

## SOMMAIRE

- Le mot du président 1
- Histoire de la création du groupe 2
- Actualités récentes 2
- À vos agendas 4
- Appel à contribution 5
- Notre sélection d'articles 6



## LE MOT DU PRÉSIDENT

Cher.ère.s sociétaires,

Créé en 2020, le Groupe Thématique de Chimie Supramoléculaire de la Société Chimique de France (SupraSCF) compte à ce jour presque 500 adhérent.e.s, démontrant le large intérêt que porte la communauté des chimistes français.es à la chimie supramoléculaire. Pour répondre au mieux à cet intérêt, les missions que se sont fixées le bureau du groupe SupraSCF sont un travail d'animation par l'organisation de manifestations scientifiques et la remise de prix, mais aussi un travail de diffusion d'informations dans la communauté.

Dans ce contexte, notre bureau est aujourd'hui très heureux de vous proposer le premier numéro d'une gazette semestrielle, *La SupInfo*, qui arrive en complément des autres canaux de diffusion d'actualités relatives à la chimie supramoléculaire tels que notre [site web](#) ou bien notre [compte twitter](#). Vous retrouverez dans *La SupInfo* toutes les rubriques qui vous plaisent déjà tant dans la gazette *EchoDCO* de la Division de Chimie Organique : un retour sur les événements marquants des six derniers mois, la présentation des événements futurs, et également une sélection d'articles récents dont les auteur.rice.s sont membres de notre groupe thématique.

Parce que cette gazette est la vôtre, nous serons bien évidemment ravis d'accueillir toutes vos suggestions pour les futurs numéros de *La SupInfo*. Au nom des membres du bureau de SupraSCF, je vous souhaite une bonne lecture.

Très cordialement,

Laurent Vial, Président du Groupe SupraSCF



## HISTOIRE DE LA CRÉATION DU GROUPE

Si le terme chimie supramoléculaire proposé par Jean-Marie Lehn est né en France en 1978 ([Acc. Chem. Res. 1978, 11, 49-57](#)), la communauté des chimistes supramoléculaires ne s'est pas constituée en entité visible, au sein de la Société Chimique de France en particulier, jusqu'à la création du Groupe thématique de Chimie Supramoléculaire (SupraSCF) en 2020.

Un élément déclencheur pour la création du groupe a sans doute été l'organisation de Supr@Lyon par Sébastien Vidal, Julien Leclaire et Christophe Bucher en 2018. Ce congrès a réuni 200 chimistes supramolécularistes, principalement français, autours de figures tutélaires comme Jean-Marie Lehn, Fraser Stoddart, Jeremy Sanders, Jean-Pierre Dutasta, David Leigh... Cet événement et les échanges que nous y avons eus nous ont fait réaliser qu'il existait une communauté active et nombreuse, mais pas d'occasion de la rassembler.

Partant du constat de la vie foisonnante de cette communauté et l'absence d'organisation, ou plutôt une dispersion dans différentes divisions de la SCF (DCO, DCC, DCP...), nous avons proposé à la SCF en 2019 la création d'un Groupe Thématique de Chimie Supramoléculaire en association avec la DCO principalement, mais également la DCC et la DCP.

Depuis le groupe a pris de l'ampleur et a organisé Supr@Strasbourg en 2021 et une journée du groupe à Lyon en 2022. Nous attendons maintenant la nouvelle journée du groupe à Montpellier en 2023 et l'organisation du congrès Supr@Paris 2024, dont l'organisation a déjà démarré !

Jean-François Nierengarten & Matthieu Sollogoub

## ACTUALITÉS RÉCENTES

### Prix du Groupe 2022

Notre Groupe a l'honneur de remettre des prix bisannuels récompensant des chercheur.euse.s remarquables dans notre discipline.

Le prix Christiane Dietrich-Buchecker est attribué à un.e chimiste de moins de 45 ans effectuant ses travaux en France et membre de la SCF depuis au moins trois ans.

Le prix André Collet est attribué à un.e chimiste confirmé.e ayant effectué des travaux de recherche reconnus au niveau national et international, et membre de la SCF depuis au moins trois ans.

## Prix André Collet 2022

Cette année, ce prix a été conjointement décerné aux Dr. Anne-Marie Caminade et Pr. Paolo Samori.

### Dr. Anne-Marie Caminade



Anne-Marie Caminade, directrice adjointe du Laboratoire de Chimie de Coordination (LCC-CNRS) à Toulouse depuis 2021, est directrice de recherche classe exceptionnelle (DRCE CNRS).

Son nom est immédiatement associé au domaine des dendrimères, dans lequel elle a été et reste la personne la plus productive au monde. Elle est à l'origine des dendrimères phosphorés, sur lesquels elle a su développer dans un premier temps une recherche fondamentale très importante et de qualité pour ensuite montrer l'étendue très large des applications de ces espèces dans des domaines aussi variés que la catalyse (métallique ou organique), la science des matériaux et la biologie / nanomédecine. Une grande partie de ses activités est liée à la chimie supramoléculaire, sous divers aspects, que ce soit des phénomènes liés à la multivalence, des associations électrostatiques, des interactions par

$\pi$ -stacking ou des liaisons hydrogène.

Sa production scientifique est remarquable. Elle entretient pour cela de nombreuses collaborations nationales et internationales: 500 publications (h index = 76, 17700 citations), 2 livres édités, 55 chapitres d'ouvrage, co-inventrice de 18 brevets prioritaires dont 16 ont été étendus à l'international, 3 brevets étant à la base de la création de 2 start-ups (Dendris et IMD-Pharma), 180 conférences invitées, Présidente de plusieurs congrès internationaux, Membre de comités éditoriaux de journaux scientifiques et fréquemment éditrice invitée.

Elle a déjà été honorée par la SCF par le Prix de la Division Chimie Organique en 2006, et par le Grand Prix Achille Le Bel en 2021.

### Pr. Paolo Samori



Paolo Samori est professeur à l'Université de Strasbourg, directeur de l'Institut de Science et d'Ingénierie Supramoléculaires (ISIS) et directeur du laboratoire de nanochimie. Il est membre étranger de l'Académie royale flamande de Belgique pour les sciences et les arts (KVAB), membre de la Royal Society of Chemistry (FRSC), membre de l'Académie européenne des sciences (EURASC), membre de l'Academia Europaea, membre de l'Académie européenne des sciences et des arts, membre de l'International Engineering and Technology Institute (IETI), Socio corrispondente, Sezione di Scienze Matematiche, Fisiche e Naturali ; Accademia Nazionale di Scienze Lettere e Arti di Modena, membre de la Materials Research Society (MRS), membre de l'Institut d'études avancées de l'Université de Strasbourg (USIAS), membre sénior de l'Institut Universitaire de France (IUF).

Paolo a publié plus de 400 articles sur la nanochimie, les sciences supramoléculaires, la chimie des matériaux et la microscopie à balayage, avec un accent particulier sur le graphène et d'autres matériaux 2D ainsi que sur les nanomatériaux organiques/polymères et hybrides fonctionnels pour des applications en optoélectronique, énergie et détection.

Il a reçu de nombreux prix prestigieux, notamment le E-MRS Graduate Student Award (1998), le MRS Graduate Student Award (2000), le prix IUPAC pour les jeunes chimistes (2001), le prix Vincenzo Caglioti (2006), le prix Nicolò Copernico (2009), le prix Guy Ourisson (2010), l'ERC Starting Grant (2010), la médaille d'argent du CNRS (2012), le prix Catalán-Sabatier (2017), le Grignard-Wittig Lectureship (2017), l'ERC Proof of Concept Grant (2017), le RSC Surfaces and Interfaces Award (2018), la médaille Blaise Pascal en science des matériaux (2018), le prix Pierre Süe (2018), l'ERC Advanced Grant (2019), le prix « Étoiles de l'Europe » (2019), l'ERC Proof of Concept Grant (2020) et le RSC/SCF Joint Lectureship in Chemical Sciences (2020).

## Prix Christine Dietrich-Buchecker 2022

### Pr. Thomas Hermans



Thomas Hermans est professeur de chimie à l'Université de Strasbourg et directeur du Laboratoire des systèmes complexes hors équilibre. Il a étudié le génie chimique et la chimie à l'Université de technologie d'Eindhoven (2000-2006), puis a obtenu un doctorat à la faculté de génie biomédical sous la direction du professeur E. W. "Bert" Meijer (2006-2010). Il a ensuite rejoint le groupe du professeur Bartosz Grzybowski à la Northwestern University en tant que chercheur postdoctoral (2010-2013).

Il a reçu l'ERC Starting Grant 2017, le Thieme Chemistry Award 2018, le Prix Guy Ourisson 2018, la Mercator Fellowship 2020, le Prix Forcheur Jean-Marie Lehn 2022, et a été Young Scientist au World Economic Forum et à la World Laureates Association 2019-2020.

L'objectif principal du groupe de recherche est d'obtenir des matériaux adaptatifs, autoréparables, autoreproduits et finalement vivants en utilisant l'auto-assemblage moléculaire dans des conditions loin de l'équilibre. Thomas est également cofondateur et directeur technique de Qfluidics, une entreprise qui travaille sur la fluidique sans paroi pour la chimie des flux et le pompage magnétostatique à faible cisaillement pour le transport de produits biologiques délicats.

## 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 2<sup>ème</sup> édition sera l'occasion pour la communauté de Chimie Supramoléculaire française de se retrouver et de partager ses 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.

Bloquez dès à présent ces dates. Au plaisir de vous retrouver à Montpellier.

Damien Bourgeois & Sébastien Ulrich, Organisateur des JCS2023




**SOCIÉTÉ CHIMIQUE DE FRANCE**  
 GROUPE THÉMATIQUE CHIMIE SUPRAMOLÉCULAIRE

**JCS2023**  
 2<sup>de</sup> Journée de Chimie Supramoléculaire  
 MONTPELLIER • 1 - 2 JUIN 2023

3 Plenary lectures • 14 Oral communications • 1 Poster session

**SAVE THE DATE**



## Supr@Paris 2024

**Supr@Paris** sera le troisième évènement d'une série de conférences en chimie supramoléculaire qui a débuté à Lyon en 2018, puis est passée par Strasbourg en 2021. Supr@Paris se tiendra à **Sorbonne Université**, au cœur de Paris, **du 15 au 17 mai 2024**.

4 sessions plénières, 1 conférence de remise de prix, 10 conférences principales, 20 communications orales et 20 communications courtes ainsi que de nombreux posters donneront l'opportunité à un maximum de personnes à différents stades de leur carrière de présenter leur science. Divers domaines de la chimie supramoléculaire seront représentés : catalyse, machines, assemblages, surfaces, nanotechnologie, molécules entrelacées, polymères... Chacun devrait y trouver son compte !

Vous trouverez toutes les informations relatives au congrès à : <https://supraparis2024.sciencesconf.org/>

Nous espérons que vous nous rejoindrez pour ce moment passionnant et unique de la science à Paris !

Matthieu Sollogoub, Président du comité d'organisation de Supr@Paris 2024



SAVE THE DATE:

**May 15-17, 2024**  
**Supr@Paris**

The 3rd French Supramolecular Chemistry Congress

*5 plenary & 10 keynote lectures,  
20 oral & 20 short communications,  
2 poster sessions*

<https://supraparis2024.sciencesconf.org> @SupraParis2024

## APPEL A CONTRIBUTION

Au-delà des publications en chimie supramoléculaire issues des laboratoires français, nous pensons que l'agrégation dans *La SupInfo* des thèses de doctorat soutenues dans le domaine est également un bon moyen d'avoir une vision large sur les recherches françaises en chimie supramoléculaire. Ainsi, nous encourageons nos adhérent.e.s à nous communiquer les détails des thèses soutenues (auteur, titre, laboratoire, résumé) dans leur équipe au cours des 6 prochains mois (oct. 2022 – mars 2023) à l'adresse suivante: [laurent.vial@univ-lyon1.fr](mailto:laurent.vial@univ-lyon1.fr)

## 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 janvier 2022-septembre 2022 dans les journaux suivants :

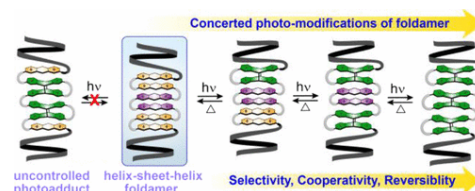
- *J. Am. Chem. Soc.*
- *Chem. Sci.*
- *Angew. Chem. Int. Ed.*
- *Chem. Comm.*
- *Chem. Eur. J.*

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

### Selective and Cooperative Photocycloadditions within Multistranded Aromatic Sheets

Gole, B.; Kauffmann, B.; Tron, A.; Maurizot, V.; McClenaghan, N.; Huc, I.; Ferrand, Y. *J. Am. Chem. Soc.* **2022**, *144*, 6894-6906

DOI: [10.1021/jacs.2c01269](https://doi.org/10.1021/jacs.2c01269)

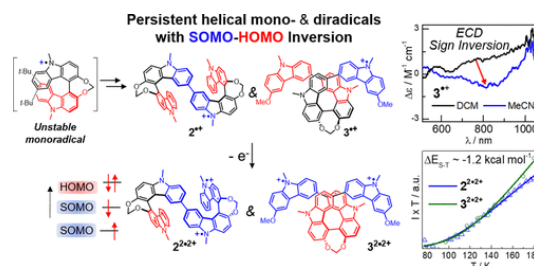


**Abstract:** A series of aromatic helix-sheet-helix oligoamide foldamers composed of several different photosensitive diaza-anthracene units have been designed and synthesized. Molecular objects up to 7 kDa were straightforwardly produced on a 100 mg scale. Nuclear magnetic resonance and crystallographic investigations revealed that helix-sheet-helix architectures can adopt one or two distinct conformations. Sequences composed of an even number of turn units were found to fold in a canonical symmetrical conformation with two helices of identical handedness stacked above and below the sheet segment. Sequences composed of an odd number of turns revealed a coexistence between a canonical fold with helices of opposite handedness and an alternate fold with a twist within the sheet and two helices of identical handedness. The proportions between these species could be manipulated, in some cases quantitatively, being dependent on solvent, temperature, and absolute control of helix handedness. Diazaanthracene units were shown to display distinct reactivity toward [4 + 4] photocycloadditions according to the substituent in position 9. Their organization within the sequences was programmed to allow photoreactions to take place in a specific order. Reaction pathways and kinetics were deciphered and product characterized, demonstrating the possibility to orchestrate successive photoreactions so as to avoid orphan units or to deliberately produce orphan units at precise locations. Strong cooperative effects were observed in which the photoreaction rate was influenced by the presence (or absence) of photoadducts in the structure. Multiple photoreactions within the aromatic sheet eventually lead to structure lengthening and stiffening, locking conformational equilibria. Photoproducts could be thermally reverted.

### Carbazole Isomerism in Helical Radical Cations: Spin Delocalization and SOMO-HOMO Level Inversion in the Diradical State

Kasemthaveechok, S.; Abella, L.; Jean, M.; Cordier, M.; Vanthuyne, N.; Guizouarn, T.; Cador, O.; Autschbach, J.; Crassous, J.; Favereau, L. *J. Am. Chem. Soc.* **2022**, *144*, 7253-7263

DOI: [10.1021/jacs.2c00331](https://doi.org/10.1021/jacs.2c00331)

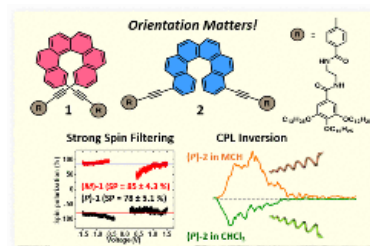


**Abstract:** We report a new molecular design to afford persistent chiral organic open-shell systems with configurational stability and an inversion in energy of the singly occupied molecular orbital (SOMO) and the highest doubly occupied molecular orbital (HOMO) for both mono- and diradical states. The unpaired electron delocalization within the designed extended helical  $\pi$ -conjugated systems is a crucial factor to reach chemical stabilities, which is not obtained using the classical steric protection approach. The unique features of the obtained helical monoradicals allow an exploration of the chiral intramolecular electron transfer (IET) process in solvents of different polarity by means of optical and chiroptical spectroscopies, resulting in an unprecedented electronic circular dichroism (ECD) sign inversion for the radical transitions. We also characterized the corresponding helical diradicals, which show near-infrared electronic circular dichroism at wavelengths up to 1100 nm and an antiferromagnetic coupling between the spins, with an estimated singlet-triplet gap ( $\Delta E_{ST}$ ) of about  $-1.2$  kcal mol $^{-1}$ . The study also revealed an intriguing double SOMO-HOMO inversion (SHI) electronic configuration for these diradicals, providing new insight regarding the peculiar energetic ordering of radical orbitals and the impact on the corresponding (chiral) optoelectronic properties.

## Mutual Monomer Orientation To Bias the Supramolecular Polymerization of [6]Helicenes and the Resulting Circularly Polarized Light and Spin Filtering Properties

Rodriguez, R.; Naranjo, C.; Kumar, A.; Matozzo, P.; Das, T.K.; Zhu, Q.R.; Vanthuyne, N.; Gomez, R.; Naaman, R.; Sanchez, L.; Crassous, J. *J. Am. Chem. Soc.* **2022**, *144*, 7709-7719

DOI: [10.1021/jacs.2c00556](https://doi.org/10.1021/jacs.2c00556)

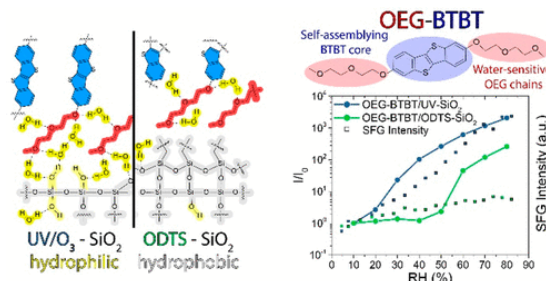


**Abstract:** We report on the synthesis and self-assembly of 2,15- and 4,13-disubstituted carbo[6]helicenes **1** and **2** bearing 3,4,5-tridodecyloxybenzamide groups. The self-assembly of these [6]helicenes is strongly influenced by the substitution pattern in the helicene core that affects the mutual orientation of the monomeric units in the aggregated form. Thus, the 2,15-substituted derivative **1** undergoes an isodesmic supramolecular polymerization forming globular nanoparticles that maintain circularly polarized light (CPL) with  $g_{lum}$  values as high as  $2 \times 10^{-2}$ . Unlike carbo[6]helicene **1**, the 4,13-substituted derivative **2** follows a cooperative mechanism generating helical one-dimensional fibers. As a result of this helical organization, [6]helicene **2** exhibits a unique modification in its ECD spectral pattern showing sign inversion at low energy, accompanied by a sign change of the CPL with  $g_{lum}$  values of  $1.2 \times 10^{-3}$ , thus unveiling an example of CPL inversion upon supramolecular polymerization. These helical supramolecular structures with high chiroptical activity, when deposited on conductive surfaces, revealed highly efficient electron-spin filtering abilities, with electron spin polarizations up to 80% for **1** and 60% for **2**, as measured by magnetic conducting atomic force microscopy.

## High-Performance Humidity Sensing in pi-Conjugated Molecular Assemblies through the Engineering of Electron/Proton Transport and Device Interfaces

Turetta, N.; Stoeckel, M.A.; de Oliveira, R.F.; Devaux, F.; Greco, A.; Cendra, C.; Gullace, S.; Gicevicius, M.; Chattopadhyay, B.; Liu, J.; Schweicher, G.; Siringhaus, H.; Salleo, A.; Bonn, M.; Backus, E.H.G.; Geerts, Y.H.; Samori, P. *J. Am. Chem. Soc.* **2022**, *144*, 2546-2555

DOI: [10.1021/jacs.1c10119](https://doi.org/10.1021/jacs.1c10119)

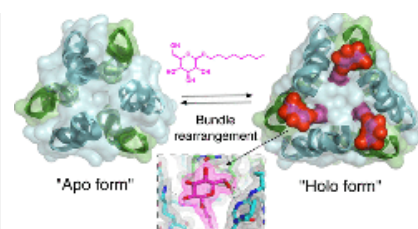


**Abstract:** The development of systems capable of responding to environmental changes, such as humidity, requires the design and assembly of highly sensitive and efficiently transducing elements. Such a challenge can be mastered only by disentangling the role played by each component of the responsive system, thus ultimately achieving high performance by optimizing the synergistic contribution of all functional elements. Here, we designed and synthesized a novel [1]benzothieno[3,2-*b*][1]benzothiophene derivative equipped with hydrophilic oligoethylene glycol lateral chains (OEG-BTBT) that can electrically transduce subtle changes in ambient humidity with high current ratios ( $>10^4$ ) at low voltages (2 V), reaching state-of-the-art performance. Multiscale structural, spectroscopical, and electrical characterizations were employed to elucidate the role of each device constituent, viz., the active material's BTBT core and OEG side chains, and the device interfaces. While the BTBT molecular core promotes the self-assembly of (semi)conducting crystalline films, its OEG side chains are prone to adsorb ambient moisture. These chains act as hotspots for hydrogen bonding with atmospheric water molecules that locally dissociate when a bias voltage is applied, resulting in a mixed electronic/protonic long-range conduction throughout the film. Due to the OEG-BTBT molecules' orientation with respect to the surface and structural defects within the film, water molecules can access the humidity-sensitive sites of the SiO<sub>2</sub> substrate surface, whose hydrophilicity can be tuned for an improved device response. The synergistic chemical engineering of materials and interfaces is thus key for designing highly sensitive humidity-responsive electrical devices whose mechanism relies on the interplay of electron and proton transport.

## Adaptive Binding of Alkyl Glycosides by Nonpeptidic Helix Bundles in Water: Toward Artificial Glycolipid Binding Proteins

Yoo, S.H.; Buratto, J.; Roy, A.; Morvan, E.; Pasco, M.; Pulka-Ziach, K.; Lombardo, C.M.; Rosu, F.; Gabelica, V.; Mackereth, C.D.; Collie, G.W.; Guichard, G. *J. Am. Chem. Soc.* **2022**, *144*, 15988-15998

DOI: [10.1021/jacs.2c05234](https://doi.org/10.1021/jacs.2c05234)

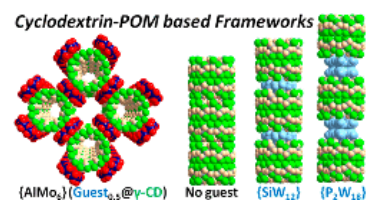


**Abstract:** Amphipathic water-soluble helices formed from synthetic peptides or foldamers are promising building blocks for the creation of self-assembled architectures with non-natural shapes and functions. While rationally designed artificial quaternary structures such as helix bundles have been shown to contain preformed cavities suitable for guest binding, there are no examples of adaptive binding of guest molecules by such assemblies in aqueous conditions. We have previously reported a foldamer 6-helix bundle that contains an internal nonpolar cavity able to bind primary alcohols as guest molecules. Here, we show that this 6-helix bundle can also interact with larger, more complex guests such as *n*-alkyl glycosides. X-ray diffraction analysis of co-crystals using a diverse set of guests together with solution and gas-phase studies reveals an adaptive binding mode whereby the apo form of the 6-helix bundle undergoes substantial conformational change to accommodate the hydrocarbon chain in a manner reminiscent of glycolipid transfer proteins in which the cavity forms upon lipid uptake. The dynamic nature of the self-assembling and molecular recognition processes reported here marks a step forward in the design of functional proteomimetic molecular assemblies.

### Chaotropic Effect as an Assembly Motif to Construct Supramolecular Cyclodextrin-Polyoxometalate-Based Frameworks

Khelifi, S.; Marrot, J.; Haouas, M.; Shepard, W.E.; Falaise, C.; Cadot, E. *J. Am. Chem. Soc.* **2022**, *144*, 4469-4477

DOI: [10.1021/jacs.1c12049](https://doi.org/10.1021/jacs.1c12049)

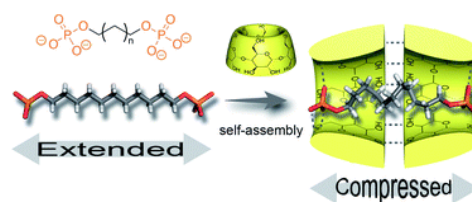


**Abstract:** In aqueous solution, low-charged polyoxometalates (POMs) exhibit remarkable self-assembly properties with nonionic organic matter that have been recently used to develop groundbreaking advances in host-guest chemistry, as well as in soft matter science. Herein, we exploit the affinity between a chaotropic POM and native cyclodextrins ( $\alpha$ -,  $\beta$ -, and  $\gamma$ -CD) to enhance the structural and functional diversity of cyclodextrin-based open frameworks. First, we reveal that the Anderson-Evans type polyoxometalate [AlMo<sub>6</sub>O<sub>18</sub>(OH)<sub>6</sub>]<sup>3-</sup> represents an efficient inorganic scaffold to design open hybrid frameworks built from infinite cyclodextrin channels connected through the disk-shaped POM. A single-crystal X-ray analysis demonstrates that the resulting supramolecular architectures contain large cavities (up to 2 nm) where the topologies are dictated by the rotational symmetry of the organic macrocycle, generating honeycomb (bnn net) and checkerboard-like (pcu net) networks for  $\alpha$ -CD (C<sub>6</sub>) and  $\gamma$ -CD (C<sub>8</sub>), respectively. On the other hand, the use of  $\beta$ -CD, a macrocycle with C<sub>7</sub> ideal symmetry, led to a distorted-checkerboard-like network. The cyclodextrin-based frameworks built from an Anderson-Evans type POM are easily functionalizable using the molecular recognition properties of the macrocycle building units. As a proof of concept, we successfully isolated a series of compartmentalized functional frameworks by the entrapment of polyiodides or superchaotropic redox-active polyanions within the macrocyclic host matrix. This set of results paves the way for designing multifunctional supramolecular frameworks whose pore dimensions are controlled by the size of inorganic entities.

### Size-dependent compression of threaded alkyldiphosphate in head to head cyclodextrin [3]pseudorotaxanes

Scelle, J.; Vervoitte, H.; Bouteiller, L.; Chamoreau, L.M.; Sollogoub, M.; Vives, G.; Hasenknopf, B. *Chem. Sci.* **2022**, *13*, 2218-2225

DOI: [10.1039/d1sc05697b](https://doi.org/10.1039/d1sc05697b)

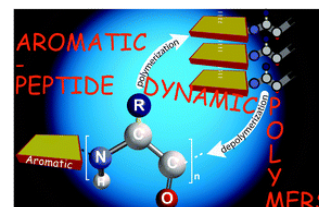


**Abstract:** The encapsulation of guests in a confined space enables unusual conformations and reactivities. In particular, the compression of alkyl chains has been obtained by self-assembled molecular capsules but such an effect has not been reported in solution for pseudorotaxane architectures. By exploiting the tendency of cyclodextrin (CD) to form head to head [3]pseudorotaxanes and the hydrogen bonding abilities of phosphate groups, we have studied the effect of the CD dimer cavity on the conformation of threaded  $\alpha,\omega$ -alkyl-diphosphate axes. The formation of [2]pseudorotaxanes and [3]pseudorotaxanes was investigated by a combination of NMR, ITC and X-ray diffraction techniques. In the solid state, the [3]pseudorotaxane with a C<sub>8</sub> axle presents a fully extended conformation with both terminal phosphate groups interacting with hydroxyl groups of the primary rim of CDs. Such hydrogen bonding interactions are also present with the C<sub>9</sub> and C<sub>10</sub> axles resulting in a compression of the alkyl chain with gauche conformations in the solid state. NMR studies have shown that this effect is maintained in solution resulting in a size-dependent progressive compression of the alkyl chain by the CD [3]pseudorotaxane architecture for C<sub>9</sub>, C<sub>10</sub> and C<sub>11</sub> axles.

### Hierarchical self-assembly of aromatic peptide conjugates into supramolecular polymers: it takes two to tango

Coste, M.; Suarez-Picado, E.; Ulrich, S. *Chem. Sci.* **2022**, *13*, 909-933

DOI: [10.1039/d1sc05589e](https://doi.org/10.1039/d1sc05589e)



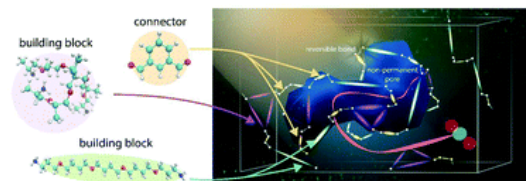
**Abstract:** Supramolecular polymers are self-assembled materials displaying adaptive and responsive “life-like” behaviour which are often made of aromatic compounds capable of engaging in  $\pi$ - $\pi$  interactions to form larger assemblies. Major advances have been made recently in controlling their mode of self-assembly, from thermodynamically-controlled isodesmic to kinetically-controlled living polymerization. Dynamic covalent chemistry has been recently implemented to generate dynamic covalent polymers which can be seen as dynamic analogues of biomacromolecules. On the other hand, peptides are readily-available and structurally-rich building blocks that can lead to secondary structures or specific functions. In this context, the past decade has seen intense research activity in studying the behaviour of aromatic-peptide conjugates through supramolecular and/or dynamic covalent chemistries. Herein, we review those impressive key achievements showcasing how aromatic- and peptide-based self-assemblies can be combined using dynamic covalent and/or supramolecular chemistry, and what it brings in terms of the structure, self-assembly pathways, and function of supramolecular and dynamic covalent polymers.



### Unravelling the pore network and gas dynamics in highly adaptive rubbery organic frameworks

Dupuis, R.; Barboiu, M.; Maurin, G. *Chem. Sci.* **2022**, *13*, 5141-5147

DOI: [10.1039/d2sc01355j](https://doi.org/10.1039/d2sc01355j)

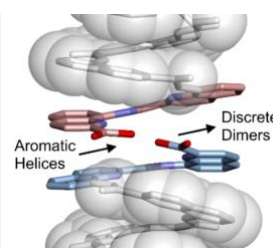


**Abstract:** Supramolecular polymers are self-assembled materials displaying adaptive and responsive “life-like” behaviour which are often made of aromatic compounds capable of engaging in  $\pi$ - $\pi$  interactions to form larger assemblies. Major advances have been made recently in controlling their mode of self-assembly, from thermodynamically-controlled isodesmic to kinetically-controlled living polymerization. Dynamic covalent chemistry has been recently implemented to generate dynamic covalent polymers which can be seen as dynamic analogues of biomacromolecules. On the other hand, peptides are readily-available and structurally-rich building blocks that can lead to secondary structures or specific functions. In this context, the past decade has seen intense research activity in studying the behaviour of aromatic-peptide conjugates through supramolecular and/or dynamic covalent chemistries. Herein, we review those impressive key achievements showcasing how aromatic- and peptide-based self-assemblies can be combined using dynamic covalent and/or supramolecular chemistry, and what it brings in terms of the structure, self-assembly pathways, and function of supramolecular and dynamic covalent polymers.

### Discrete Stacked Dimers of Aromatic Oligoamide Helices

Bindl, D.; Mandal, P.K.; Allmendinger, L.; Huc, I. *Angew Chem. Int. Ed.* **2022**, *61*, e202116509

DOI: [10.1002/anie.202116509](https://doi.org/10.1002/anie.202116509)

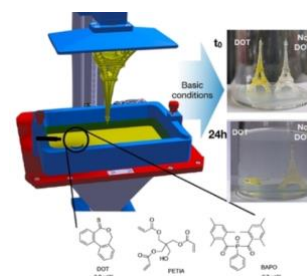


**Abstract:** Tight binding was observed between the C-terminal cross section of aromatic oligoamide helices in aqueous solution, leading to the formation of discrete head-to-head dimers in slow exchange on the NMR timescale with the corresponding monomers. The nature and structure of the dimers was evidenced by 2D NOESY and DOSY spectroscopy, mass spectrometry and X-ray crystallography. The binding interface involves a large hydrophobic aromatic surface and hydrogen bonding. Dimerization requires that helices have the same handedness and the presence of a C-terminal carboxy function. The protonation state of the carboxy group plays a crucial role, resulting in pH dependence of the association. Dimerization is also influenced by neighboring side chains and can be programmed to selectively produce heteromeric aggregates.

### Thionolactone as a Resin Additive to Prepare (Bio)degradable 3D Objects via VAT Photopolymerization

Gil, N.; Thomas, C.; Mhanna, R.; Mauriello, J.; Maury, R.; Leuschel, B.; Malval, J.-P.; Clement, J.-L.; Gignes, D.; Lefay, C.; Soppera, O.; Guillaneuf, Y. *Angew Chem. Int. Ed.* **2022**, *61*, e202117700

DOI: [10.1002/anie.202117700](https://doi.org/10.1002/anie.202117700)

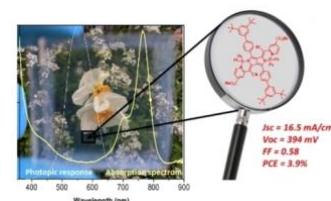


**Abstract:** Three-dimensional (3D) printing and especially VAT photopolymerization leads to cross-linked materials with high thermal, chemical, and mechanical stability. Nevertheless, these properties are incompatible with requirements of degradability and re/upcyclability. We show here that thionolactone and in particular dibenzo[*c,e*]-oxepane-5-thione (DOT) can be used as an additive (2 wt %) to acrylate-based resins to introduce weak bonds into the network via a radical ring-opening polymerization process. The low amount of additive makes it possible to modify the printability of the resin only slightly, keep its resolution intact, and maintain the mechanical properties of the 3D object. The resin with additive was used in UV microfabrication and two-photon stereolithography setups and commercial 3D printers. The fabricated objects were shown to degrade in basic solvent as well in a homemade compost. The rate of degradation is nonetheless dependent on the size of the object. This feature was used to prepare 3D objects with support structures that could be easily solubilized.

### Transparent and Colorless Dye-Sensitized Solar Cells Based on Pyrrolopyrrole Cyanine Sensitizers

Baron, T.; Naim, W.; Nikolinakos, I.; Andrin, B.; Pellegrin, Y.; Jacquemin, D.; Haacke, S.; Sauvage, F.; Odobel, F. *Angew Chem. Int. Ed.* **2022**, *61*, e202207459

DOI: [10.1002/anie.202207459](https://doi.org/10.1002/anie.202207459)

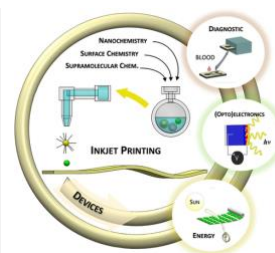


**Abstract:** The development of transparent solar cells extends the applications of photovoltaics by offering the opportunity to substitute the gigantic surface coverage of windows by solar panels to produce electricity. Herein, we report a new family of NIR-sensitizers based on pyrrolopyrrole cyanine dyes, particularly efficient for the development of fully transparent and colorless dye-sensitized solar cells since a record efficiency of 2.5 % was achieved with an average visible transmittance (AVT) of 76 % and a color rendering index (CRI) of 93.

## Challenges, Prospects, and Emerging Applications of Inkjet-Printed Electronics: A Chemist's Point of View

Lemarchand, J.; Bridonneau, N.; Battaglini, N.; Carn, F.; Mattana, G.; Piro, B.; Zrig, S.; Noel, V. *Angew Chem. Int. Ed.* **2022**, *61*, e202200166

DOI: [10.1002/anie.202200166](https://doi.org/10.1002/anie.202200166)

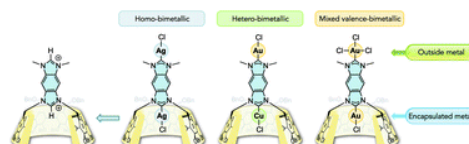


**Abstract:** Driven by the development of new functional inks, inkjet-printed electronics has achieved several milestones upon moving from the integration of simple electronic elements (e.g., temperature and pressure sensors, RFID antennas, etc.) to high-tech applications (e.g. in optoelectronics, energy storage and harvesting, medical diagnosis). Currently, inkjet printing techniques are limited by spatial resolution higher than several micrometers, which sets a redhibitory threshold for miniaturization and for many applications that require the controlled organization of constituents at the nanometer scale. In this Review, we present the physico-chemical concepts and the equipment constraints underpinning the resolution limit of inkjet printing and describe the contributions from molecular, supramolecular, and nanomaterials-based approaches for their circumvention. Based on these considerations, we propose future trajectories for improving inkjet-printing resolution that will be driven and supported by breakthroughs coming from chemistry.

## Janus-type homo-, hetero- and mixed valence-bimetallic complexes with one metal encapsulated in a cyclodextrin

Wen, Z.H.; Maisonhaute, E.; Zhang, Y.M.; Roland, S.; Sollogoub M. *Chem. Comm.* **2022**, *58*, 4516-4519

DOI: [10.1039/d2cc00219a](https://doi.org/10.1039/d2cc00219a)

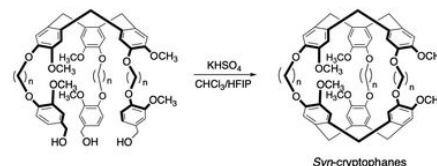


**Abstract:** Bis-azolium salts with one azolium capping a perbenzylated  $\alpha$ -cyclodextrin have been designed to generate Janus-type bimetallic complexes with various combinations of copper, silver, gold or palladium salts. Encapsulation of one metal center inside the cavity allowed (trans)metalation and oxidation reactions to be controlled at selected positions. In particular, it was possible to oxidize Au<sup>I</sup> into Au<sup>III</sup> selectively on the position outside the cavity of the cyclodextrin on the bis-Au<sup>I</sup> Janus complex.

## Access to the Syn diastereomers of cryptophane cages using HFIP

Della-Negra, O.; Cirillo, Y.; Brotin, T.; Dutasta, J.-P.; Saaidi, P.-L.; Chatelet, B.; Martinez, A. *Chem. Comm.* **2022**, *58*, 3330-3333

DOI: [10.1039/d1cc06607b](https://doi.org/10.1039/d1cc06607b)

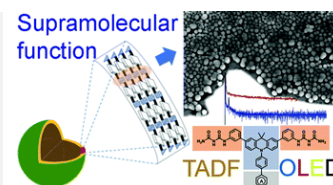


**Abstract:** Cryptophane cages can adopt either an *anti* or *syn* configuration that present different recognition properties. While the synthesis of *anti*-cryptophanes is well reported, the synthesis of *syn*-cryptophanes remains a challenge. Herein, we demonstrate that the use of HFIP as a co-solvent during the second ring closure reaction significantly affects the regioselectivity, providing easier access to the *syn*-cryptophane stereoisomers.

## Supramolecular gating of TADF process in self-assembled nano-spheres for high-resolution OLED applications

Hsieh, Y.-Y.; Sanchez, R.S.; Raffy, G.; Shyue, J.-J.; Hirsch, L.; Del Guerzo, A.; Wong, K.-T.; Bassani, D.M. *Chem. Comm.* **2022**, *58*, 1163-1166

DOI: [10.1039/d1cc06120h](https://doi.org/10.1039/d1cc06120h)



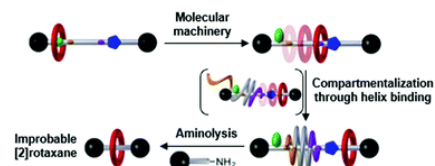
**Abstract:** Acridine-based donor–acceptor chromophores exhibiting E-type delayed fluorescence were substituted with bis-biuret H-bonding motifs to induce the formation of hollow spheres which can be deposited from solution to form the active component of OLED devices. In solution, the contribution of the delayed component is sensitive to disruption of the aggregates.

### [3]Foldarotaxane-mediated synthesis of an improbable [2]rotaxane

Koehler, V.; Gauthier, M.; Yao, C.H.; Fournel-Marotte, K.; Waeles, P.; Kauffmann, B.; Huc, I.; Coutrot, F.; Ferrand, Y. *Chem. Comm.* **2022**, *58*, 8618-8621

DOI: [10.1039/d2cc03066g](https://doi.org/10.1039/d2cc03066g)

**Abstract:** The wrapping of an aromatic oligoamide helix around an active ester-containing [2]rotaxane enforced the sliding and the sequestration of the surrounding macrocycle around a part of the axle for which it has no formal affinity. The foldamer-mediated compartmentalization of the [2]rotaxane shuttle was subsequently used to prepare an improbable rotaxane.

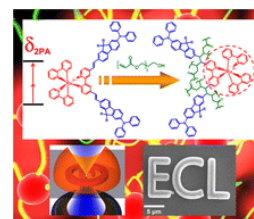


### Micropatterning of electrochemiluminescent polymers based on multipolar Ru-complex two-photon initiators

Mhanna, R.; Durand, N.; Savel, P.; Akdas-Kilic, H.; Abdallah, S.; Versace, D.-L.; Soppera, O.; Fillaut, J.-L.; Sojic, N.; Malval, J.-P. *Chem. Comm.* **2022**, *58*, 9678-9681

DOI: [10.1039/d2cc04159f](https://doi.org/10.1039/d2cc04159f)

**Abstract:** In this work, we present an original stereolithography strategy based on multibranching Ru-complexes with a high two-photon initiating ability allowing the 'one-pot' direct laser writing of ECL-active materials deposited onto electro-active surfaces at the  $\mu\text{m}$  scale.

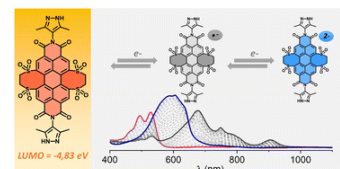


### New sulfonated perylene diimide pyrazolate ligands: a simple route toward n-type redox-active hybrid materials

Monnier, V.; Odobel, F.; Diring, S. *Chem. Comm.* **2022**, *58*, 9429-9432

DOI: [10.1039/d2cc02427f](https://doi.org/10.1039/d2cc02427f)

**Abstract:** We report the synthesis and the in depth electrochemical study of two novel electron accepting sulfonated perylene diimide pyrazolate ligands. Bridging the sulfone moieties of the perylene core unexpectedly affected the optical and electronic properties as evidenced by spectroelectrochemical investigation. Notably, we achieved a significant lowering of the LUMO level to  $-4.83\text{ eV}$ , ranking the ligand among the best electron acceptors via a straightforward synthetic procedure. These ligands can be foreseen for the development of n-type functional materials.

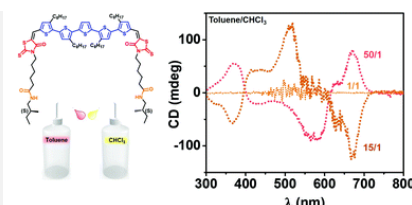


### Chirality inversion in hydrogen-bonded rhodanine-oligothiophene derivatives by solvent and temperature

Garcia, A.M.; Ruiz-Carretero, A. *Chem. Comm.* **2022**, *58*, 529-532

DOI: [10.1039/d1cc05945a](https://doi.org/10.1039/d1cc05945a)

**Abstract:** The self-assembly process of hydrogen-bonded quinquethiophene-rhodanine derivatives has been explored as a function of solvent and temperature. We demonstrate the divergent supramolecular chirality emerging from a single enantiomer by subtle changes in solvent mixtures and sample preparation protocol. Spectroscopic techniques have proved the presence of aggregates where H-bonding interactions play a crucial role.

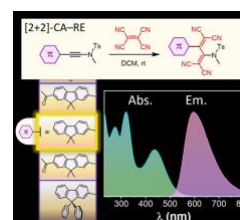


### Synthesis and Photophysical Properties of 1,1,4-Tetracyanobutadienes Derived from Ynamides Bearing Fluorophores

Philippe, C.; Bui, A.T.; Beau, M.; Bloux, H.; Riobe, F.; Mongin, O.; Roisnel, T.; Cordier, M.; Paul, F.; Lemiegre, L.; Trolez, Y. *Chem. Eur. J.* **2022**, *28*, e202200025

DOI: [10.1002/chem.202200025](https://doi.org/10.1002/chem.202200025)

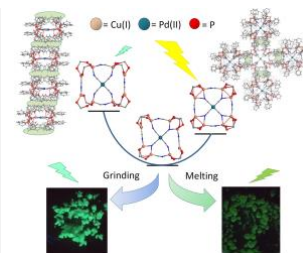
**Abstract:** 1,1,4-Tetracyanobutadienes (TCBDs) derived from ynamides and bearing diverse fluorene-based chromophores or other tricyclic aromatic hydrocarbons were prepared. The conceived sulfonamido-TCBDs showed remarkable photophysical properties covering a large range of wavelengths from the visible region to the NIR. They displayed an environment-sensitive emission that was observed in nonpolar solvents and in the solid state but was very weak in dichloromethane. Quantum yields in cyclohexane reached values up to 7.8%.



### Impact of Intermolecular Non-Covalent Interactions in a (Cu<sub>8</sub>Pd<sub>11</sub>)-Pd-I Discrete Assembly: Conformers' Geometries and Stimuli-Sensitive Luminescence Properties

Moutier, F.; Schiller, J.; Lecourt, C.; Khalil, A.M.; Delmas, V.; Calvez, G.; Costuas, K.; Lescop, C. *Chem. Eur. J.* **2022**, *28*, e202104497

DOI: [10.1002/chem.202104497](https://doi.org/10.1002/chem.202104497)

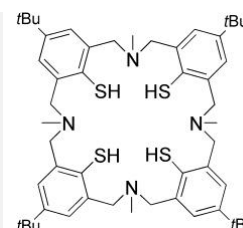


**Abstract:** A combined experimental and computational study highlights the crucial role played by intermolecular non-covalent weak-interactions in the conformer selection, the solid-state organization and the photophysical properties observed in a series of phases of a Cu<sub>8</sub>Pd<sub>11</sub> multimetallic assembly. Rationalization of the structure/properties relationships allows understanding their mechanical and thermal stimuli-sensitive responses.

### Expanded Mercaptocalixarenes: A New Kind of Macrocyclic Ligands for Stabilization of Polynuclear Thiolate Clusters

Schleife, F.; Bonnot, C.; Chambron, J.-C.; Borner, M.; Kersting, B. *Chem. Eur. J.* **2022**, *28*, e202104255

DOI: [10.1002/chem.202104255](https://doi.org/10.1002/chem.202104255)

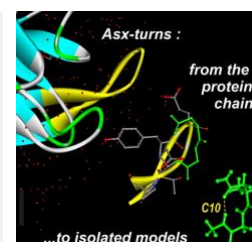


**Abstract:** The synthesis of expanded mercaptocalix[4]arenes, in which four 4-tert-butyl-thiophenolato units are joined by -CH<sub>2</sub>NRCH<sub>2</sub>- and -CH<sub>2</sub>NR(CH<sub>2</sub>)<sub>3</sub>NRCH<sub>2</sub>- linkers, has been achieved. The new macrocycles do not show the conformational isomerism typical of the parent mercaptocalix[4]arenes. The potential of these macrocycles to form mixed-ligand complexes with first row-transition metal ions is demonstrated.

### Characterization of Asx Turn Types and Their Connate Relationship with beta-Turns

D'mello, V.C.; Goldsztejn, G.; Mundlapati, V.R.; Brenner, V.; Gloaguen, E.; Charnay-Pouget, F.; Aitken, D.J.; Mons, M. *Chem. Eur. J.* **2022**, *28*, e202200969

DOI: [10.1002/chem.202104328](https://doi.org/10.1002/chem.202104328)

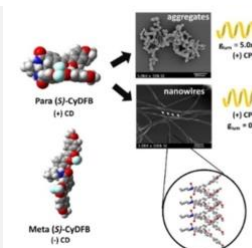


**Abstract:** One good turn promotes another: The Asx turn, a H-bonded, local secondary structure of the asparagine residue was investigated in the gas phase using laser spectroscopy and quantum chemistry studies of relevant model peptides. Comparison of these models with crystallized proteins supports the premise that Asx turns foster or stabilize the classical  $\beta$ -turn structures, and even promote  $\beta$ -bulges when Asn is followed by a Gly residue.

### Circularly Polarized Luminescence and Circular Dichroism of Bichromophoric Difluoroboron-beta-diketonates: Inversion and Enhanced Chirality Based on Spatial Arrangements and Self-Assembly

Panis, J.A.; Louis, M.; Brosseau, A.; Katao, S.; de los Reyes, F.; Nakashima, T.; Metivier, R.; Allain, C.; Kawai, T. *Chem. Eur. J.* **2022**, *28*, e2022010

DOI: [10.1002/chem.202201012](https://doi.org/10.1002/chem.202201012)



**Abstract:** Two bichromophoric difluoroboron  $\beta$ -diketonates (DFBs) with different connections to a chiral cyclohexanediamine bridge display inversion of chirality. When using different solvent systems, para Cy-DFB shows self-assembly in spherical aggregates with enhanced chiroptical properties as compared with solution state. Ultrasonication and heating induces the formation of supramolecular assembled nanowires with higher g value of 0.015.

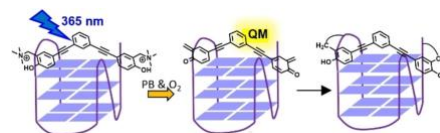


### Photoactivatable V-Shaped Bifunctional Quinone Methide Precursors as a New Class of Selective G-quadruplex Alkylating Agents

Lena, A.; Benassi, A.; Stasi, M.; Saint-Pierre, C.; Freccero, M.; Gasparutto, D.; Bombard, S.; Doria, F.; Verga, D. *Chem. Eur. J.* **2022**, *28*, e202200734

DOI: [10.1002/chem.202200734](https://doi.org/10.1002/chem.202200734)

**Abstract:** G4 ligand Quinone Methide precursors. A new family of G-quadruplex alkylating compounds able to generate quinone methides (QM) through photochemical activation has been designed and synthesized. In the presence of the human telomeric sequence, ammonium salt precursors showed the ability to generate mono- and crosslinking products identified both by gel and MALDI-ToF mass spectrometry analysis.

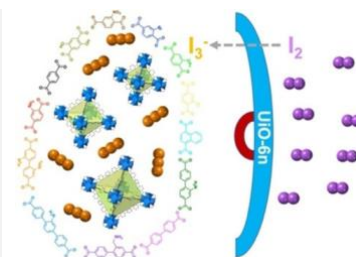


### Capture of Gaseous Iodine in Isorecticular Zirconium-Based UiO-n Metal-Organic Frameworks: Influence of Amino Functionalization, DFT Calculations, Raman and EPR Spectroscopic Investigation

Leloire, M.; Walshe, C.; Devaux, P.; Giovine, R.; Duval, S.; Bousquet, T.; Chibani, S.; Paul, J.-F.; Moissette, A.; Vezin, H.; Nerisson, P.; Cantrel, L.; Volkringer, C.; Loiseau, T. *Chem. Eur. J.* **2022**, *28*, e202104437

DOI: [10.1002/chem.202104437](https://doi.org/10.1002/chem.202104437)

**Abstract:** Conversion of  $I_2$  into  $I_3^-$  species trapped within UiO-n. The adsorption of gaseous iodine in UiO-n MOF-like materials has been systematically studied by analyzing kinetic curves. They show the conversion of trapped  $I_2$  into anionic species  $I_3^-$ , which is enhanced by the existence of amino groups functionalizing the organic linkers.



### Chalcogen Bonding with Diaryl Ditellurides: Evidence from Solid State and Solution Studies

Weiss, R.; Aubert, E.; Gros Lambert, L.; Pale, P.; Mamane, V. *Chem. Eur. J.* **2022**, *28*, e202200395

DOI: [10.1002/chem.202200395](https://doi.org/10.1002/chem.202200395)

**Abstract:** Diaryl ditelluride derivatives bearing different functional groups were prepared with the aim to study their ability to interact through chalcogen bonding (ChB). Rectangular  $Te_4$  and triangular  $Te_3$  motifs were observed in the solid-state as a result of intermolecular  $Te \cdots Te$  ChB. In solution, the use of the very sensitive  $^{125}Te$ ,  $^{17}O$  NMR analyses as well as  $^{19}F$ - $^1H$  HOESY allowed unambiguous detection of a  $Te \cdots O$  chalcogen bond between the diaryl ditellurides and phosphine oxides.

