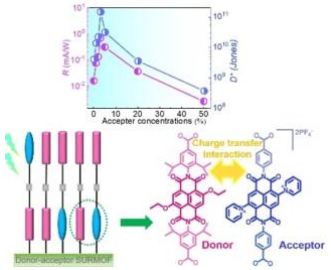
***Abstract*:** Light-dependent reduction of carbon dioxide (CO2) into value-added products can be catalyzed by a variety of molecular complexes. Here we report a rare example of a structurally characterized artificial enzyme, resulting from the combination of a heme binding protein, heme

oxygenase, with cobalt-protoporphyrin IX, with good activity for the photoreduction of CO2 to carbon monoxide (CO). Using a copper-based photosensitizer, thus making the photosystem free of noble metals, a large turnover frequency value of ~616 h–1, a turnover value of ~589, after 3 h reaction, and a CO vs H2 selectivity of 72% were obtained, establishing a record among previously reported artificial CO2 reductases. Thorough photophysical studies allowed tracking of reaction intermediates and provided insights into the reaction mechanism. Thanks to a high-resolution crystal structure of the artificial enzyme, both in the absence and in the presence of the protein-bound CO2 substrate, a rational site-directed mutagenesis approach was used to study the effect of some modifications of the active site on the activity.

Regulated Charge Transfer in Donor-Acceptor Metal–Organic Frameworks for Highly-Sensitive Photodetectors

Z. Xu, A. Chandresh, A. Mauri, M. Esmaeilpour, V. Monnier, F. Odobel, L. Heinke, W. Wenzel, M. Kozlowska, S. Diring, R. Haldar, C. Wöll

Angew. Chem. Int. Ed. **2024**, e202414526

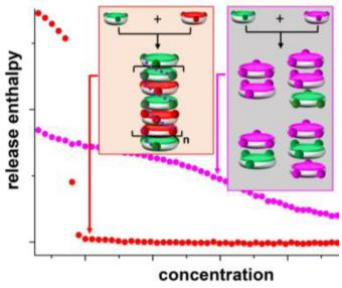


***Abstract*:** A layer-by-layer approach is used to grow naphthalenediimide-based donor-acceptor MOF thin films for efficient free charge generation in response to light. Interestingly, we find that the optimum photocurrent response is obtained at a low optimal doping concentration of acceptor, which outperforms traditional donor-MOF thin films by a factor of forty.

Enhanced Stability and Properties of Benzene-1,3,5-Tricarboxamide Supramolecular Copolymers through Engineered Coupled Equilibria

H. Kong, A. Valverde-González, R. Maruchenko, L. Bouteiller, M. Raynal

Angew. Chem. Int. Ed. **2024**, e202421991

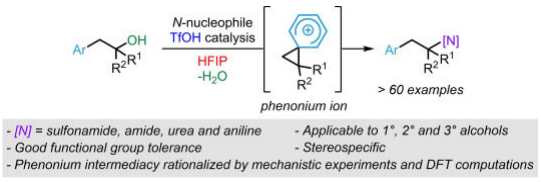


***Abstract*:** Replacing an ester by an ether function in the side chain of a chiral benzene1,3,5-tricarboxamide (BTA) monomer (magenta and red disks, resp.) greatly favours its copolymerization with achiral BTA monomers (green disk), due to the minimization of competing species. The resulting supramolecular copolymers exhibit greater stability which translates into better catalytic and rheological properties.

Triflic Acid-Catalyzed Dehydrative Amination of 2-Arylethanols with Weak N-Nucleophiles in Hexafluoroisopropanol

M. Van Hoof, R. J. Mayer, J. Moran, D. Lebœuf

Angew. Chem. Int. Ed. **2024**, e202417089

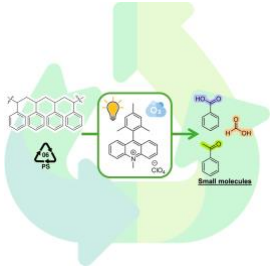


***Abstract*:** We report a catalytic deoxyamination of 2-arylethanols in hexafluoroisopropanol, which directly installs various amino groups, including sulfonamides, amides, ureas and anilines. The transformation relies on the intermediacy of a phenonium ion, whose formation was rationalized by mechanistic experiments and DFT calculations.

Reassessing the Photochemical Upcycling of Polystyrene Using Acridinium Salts

A.-L. De Abreu, D. Taton, D. M. Bassani

Angew. Chem. Int. Ed. **2024**, e202418680



***Abstract*:** It's all about oxygen! Photochemical upcycling of polystyrene occurs efficiently using an acridinium photocatalyst even under solar irradiation. However, contrary to expectations, the mechanism proceeds through the generation of reactive oxygen species.

Localized Oxidative Catalytic Reactions Triggered by Cavitation Bubbles Confinement on Copper Oxide Microstructured Particles.

V. Mahendran, Q. Thang Trinh, X. Zhangyue, U. Jonnalagadda, T. Gould, N.-T. Nguyen, J. Kwan, T. S. Choksi, W. Liu, S. Valange, F. Jérôme, P. N. Amaniampong

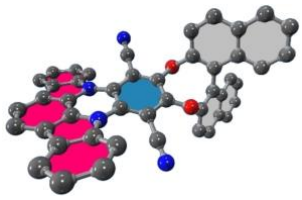
Angew. Chem. Int. Ed. **2024**, e202416543

***Abstract*:** Localised oxidative catalytic reactions triggered by cavitation bubbles confinement on copper oxide microstructured particles.We exploit here a concept of CuO particle design with multiple gas-stabilizing sites, engineered to function as cavitation nuclei and catalysts. This concept facilitates selective and localised acoustic energy transfer directly to the catalyst surface, minimising the undesired dissipation of acoustic energy into the bulk solution while demonstrating superior cavitation properties at lower acoustic pressure amplitudes towards catalytic oxidative reactions.

Control of Dynamic Chirality in Donor-Acceptor Fluorophores

M. Coehlo, L. Frédéric, L. Poulard, N. Ferdi, L. Estaque, A. Desmarchelier, G. Clavier, J.-P. Dognon, L. Favereau, M. Giorgi, J.-V. Naubron, G. Pieters

Angew Chem. Int. Ed. **2025**, e202414490

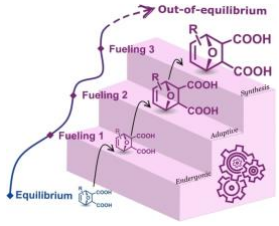


***Abstract*:** We present a molecular design where the dynamic chirality of donor-acceptor fluorophores is controlled using a configurationally stable chiral unit. Beyond illustrating the potential of dynamic chirality control to facilitate the access to chiral functional materials, this work highlight the positive influence of chiral perturbation from the configurationally stable chiral unit on the dissymmetry factors of the dynamically chiral fluorophores.

Progressive Endergonic Synthesis of Diels–Alder Adducts Driven by Chemical Energy

S. Al Shehimy, H.-D. Le, S. Amano, S. Di Noja, L. Monari, G. Ragazzon

Angew Chem. Int. Ed. **2024**, e202411554

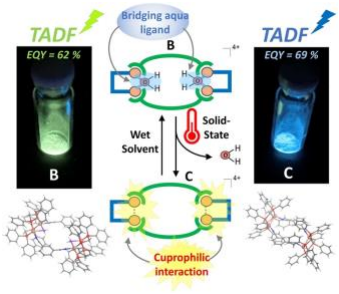


***Abstract*:** Going uphill. While most chemical reactions proceed towards equilibrium, we describe herein how to drive Diels–Alder reactions away from equilibrium (ΔG >0) using the hydration energy of carbodiimides. Our strategy yielded products up to 400 % of what thermodynamics would allow at equilibrium. Progressive accumulation upon repeated fueling cycles unlocks adaptive behaviors in chemical reaction networks.

High-Temperature Solid-State Post-Synthetic Modification of Highly Luminescent Cu(I) Metallacycles toward New Luminescent Thermic Tracers

A. Schlachter, C. Xu, J. Schiller, R. Utrera Melero, S. Kerneis, G. Calvez, K. Costuas, M. Scheer, C. Lescop

Angew Chem. Int. Ed. **2025**, e202413151

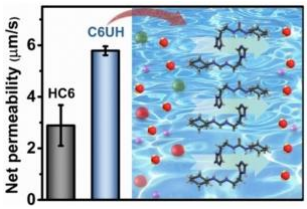


***Abstract*:** The TADF luminescent Cu(I) metallacycle **B** carrying unusual semi-bridging aqua ligands has been prepared in a one-step high-yield reaction. When **B** is heated markedly above room temperature, a solid-state reaction affords a new metallacycle **C** displaying TADF luminescence different from that of **B**. The removal of the aqua ligands and the formation of cuprophilic interactions makes this transition an innovative example of a solid-state photoactive tracer.

Partitioning / Self-assembly of Artificial Water Channels - Toward Controlled Permselectivity through Bilayer Membrane

D.-D. Su, A. van der Lee, M. Barboiu

Angew Chem. Int. Ed. **2025**, e202413816

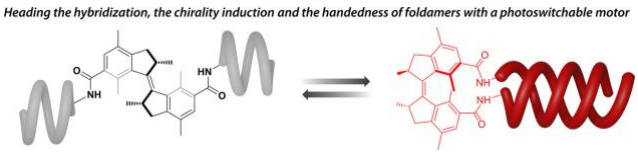


***Abstract*:** Cycloalkyl imidazole dimers have been used to generate biomimetic water channels through intermolecular hydrogen bonding interactions with superior water net permeability as well as ion rejection. This work will bring more possibilities for the design of artificial water channels with attached cycloalkyl components, and further may have applications in practical membrane support for water treatment.

Light- and Temperature-Controlled Hybridization, Chiral Induction and Handedness of Helical Foldamers

Y. Aidibi, S. Azar, L. Hardoin, M. Voltz, S. Goeb, M. Allain, M. Sallé, R. Costil, D. Jacquemin, B. Feringa, D. Canevet

Angew Chem. Int. Ed. **2025**, e202413629

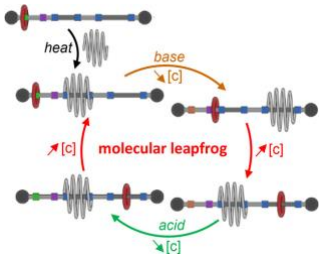


***Abstract*:** Controlling the single or multiple helical state as well as the chirality of helical foldamers is currently in the limelight. In this context, this work demonstrates to which extent grafting a photo-responsive unidirectional motor on foldamer skeletons is relevant to tackle these challenges. To the best of our knowledge, this work constitutes the first example of photoswitchable handedness of foldamer-based double helices.

Cascading Macrocycle and Helix Motions in a Foldarotaxane Molecular Shuttle

R. Hess, M. Brenet, H. Rajaonarivelo, M. Gauthier, V. Koehler, P. Waelès, I. Huc, Y. Ferrand, F. Coutrot

Angew Chem. Int. Ed. **2024**, e202413977

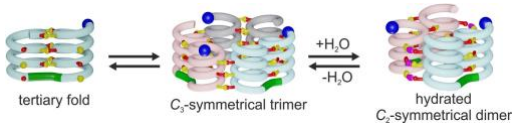


***Abstract*:** A foldarotaxane molecular shuttle is reported that operates through orchestrated interdependent motions of the macrocycle and foldamer. Depending on the pH and concentration, stable and metastable states could be obtained. In particular, shuttling of the macrocycle triggered the gliding of the foldamer away from its best station. Conversely, the foldamer unit could compartmentalize the rotaxane axle and trap the macrocycle away from its best station.

Abiotic Foldamer Quaternary Structures

S. Wang, L. Allmendinger, I. Huc

Angew Chem. Int. Ed. **2024**, e202413252



***Abstract*:** The introduction of hydrogen bond donors at precise locations at the periphery of a stable aromatic foldamer helix-turn-helix tertiary fold led to its aggregation in chloroform to produce genuine discrete abiotic quaternary structures in which the tertiary folds are preserved. The quaternary structures were assigned to C3-symmetrical trimer corresponding to the initial design, and to an unexpected hydrated C2-symmetrical dimer.

Carbon Dot Synthesis and Purification: Trends, Challenges and Recommendations

Y. Hu, O. Seivert, Y. Tang, H. Enis Karahan, A. Bianco

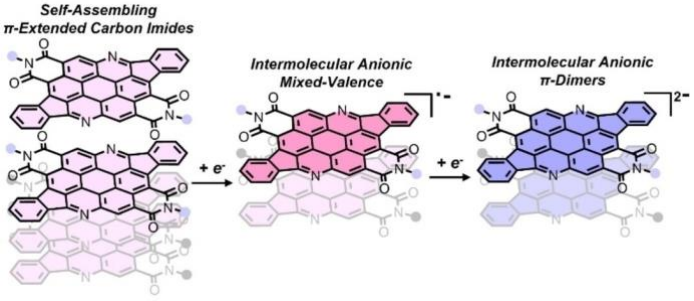
Angew Chem. Int. Ed. **2024**, e202412341

***Abstract*:** This Review analyzes the current trends and challenges in the synthesis and purification of carbon dots prepared through various methods and using a wide variety of precursors. Diverse purification techniques, including centrifugation, filtration, dialysis, column chromatography, and electrophoresis, are systematically and thoroughly described, along with pointing out the gaps in the synthesis, purification, and assessment of CD purity.

Intermolecular Anionic Mixed-Valence and π-Dimer Complexes of ortho-Pentannulated Bisazacoronene Diimide

A. H. G. David, M. Roger, O. Alévêque, H. Melnychenko, L. Le Bras, M. Allain, A. Gapin, D. Canevet, O. Ségut, E. Levillain, A. Goujon

Angew Chem. Int. Ed. **2025,** e202413616



***Abstract*:** The electrochemical reduction of ortho-pentannulated bisazacoronene diimides in a non-aqueous solvent has led to the serendipitous discovery of intermolecular anionic mixed-valence and π-dimer species. The observation of this phenomenon provides insights into the fundamental behaviour of supramolecular organic semiconductors, thereby paving the way for the development of novel electronic devices and electron-deficient materials.

Cobalt Tetracationic 3,4-Pyridinoporphyrazine for Direct CO_2 to Methanol Conversion Escaping the CO Intermediate Pathway

C. Zhang, J. Follana-Berná, D. Dragoe, Z. Halime, P. Gotico, A. Sastre-Santos, A. Aukauloo

Angew Chem. Int. Ed. **2024**, e202411967

***Abstract*:** In this study, we investigate the electrocatalytic properties of tetracationic cobalt (II) tetrapyridinoporphyrazine (**CoTmTPyPz**) for CO_2 reduction in a heterogeneous medium when adsorbed on carbon nanotubes (CNT) at a carbon paper (CP) electrode. Unlike previous reports on cobalt-based phthalocyanine electrocatalysis, which suggested CO as an intermediate in the reduction to methanol, our findings indicate that **CoTmTPyPz** does not reduce CO to methanol, thereby excluding a mechanistic pathway where CO is an intermediate.

Phosphetene-Based Polyaromatics: Structure-Property Relationships and Chiroptical Tuning

H. Lauwick, E. Kertész, K. Noel Garami, W. Huadsai, M. P. Duffy, R. Foundi, A. Chemin, T. Roisnel, N. Vanthuyne, Z. Benkő, P.-A. Bouit, M. Hissler

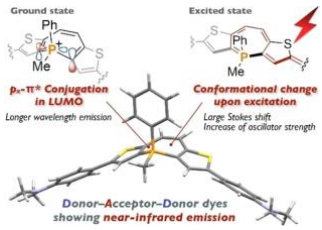
Angew Chem. Int. Ed. **2024**, e202409988

***Abstract*:** The synthesis of phosphetene rings (4-membered P-ring) flanked with PAH systems is described. Although neither the P centre nor the four-membered ring participate in the frontier orbitals, both structural features play an important role in modulating the symmetry of the orbitals, resulting in chiroptical properties. The stereogenic P-atom was used as a chiral perturbator to induce circularly polarized luminescence of the polyaromatic system.

Dithieno[3,2-b; 2′,3′-f]phosphepinium-Based Near-Infrared Fluorophores: px–π* Conjugation Inherent to Seven-Membered Phosphacycles

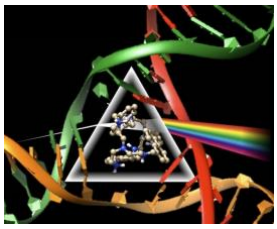
K. Andoh, M. Murai, P.-A. Bouit, M. Hissler, S. Yamaguchi

Angew Chem. Int. Ed. **2024**, e202410204



***Abstract*:** A seven-membered-ring phosphepinium has been developed as the key core skeleton for near-infrared (NIR) dyes. The low-lying px orbital in the phosphonium moiety and the bent conformation of the seven-membered ring lead to a stabilization of the LUMO via a "px–π* conjugation". The observed intense emission with a large Stokes shift was attributed to a large structural relaxation with a contribution from a quinoidal resonance structure in the excited state.

Structural Optimization of Azacryptands for Targeting Three-Way DNA Junctions

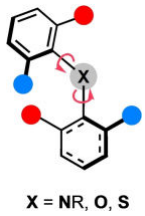


A. Pipier, T. Chetot, A. Kalamatianou, N. Martin, M. Caroff, S. Britton, N. Chéron, L. Trantírek, A. Granzhan, D. Monchaud

Angew Chem. Int. Ed. **2024**, e202409780

***Abstract*:** Great gig in the strands. We report on the characterization of azacryptands, small-molecule ligands that display high affinity and selectivity for a three-strand DNA structure known as a three-way DNA junction (TWJ), which makes them ideal molecular tools to interrogate the cellular relevance of TWJs and their potential as novel anticancer targets.

Enantioselective Synthesis of Heteroatom-Linked Non-Biaryl Atropisomers

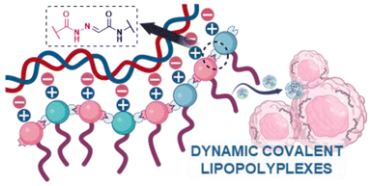


A. Naghim, J. Rodriguez, O. Chuzel, G. Chouraqui, D. Bonne

Angew Chem. Int. Ed. **2024**, e202407767

***Abstract*:** The successful atroposelective synthesis of heteroatom-linked non-biaryl atropisomers marks a significant milestone in organic synthesis. Unlike conventional atropisomers, these unique molecules display generally lower enantiomerization barriers due to possible concerted bond rotations. Through innovative strategies, chemists have succeeded in controlling the atroposelectivity of these reactions, enabling the construction of original optically active molecular structures.

Amphiphilic dynamic covalent polymer vectors of siRNA

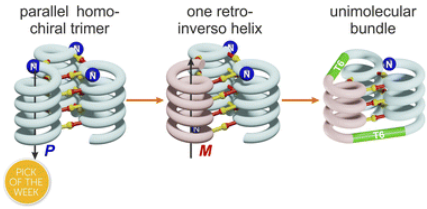


J. García Coll, P. Trousselier, S. Dattram Pawar, Y. Bessin, L. Lichon, J. Leblond Chain, E. Sachon, N. Bettache, S. Ulrich

Chem. Sci **2025**, Advance Article

***Abstract*:** Dynamic covalent polymers (DCPs) recently emerged as smart siRNA delivery vectors, which dynamically self-assemble through siRNA templating and depolymerize in a controlled manner. Herein, we report the dynamic combinatorial screening of cationic and amphiphilic peptide-based monomers. We provide experimental evidence, by mass spectrometry analyses, of the siRNA-templated formation of DCPs, and show that amphiphilic DCPs display superior activity in terms of siRNA complexation and delivery in cells. Thus, the work describes a new type of siRNA vector based on dynamic covalent lipopolyplexes, which feature improved activity as well as better nano-structuration compared to previous generations of DCPs.

Design of an abiotic unimolecular three-helix bundle

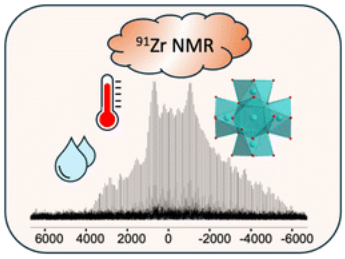


S. Wang, J. Sigl, L. Allmendinger, V. Maurizot, I. Huc

Chem. Sci. **2025**,*16*, 1136-1146

***Abstract*:** Starting from the solid state structure of C_3-symmetrical homochiral parallel trimolecular bundle of three aromatic helices held together by intermolecular hydrogen bonds, we have used simple rational principles and molecular modelling to design a similar heterochiral structure where one helix had an opposite orientation and handedness. A rigid and a flexible linker to connect these helices and transform the bundle into a unimolecular object were designed and synthesized. Model sequences with two helices and one linker were then prepared. Their conformations were investigated in solution by nuclear magnetic resonance and circular dichroism, in the solid state by X-ray crystallography, and by molecular dynamics simulations, overall supporting the initial design. A final 6.9 kDa unimolecular three-helix bundle was then prepared using a fragment condensation approach. Solution studies support the formation of the targetted tertiary fold in the case of the rigid linker, thereby validating the overall approach.

Probing the water adsorption and stability under steam flow of Zr-based metal–organic frameworks using 91Zr solid-state NMR spectroscopy

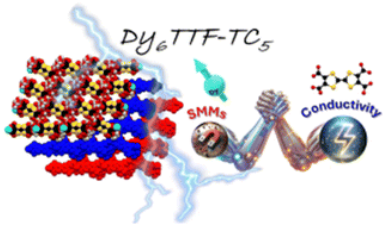


A. Nadol, F. Venel, R. Giovine, M. Leloire, C. Volkringer, T. Loiseau, C. Gervais, C. Mellot-Draznieks, B. Doumert, J. Trébosc, O. Lafon, F. Pourpoint

Chem. Sci. **2025**,*16*, 69-82

***Abstract*:** The stability of metal–organic frameworks (MOFs) in the presence of water is crucial for a wide range of applications, including the production of freshwater, desiccation, humidity control, heat pumps/chillers and capture and separation of gases. In particular, their stability under steam flow is essential since most industrial streams contain water vapor. Nevertheless, to the best of our knowledge, the stability under steam flow of Zr-based MOFs, which are among the most widely studied MOFs, has not been investigated so far. We explore it herein for three UiO-like Zr-based MOFs built from the same Zr cluster but distinct organic linkers at temperature ranging from 80 to 200 °C. We demonstrate the possibility of acquiring their 91Zr NMR spectra using high magnetic field (18.8 T) and low temperature (140 K) and of interpreting them by comparing experimental data with NMR parameters calculated by DFT. NMR observation of this challenging isotope combined with more conventional techniques, such as N2 adsorption, X-ray diffraction, IR, and 1H and 13C solid-state NMR spectroscopies, provides information not only on the possible collapse of the MOF framework but also on the adsorption of molecules into the pores. We notably show that UiO-66(Zr) and UiO-66-Fum(Zr) built from terephthalate and fumarate linkers, respectively, are stable over 24 h (and even over 7 days for UiO-66(Zr)) under steam flow at all investigated temperatures, whereas UiO-67-NH2 containing a 2-amino-[1,1′-biphenyl]-4,4′-dicarboxylate linker degrades under steam flow at temperatures ranging from 80 to 150 °C but is preserved at 200 °C. The lower stability of UiO-67-NH2 stems from its larger pores and its weaker Zr–O coordination bonds, whereas its preservation at 200 °C results from a more limited condensation of water in the pores.

A highly conducting tetrathiafulvalene-tetracarboxylate based dysprosium(iii) 2D metal–organic framework with single molecule magnet behaviour

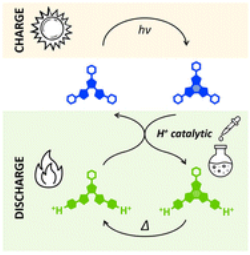


F. Manna, M. Oggianu, P. Auban-Senzier, G. Novitchi, E. Canadell, M. Laura Mercuri, N. Avarvari

Chem. Sci. **2024**, *15*, 19247-19263

***Abstract*:** The synthesis and whole characterization by a multitechnique approach of an unprecedented dysprosium(III) 2D metal organic framework (MOF), involving the redox-active tetrathiafulvalene (TTF)-based linker TTF-tetracarboxylate (TTF-TC), are herein reported. The single-crystal X-ray structure, formulated as $[Dy_6(TTF\text{-}TC)_5(H_2O)_{22}]\cdot 21H_2O$ (**1**), reveals a complex 2D topology, with hexanuclear Dy_6 clusters as secondary building units (SBUs) interconnected by five linkers, stacked almost parallel in each layer and eclipsed along the [111] direction, leading to the formation of 1D channels filled by water molecules. The mixed valence of the TTF units is confirmed by both bond distance analysis, Raman microscopy and diffuse reflectance spectroscopy, and further supported by band structure calculations, which also predict activated conductivity for this material. Thanks to efficient TTF stacking and partial oxidation, **1** shows semiconducting behavior, with, however, a record conductivity value of 1 mS cm^{-1} at room temperature, when compared to the previously reported TTF-based MOFs. Furthermore, temperature and magnetic field dependent ac (alternative current) magnetic susceptibility measurements demonstrate field induced slow relaxation of magnetization, accounting for two independent relaxation processes, with an energy barrier (U_{eff}/K) of around 12 K, typical for dysprosium carboxylate complexes. The herein reported 2D Dy-MOF provides a valuable master plan for coexistence of conducting π-TTF stacks and highly anisotropic Dy^{III} SMM properties.

Acid-sensitive photoswitches: towards catalytic on-demand release of stored light energy



L. Chocron, N. Baggi, E. Ribeiro, V. Goetz, P. Yu, K. Nakatani, R. Métivier

Chem. Sci. **2024**, *15*, 16034-16039

***Abstract*:** Photochromic compounds are promising for a variety of applications, including molecular solar thermal (MOST) energy storage. The energy release step and cyclability are critical issues to be addressed for the development of this technology. We report herein the synthesis and characterization of two diarylethene molecules featuring one (**1**) or two (**2**) pyridine groups as protonatable moieties. Upon UV irradiation, both molecules undergo a cyclization reaction from the open form (OF) to the closed form (CF). Both CF are stable for a few days in acetonitrile, and the addition of acid leads to a 600 (**1**) or 1500-fold (**2**) acceleration of the ring-opening reaction, even in catalytic amounts. A kinetic model is proposed to simulate the reaction, elucidating the contribution of each step to the kinetics and evidencing the importance of the kinetic control over the protonation thermodynamic equilibrium. Data fitting leads to the rates of elementary steps and turnover numbers (TON). Following a complete reaction cycle, neutralization of the acid by an equivalent amount of base allowed further cycles. This study represents a significant advancement in the cyclability and the control of the on-demand triggering of the energy-releasing ring-opening reaction of diarylethenes for future MOST applications.

Nanoconfinement of polyoxometalates in cyclodextrin: computational inspections of the binding affinity and experimental demonstrations of reactivity modulation

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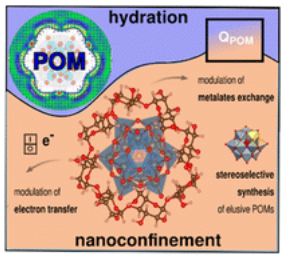
Chem. Sci. **2024**, *15*, 15849-15857



***Abstract*:** Chaotropic polyoxometalates (POMs) form robust host–guest complexes with γ-cyclodextrin (γ-CD), offering promising applications in catalysis, electrochemical energy storage, and nanotechnology. In this article, we provide the first computational insights on the supramolecular binding mechanisms using density-functional theory and classical molecular dynamics simulations. Focusing on the encapsulation of archetypal Keggin-type POMs ($PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$ and $BW_{12}O_{40}^{5-}$), our findings reveal that the lowest-charged POM, namely $PW_{12}O_{40}^{3-}$ spontaneously confines within the wider rim of γ-CD, but $BW_{12}O_{40}^{5-}$ does not exhibit this behaviour. This striking affinity for the hydrophobic pocket of γ-CD originates from the structural characteristics of water molecules surrounding $PW_{12}O_{40}^{3-}$. Moreover, through validation using ^{31}P NMR spectroscopy, we demonstrate that this nanoconfinement regulates drastically the POM reactivity, including its capability to undergo electron transfer and intermolecular metalate Mo/W exchanges. Finally, we exploit this nanoconfinement strategy to isolate the elusive mixed addenda POM $PW_{11}MoO_{40}^{3-}$.

Synthesis of polyurethanes through the oxidative decarboxylation of oxamic acids: a new gateway toward self-blown foams

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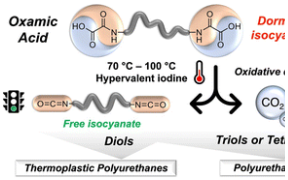
Chem. Sci. **2024**, *15*, 13475-13485

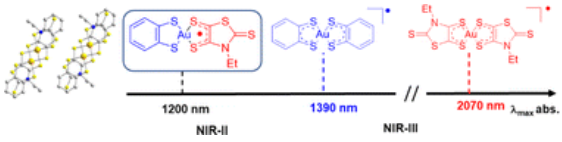


***Abstract*:** Polyurethane (PU) thermoplastics and thermosets were prepared through the step-growth polymerization of *in situ* generated polyisocyanates through the decarboxylation of polyoxamic acids, in the presence of phenyliodine diacetate (PIDA), and polyols. The CO_2 produced during the reaction allowed the access to self-blown polyurethane foams through an endogenous chemical blowing. The acetic acid released from ligand exchange at the iodine center was also shown to accelerate the polymerization reaction, avoiding the recourse to an additional catalyst. Changing simple parameters during the production process allowed us to access flexible PU foams with a wide range of properties.

Mixed-ligand, radical, gold bis(dithiolene) complexes: from single-component conductors to controllable NIR-II absorbers

H. Kharraz, P. Alemany, E. Canadell, Y. Le Gal, T. Roisnel, H. Cui, K. H. Kim, M. Fourmigué, D. Lorcy

Chem. Sci. **2024**, *15*, 11604-11616



***Abstract*:** Neutral radical bis(dithiolene) gold complexes $[Au(dt)_2]^{\cdot}$ are known to exhibit a strong absorption in the 1400–2000 nm NIR absorption range. Here, we demonstrate that the NIR signature of mixed-ligand bis(dithiolene) gold complexes $[Au(dt_A)(dt_D)]^{\cdot}$ associating two different dithiolene, dt_A and dt_D, is found at higher energy, out of the range of the homoleptic analogs $[Au(dt_A)_2]^{\cdot}$ and $[Au(dt_D)_2]^{\cdot}$, in the looked-after NIR-II 1000–1400 nm absorption range. An efficient synthetic approach towards precursor mixed-ligand monoanionic gold bis(dithiolene) complexes $[Au(dt_A)(dt_D)]^{-1}$ is reported. Using this strategy, no symmetrical complexes are formed and, upon electrocrystallization, no scrambling was observed in solution, allowing for the isolation of radical gold bis(dithiolene) complex such as $[Au(bdt)(Et\text{-}thiazdt)]^{\cdot}$ (bdt: benzene-1,2-dithiolate; Et-thiazdt: *N*-ethyl-thiazoline-2-thione-3,4-dithiolate), which behaves as a single-component conductor. It is shown from theoretical calculations that the spin polarization induced by electron repulsions leads to a strong localization of the spin–orbitals, and provides a sound basis to understand, (i) the different ligand-based oxidation potentials, (ii) the NIR optical absorption at notably higher energies and (iii) the larger potential difference of the two redox processes than in the parent symmetric complexes. The solid-state properties of the radical complex $[Au(bdt)(Et\text{-}thiazdt)]^{\cdot}$ are the consequence of a strongly 1D electronic structure with weakly dimerized chains and electronic localization favoring a semiconducting behavior, stable under pressures up to 18.2 GPa. Altogether, the versatility of the preparation method of $[Au(dt_A)(dt_D)]^{-1}$ salts opens the route for a wide library of different mixed-ligand radical complexes $[Au(dt_A)(dt_D)]^{\cdot}$ with simultaneously an adaptable absorption in the NIR-II range and the rich structural chemistry of single-component conductors.

Repurposing a supramolecular iridium catalyst via secondary Zn···O=C weak interactions between the ligand and substrate leads to ortho-selective C(sp2)–H borylation of benzamides with unusual kinetics

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Chem. Sci. **2024**, *15*, 11794-11806

***Abstract*:** The iridium-catalyzed C–H borylation of benzamides typically leads to meta and para selectivities using state-of-the-art iridium-based N,N-chelating bipyridine ligands. However, reaching ortho selectivity patterns requires extensive trial-and-error screening via molecular design at the ligand first coordination sphere. Herein, we demonstrate that triazolylpyridines are excellent ligands for the selective iridium-catalyzed ortho C–H borylation of tertiary benzamides and, importantly, we demonstrate the almost negligible effect of the first coordination sphere in the selectivity, which is so far unprecedented in iridium C–H bond borylations. Remarkably, the activity is dramatically enhanced by exploiting a remote Zn···O=C weak interaction between the substrate and a rationally designed molecular-recognition site in the catalyst. Kinetic studies and DFT calculations indicate that the iridium-catalyzed C–H activation step is not rate-determining, this being unique for remotely controlled C–H functionalizations. Consequently, a previously established supramolecular iridium catalyst designed for meta-borylation of pyridines is now compatible with the ortho-borylation of benzamides, a regioselectivity switch that is counter-intuitive regarding precedents in the literature. In addition, we highlight the role of the cyclohexene additive in avoiding the formation of undesired side-products as well as accelerating the HBpin release event that precedes the catalyst regeneration step, which is highly relevant for the design of powerful and selective iridium borylating catalysts.