

SOMMAIRE

- Le mot du président 1
- Actualités récentes 2
- Prix du groupe 2024 3
- Un point sur... 5
- Notre sélection d'articles 7



LE MOT DU PRÉSIDENT

Cher-ère-s sociétaires,

Nous sommes particulièrement heureux de vous avoir vu si nombreux à l'occasion de Supr@Paris en mai dernier, notre congrès international englobant tous les domaines de la chimie supramoléculaire. Grâce à une organisation superbement orchestrée par Matthieu Sollogoub, cet événement s'enracine encore plus durablement dans le paysage des événements incontournables en chimie supramoléculaire. Nous vous donnons rendez-vous pour la prochaine édition à Angers en 2027 !

Nous sommes également ravis d'annoncer les lauréats des prix 2024 du groupe Supr@SCF : Ling Peng et Mihail Barboiu ont conjointement reçu le prix André Collet, Nicolas Giuseppone a été honoré du prix Henry Le Chatelier, et Clément Falaise a été récompensé par le prix Christiane Dietrich-Buchecker. Félicitations à eux pour ces distinctions amplement méritées !

Vous trouverez aussi dans ce numéro une brillante introduction à la topologie moléculaire et à la chiralité topologique par Jean-Claude Chambron.

Finalement, ne manquez pas « Notre sélection d'articles » publiés au cours des 8 derniers mois par nos sociétaires.

Au nom des membres du bureau, je vous souhaite une bonne lecture et un bel été !

Bien cordialement,

Laurent Vial, Président du Groupe Supr@SCF



ACTUALITÉS RÉCENTES

Supr@Paris 2024

La conférence Supr@Paris s'est tenue sur le site des Cordeliers, à Paris, du 15 au 17 Mai dernier.

Le comité d'organisation local, chapeauté par M. Sollogoub, comprenait 3 membres du bureau du groupe de Chimie Supramoléculaire. Plus de 250 participants de 20 pays ont participé de façon active sur les deux jours et ½ de la conférence ! Les 4 conférences plénières, les 10 « keynotes » et les 22 présentations orales d'excellente qualité ont couvert un champ extrêmement vaste des thématiques de la chimie supramoléculaire, permettant ainsi de mettre en relation des scientifiques à tous les stades de leur carrière et venant d'horizons thématiques et géographiques variés.

Il apparaît ainsi que la chimie supramoléculaire est une discipline extrêmement dynamique et que la nouvelle série des conférences Supr@, après Supr@Lyon et Supr@Strasbourg, constitue une vitrine exceptionnelle pour notre communauté à l'international. Cet engouement scientifique, conjugué au soutien des sponsors et des institutions et à l'aide de nombreux étudiants, ont fait de cet événement un succès !

Prochaine édition à Angers en 2027, nous avons hâte de vous y retrouver !



PRIX DU GROUPE 2024

Prix André Collet

Ce prix a été conjointement décerné au Dr Ling Peng et au Dr Mihail Barboiu.

Dr Ling Peng



Ling Peng, directrice de recherche de classe exceptionnelle au CNRS, est responsable de l'équipe Biomolécules et Biomatériaux du Centre Interdisciplinaire de Nanoscience de Marseille (CINaM). Depuis son entrée au CNRS, Ling Peng travaille activement à l'interface de la chimie et de la biologie.

Les travaux du Dr Peng dans la chimie des dendrimères supramoléculaires capables de s'auto-assembler ont inspiré et transformé le domaine de la science des dendrimères pour les applications biomédicales. Elle a développé une approche supramoléculaire véritablement innovante pour la synthèse de dendrimères fondée sur l'auto-assemblage de briques moléculaires amphiphiles. Ces briques moléculaires amphiphiles peuvent être facilement

conçues et rapidement synthétisées, pour former après auto-assemblage une grande variété de dendrimères supramoléculaires. Il est particulièrement remarquable que ces dendrimères supramoléculaires sont modulables et adaptatifs pour former des complexes d'inclusion et encapsuler des molécules invitées, y compris des agents thérapeutiques, des acides nucléiques et des agents d'imagerie pour différentes applications biomédicales. Ce concept pionnier a permis aux scientifiques de concevoir des dendrimères supramoléculaires de tailles, formes, propriétés et fonctions diverses pour des applications spécifiques.

Dr Ling Peng est co-auteur de plus de 160 publications internationales et de 7 brevets. Son équipe de recherche est labellisée par la Ligue contre le Cancer depuis 2016. Elle est membre distinguée de la Société Chimique de France, et a déjà été honorée par le prix du Dr et de Mme Henri Labbé de l'Académie des Sciences et le Grand Prix SCF SUD PACA.

Dr Mihail Barboiu



Mihail Barboiu est Directeur de Recherche de Classe Exceptionnelle au CNRS et responsable de l'équipe Nanosystèmes Supramoléculaires Adaptatifs. Il a apporté des contributions très significatives à la recherche en chimie supramoléculaire et en chimie constitutionnelle dynamique, où il s'agit de générer des systèmes supramoléculaires fonctionnels à partir de blocs moléculaires qui interagissent et s'échangent de manière réversible. L'auto-assemblage contrôlé de composants peut permettre la circulation très efficace d'informations structurelles du niveau moléculaire vers des systèmes ayant une dimension nanométrique ou même micrométrique. A ce niveau, il est bon de rappeler les nombreuses études qui ont exploré les architectures de canaux ioniques artificiels comme systèmes potentiels de la conduction naturelle des ions. De façon étonnante on constate beaucoup moins d'apports et de progrès

dans le domaine des canaux d'eau synthétiques. Or, le développement biomimétique de canaux d'eau et de pores contribue à une meilleure connaissance de la fonction de transport sélectif d'eau des canaux naturels, les Aquaporines, pour offrir de nouvelles stratégies afin de fabriquer des systèmes de purification de l'eau hautement sélectifs. C'est le mérite du Dr Barboiu d'être devenu un pionnier du développement des premiers canaux d'eau artificiels ! Il a décrit comment ces systèmes peuvent répondre à son premier objectif du maintien d'une fonction naturelle, il a apporté de nombreuses connaissances dans le domaine des canaux d'eau artificiels biomimétiques, et il a réalisé des découvertes capitales pour l'avenir. En même temps, ces canaux d'eau synthétiques sont des modèles d'étude de l'hydrodynamique de l'eau à l'échelle moléculaire applicables à de nombreux scénarios biologiques mais aussi pour des applications industrielles comme le dessalement ou la purification de l'eau.

Mihail Barboiu est auteur de plus de 350 publications internationales et de 7 brevets. Il a présenté plus de 450 conférences invités et orales dans des manifestations internationales. Il a supervisé plus de 100 post doctorants, doctorants et étudiants de master.

Membre de la Société Chimique de France depuis 1999, il a obtenu le Titre de reconnaissance de la SCF pour les travaux en 2015. L'Académie des sciences et la Société Chimique de Roumanie l'ont également honoré par l'attribution du prix « du mérite » de l'académie (2008) et la médaille Costin Nenitescu de la SCR (2007). Le Dr Barboiu a reçu le RSC Surfaces

and Interfaces Award 2015 et a été nommé Fellow of the Royal Society of Chemistry (FRSC). Il a reçu le Mid-Carrer Award 2014 de la part de la Société de Chimie Coréenne, et l'European Young Investigator Award 2004 de l'European Science Fondation et EUHORCS. Ce dernier prix, considéré comme précurseur de l'ERC est le premier obtenu par un candidat de l'Institut de Chimie du CNRS en 2004.

Prix Henry Le Chatelier

Pr Nicolas Giuseppone



Nicolas Giuseppone effectue ses études supérieures à l'Université Paris-Saclay et y obtient son Doctorat sur l'utilisation des iodures de lanthanide en catalyse asymétrique au laboratoire du Professeur H.B. Kagan sous la direction du Dr. Jacqueline Collin. Puis il rejoint en tant que chercheur post-doctoral le laboratoire du Professeur K.C. Nicolaou au Scripps Research Institute de La Jolla (Université de San Diego, Californie). Il y travaille sur la première synthèse totale de la Diazonamide A, un anticancéreux d'origine marine. Après une année, il est recruté par le CNRS en tant que chargé de recherche et rejoint le laboratoire du Professeur Jean-Marie Lehn pour y démarrer des recherches dans le domaine de la chimie supramoléculaire. En 2008, il est

nommé Professeur de Chimie à l'Université de Strasbourg et crée sa propre équipe de recherche à l'Institut Charles Sadron (UPR CNRS). Il reçoit une bourse du Conseil Européen de la Recherche (ERC) en 2010, est nommé membre junior de l'Institut Universitaire de France en 2013, et il est promu Professeur Classe Exceptionnel (PCE2) en 2020.

Il a été sous-directeur de l'Institut Charles Sadron de 2012 à 2023, et directeur de la Fédération de Recherche sur les Matériaux et les Nanosciences du Grand Est de 2018 à 2023. Il est également le référent à l'Intégrité Scientifique de l'Université de Strasbourg depuis 2017.

Il devient membre senior de l'Institut Universitaire de France en 2023 (chaire fondamentale) et reçoit la Médaille d'Argent du CNRS en 2024.

Ses travaux de recherches utilisent la chimie supramoléculaire et les moteurs moléculaires pour concevoir de nouveaux systèmes actifs hors équilibre et des matériaux intelligents capables d'interagir avec leur environnement.

Prix Christiane Dietrich-Buchecker

Dr Clément Falaise



Clément Falaise est chargé de recherche au sein de l'Institut Lavoisier de Versailles. Il a obtenu son doctorat en 2014 à l'Université de Lille, sous la direction de Thierry Loiseau (UCCS), en travaillant sur la chimie de coordination des actinides tétravalents. Il a ensuite rejoint le groupe de May Nyman (Oregon State University) où ses travaux portaient sur la compréhension des mécanismes de formation des nano-édifices d'uranyle en solution aqueuse, puis le groupe de Stéphane Cordier (ISCR) pour développer des systèmes supramoléculaires à base de clusters luminescents.

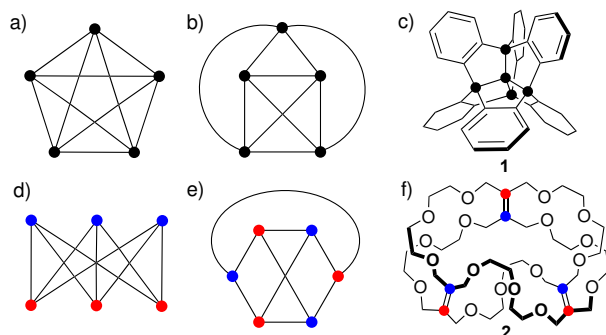
Depuis 2017, ses recherches se concentrent sur la physico-chimie des polyanions inorganiques (polyoxométallates, clusters métalliques, clusters de bore) en solution aqueuse. Il étudie l'origine du caractère (super)chaotrope des polyanions et exploite cette propriété, encore ignorée il y a 10 ans, afin d'associer les polyanions avec une grande variété de substances organiques non-ioniques (surfactants ou macrocycles organiques). Sa maîtrise des processus de reconnaissances moléculaires amplifiés par l'effet chaotrope lui permet de concevoir des complexes hôte-invité commutables, des structures hybrides poreuses, des vésicules multi-lamellaires, ou encore des microtubules artificiels.

Ses travaux ont été valorisés à travers une soixantaine de publications et différents contrats de recherche (ANR, MOMENTUM-CNRS, EMERGENCE@INC). Depuis 2021, il est membre du comité national de la recherche scientifique (section 14).

UN POINT SUR...LA TOPOLOGIE MOLÉCULAIRE ET LA CHIRALITÉ TOPOLOGIQUE

La topologie intrinsèque. Une molécule est décrite par sa composition atomique et les liaisons entre les atomes, d'une part, les longueurs de ces liaisons ainsi que les angles qu'elles font entre elles, d'autre part. Les premières sont des caractéristiques topologiques, les secondes, les caractéristiques géométriques. Ces caractéristiques topologiques sont dites intrinsèques, car elles sont indépendantes de toute représentation dans l'espace 3D. Sachant qu'un graphe est un ensemble de sommets interconnectés au moyen d'arêtes, la topologie intrinsèque d'une molécule peut être décrite par le graphe moléculaire dans lequel les sommets sont les atomes et les arêtes les liaisons qu'ils ont entre eux. Les liaisons considérées à l'origine étaient les liaisons covalentes, mais les développements de la chimie supramoléculaire, grâce à l'utilisation de liaisons pouvant donner lieu à des phénomènes d'échange (liaisons covalentes dynamiques et de coordination), ont permis la synthèse, sous contrôle thermodynamique, de molécules de topologies de plus en plus complexes.

Les graphes non plans. Les molécules sont des objets tridimensionnels que l'on a l'habitude de représenter dans le plan grâce à une projection. Pour les molécules les plus complexes les contraintes géométriques imposent que certaines liaisons se croisent entre elles. Cependant, ces croisements sont levés, dans la plupart des cas, si l'on réduit la représentation de la molécule à la "présentation" de son graphe, non soumis à des contraintes géométriques. Le graphe correspondant est alors dit plan, comme l'est le graphe-circuit d'un macrocycle. Mais ce n'est pas le cas des



molécules **1** et **2** de la Figure 1 dont le graphe contient l'un et l'autre, respectivement, des graphes de Kuratowski K_5 et $K_{3,3}$, les graphes dont la présentation dans le plan ne peut être réduite à moins d'un croisement. K_5 est le graphe complet à cinq sommets (Figures 1a et 1b) et $K_{3,3}$ le graphe bipartite complet à deux ensembles de trois sommets différenciés par deux couleurs (Figures 1d et 1e).

Figure 1. (Haut) présentations du graphe K_5 (a) à 5 croisements et (b) à 1 croisement. (c) Le centrohexaindane **1** dont le graphe contient K_5 . (Bas) présentations du graphe $K_{3,3}$: (d) à 9 croisements et (e) à 1 croisement. (f) L'échelle de Möbius moléculaire **2** dont le graphe contient $K_{3,3}$.

La topologie extrinsèque. Il existe une seconde propriété topologique, la topologie extrinsèque. Elle est appelée ainsi, car elle n'apparaît que lorsque la molécule est déployée (en topologie on dit "plongée") dans l'espace tridimensionnel. La topologie intrinsèque d'un [2]catenane, molécule dans laquelle deux macrocycles sont entrelacés, est décrite au moyen de deux graphes-circuits, que l'on représente dans le plan par deux cercles disjoints. La topologie extrinsèque d'un [2]catenane, décrite par l'entrelacement des anneaux, est appelée le lien de Hopf, dont une vue en perspective est représentée à la Figure 2a. Un autre "plongement" dans l'espace 3D de deux graphes-circuits est le lien de Salomon, matérialisé en chimie par un [2]catenane doublement entrelacé, et dont une vue en perspective est représentée à la Figure 2b. Si l'on s'intéresse maintenant aux systèmes décrits par trois graphes-circuits, une topologie remarquable est celle du lien des Borromées (Figure 2c), plongement des trois graphes-circuits dans lequel ils sont séparés deux à deux mais unis par le troisième. Un certain nombre de molécules à topologie du lien des Borromées a aussi été synthétisé.

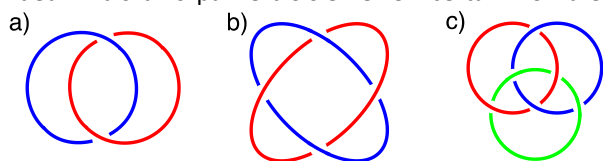
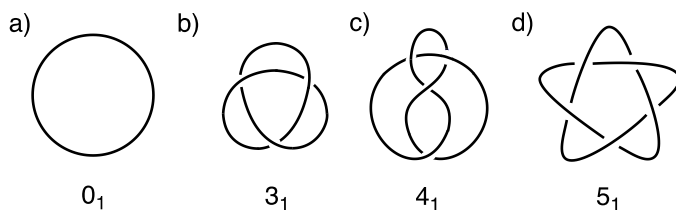


Figure 2. (a) Lien de Hopf matérialisé par un [2]catenane ; (b) lien de Salomon matérialisé par un [2]catenane doublement entrelacé ; noter que le lien de Salomon est chiral (énantiomère droit représenté) ; (c) lien des Borromées.

La topologie de nœud. La topologie extrinsèque évidente du macrocycle est appelée " nœud trivial". Mais on peut imaginer toutes sortes d'autres topologies extrinsèques pour le graphe-circuit. Ce sont celles constituées par les nœuds non triviaux. La Figure 3 reproduit les diagrammes du début de la série des nœuds notés N_m , où N est le nombre minimum de croisements lorsque l'on projette la représentation 3D du nœud dans le plan, et m est le numéro d'ordre dans la série à N croisements. Parmi ceux-ci, les nœuds dits premiers sont ceux qui ne peuvent pas être décomposés en nœuds plus simples. Les nœuds 3_1 et 5_1 sont les premiers de la série des nœuds dits toriques, car ils peuvent être plongés à la surface d'un tore. Depuis la première synthèse d'un composé ayant la topologie du nœud 3_1 par Dietrich-Buchecker et Sauvage, d'autres exemples de molécules présentant la même topologie ou des topologies plus

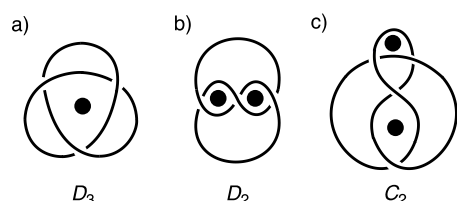


complexes, comme le nœud de huit 4_1 et le nœud 5_1 ont été synthétisées, notamment dans les groupes de Jin et de Leigh, respectivement.

Figure 3. Diagramme (a) du nœud trivial ainsi que ceux des trois nœuds premiers les plus simples: (b) le nœud trifolié ; (c) le nœud de huit ; (d) le nœud pentafolié.

Les aspects synthétiques. La synthèse raisonnée de molécules présentant des caractéristiques topologiques extrinsèques a démarré dans les années 1960 avec les travaux de Lüttringhaus et Schill, puis Schill et coll. Elle a connu une impulsion déterminante à partir des années 1980 quand Sauvage et coll., d'une part, Stoddart et coll., d'autre part, ont introduit l'usage de templates (cations de transition pour le premier, interactions supramoléculaires pour le second). Dans les années 1990, Hunter, puis Vögtle et coll. ont démontré l'intérêt des liaisons hydrogène pour diriger l'entrelacement de fragments moléculaires et synthétiser caténanes et nœuds. Par la suite, Sanders et coll. ainsi que Stoddart et coll. ont mis à profit les propriétés des liaisons covalentes dynamiques (respectivement ponts disulfure et fonctions imine) associées à des effets template pour synthétiser des molécules présentant une grande diversité de topologies extrinsèques. Leigh et coll. ont introduit le concept de template actif qui ajoute à l'effet structural du template classique une action catalytique dans la formation de liaisons-clés pour l'obtention de la topologie visée. La voie la plus efficace pour synthétiser des molécules ayant la topologie du lien de Borromées est celle de la chimie de coordination supramoléculaire (utilisation de métalla-macrocycles).

La chiralité topologique. La présentation classique du nœud trifolié est de symétrie D_3 (Figure 4a). On peut imaginer d'autres présentations comme celle de symétrie D_2 (Figure 4b), ainsi que celle de symétrie C_2 (Figure 4c). Ces trois présentations ont permis d'élaborer des stratégies de synthèse de nœuds moléculaires trifoliés utilisant des cations métalliques comme templates. Les symétries de ces trois présentations indiquent qu'une molécule ayant la topologie du nœud trifolié est chirale. Elle existe donc sous forme de deux énantiomères, un nœud trifolié gauche et un nœud trifolié droit, ce dernier à la Figure 4. Le dédoublement du nœud trifolié moléculaire par cristallisation fractionnée de paires de diastéréoisomères a été rapporté par Sauvage et coll. Des synthèses stéréosélectives ont été publiées par la suite (Sauvage, von Zelewski et coll., Leigh et coll.). Les énantiomères du nœud trifolié sont dits énantiomères topologiques et la chiralité du nœud trifolié est qualifiée de topologique. Cela signifie que l'on ne peut pas transformer un énantiomère en un autre par déformation continue, sans passage d'une liaison à travers une autre. Par opposition,



les molécules chirales dont le graphe est plan ont une chiralité euclidienne car celle-ci résulte uniquement de leurs propriétés géométriques.

Figure 4. Diagrammes de trois présentations du nœud trifolié droit différant par leur symétrie. Les disques en noir représentent les cations métalliques-templates dont les géométries de coordination sont (a) octaédrique et (b) et (c) tétraédriques.

La nature topologique de la chiralité du nœud trifolié est une conséquence de sa topologie : elle est inconditionnelle. Il en est de même de celle du lien de Salomon (Figure 2b). En revanche, le lien de Hopf est doué de chiralité topologique si et seulement si son graphe-circuit est orienté. Cela se traduit, en chimie, par la synthèse et l'utilisation de macrocycles de symétrie σ_h . Cependant, la chiralité de certains nœuds n'est pas nécessairement de nature topologique. Tel est le cas du nœud de huit (Figure 3c), dont on démontre de façon très simple qu'il est possible de convertir l'énantiomère droit en énantiomère gauche par déformation continue. Notons aussi que la chiralité topologique peut être aussi de nature intrinsèque : tel est le cas, par exemple, de l'échelle de Möbius moléculaire **2** de la Figure 1f.

Stéréochimie topologique : H. L. Frisch, E. Wasserman, *J. Am. Chem. Soc.* **1961**, *83*, 3789 ; D. M. Walba, *Tetrahedron* **1985**, *41*, 3161 ; J.-C. Chambron, C. Dietrich-Buchecker, J.-P. Sauvage, *Top. Cur. Chem.* **1993**, *165*, 131 ; C. Liang, K. Mislow, *J. Math. Chem.* **1994**, *15*, 245.

Caténanes : C. Dietrich-Buchecker, J.-P. Sauvage, *Chem. Rev.* **1987**, *87*, 795 ; D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725 ; G. Gil-Ramírez, D. A. Leigh, A. J. Stephens, *Angew. Chem. Int. Ed.* **2015**, *54*, 6110.

Nœuds : C. Dietrich-Buchecker, J.-P. Sauvage, *New. J. Chem.* **1992**, *16*, 277 ; C. Dietrich-Buchecker, B. X. Colasson, J.-P. Sauvage, *Top. Curr. Chem.* **2005**, *249*, 261 ; R. S. Forgan, J.-P. Sauvage, J. F. Stoddart, *Chem. Rev.* **2011**, *111*, 9, 5434 ; J. E. Beves, B. A. Blight, C. J. Campbell, D. A. Leigh, R. T. McBurney, *Angew. Chem. Int. Ed.* **2011**, *40*, 9260 ; S. D. P. Fielden, D. A. Leigh, S. L. Woltering, *Angew. Chem. Int. Ed.* **2017**, *56*, 11166.

Anneaux des Borromées : S. J. Cantrill, K. S. Chichak, A. J. Peters, J. F. Stoddart, *Acc. Chem. Res.* **2005**, *38*, 1.

Cet article a été rédigé par **Jean-Claude Chambron**, DR CNRS à l'Université de Strasbourg

jcchambron@unistra.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 novembre 2023 - juin 2024 dans les journaux suivants :

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

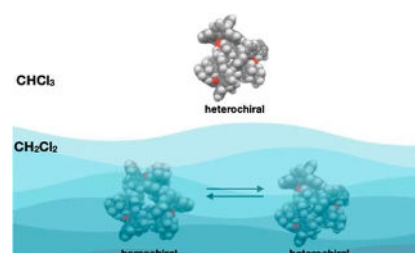
Cette sélection est évidemment non exhaustive.

Circular Heterochiral Titanium-Based Self-Assembled Architectures

P. Mobian, D.-J. Pham, A. Chaumont, L. Barloy, G. Khalil, N. Kyritsakas

J. Am. Chem. Soc. **2024**, *146*, 14067–14078

DOI: [10.1021/jacs.4c02352](https://doi.org/10.1021/jacs.4c02352)



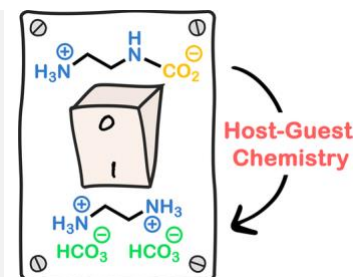
Abstract: Circular trinuclear helicates have been synthesized from a bis-biphenol strand (LH₄), titanium isopropoxide, and various diimine ligands. These self-assembled architectures constructed around three TiO₄N₂ nodes have a heterochiral structure (C₁ symmetry) when 2,2'-bipyridine (A), 4,4'-dimethyl-2,2'-bipyridine (B), 4,4'-bromo-2,2'-bipyridine (C), or 4,4'-dimethyl-2,2'-bipyrimidine (D) is employed. Within these complexes, one nitrogen ligand is *endo*-positioned inside the metallo-macrocycle, whereas the other two diimine ligands point outside the helicate framework. This investigation highlights that the nitrogen ligand which does not participate in the helicate framework of the complex controls the overall symmetry of the helicate since the 2,2'-bipyrimidine chelate (F) ends in the formation of a homochiral aggregate (C₃ symmetry). The lack of symmetry found in the solid state for the trinuclear species ([Ti₃L₃(B)₃], [Ti₃L₃(C)₃], and [Ti₃L₃(D)₃]) is observed for these complexes in solution (dichloromethane or chloroform). Remarkably, the 2,2'-bipyrazine ligand (ligand E) ends in the formation of a hexameric aggregate formulated as [Ti₆L₆(E)₆], whereas the use of 4,4'-dimethyl-2,2'-bipyrimidine (ligand D) permits to generate the dinuclear complexes ([Ti₂L(D)₂(OⁱPr)₄] and [Ti₂L₂(D)₂]) in addition to the trimeric structure [Ti₃L₃(D)₃]. The behavior of [Ti₃L₃(A)₃] in solution, on the other hand, is unique since an equilibrium between the homochiral and the heterochiral form is reached within 17 days after the complex has been dissolved in dichloromethane (C₃-[Ti₃L₃(A)₃]/C₁-[Ti₃L₃(A)₃] ratio = 0.3). In chloroform, the heterochiral form of [Ti₃L₃(A)₃] is stable for the same period of time, evidencing the dependence of this stereochemical transformation toward the solvent medium. The thermodynamic and kinetic parameters linked to this stereochemical equilibrium have been obtained and point to the fact that the transformation is intramolecular and not induced by the presence of external ligands. The thermodynamic constant of the C₁-[Ti₃L₃(A)₃]/C₃-[Ti₃L₃(A)₃] equilibrium is found to be $K = 0.34 \pm 10\%$. Further evidence to rationalize this solvent-induced symmetry switch is obtained via a DFT calculation and classical molecular dynamics. In particular, this computational investigation elucidates the reason why the stereochemical transformation of a heterochiral architecture into a homochiral structure is possible only for a trinuclear assembly containing ligand A.

Switching between Nonisoenergetic Dynamic Covalent Reactions Using Host-Guest Chemistry

T. Chetot, F. Marocco Stuardi, A. Forot, M. Ducreux, A. Baudouin, E. Chefdeville, F. Perret, L. Vial, J. Leclaire

J. Am. Chem. Soc. **2024**, *146*, 13580-13587

DOI: [10.1021/jacs.4c03400](https://doi.org/10.1021/jacs.4c03400)



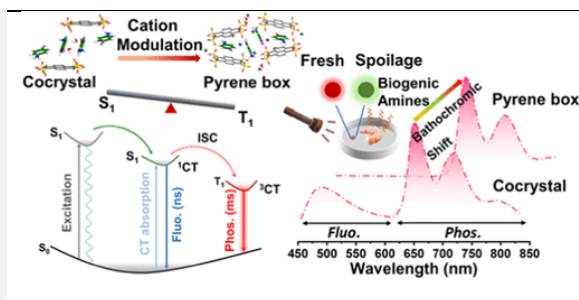
Abstract: CO₂ reacts with simple amines in the presence of water to generate dynamic combinatorial libraries of majority (i.e., ammonium carbamates) and minority (i.e., ammonium carbonates) nonisoenergetic covalent adducts. Over the past two decades, our laboratory has reported on a new class of cavitands, namely, dyn[n]arenes, from which a polyanionic macrocycle is a highly efficient receptor for linear polyammoniums that forms [2]pseudorotaxanes in water at neutral pH. Herein, we demonstrate that the formation of [2]pseudorotaxanes shifts the equilibrium of CO₂ capture by polyamines in water toward the quasi-exclusive formation of carbonate adducts, providing the first example of a switch between two competitive and reversible covalent processes triggered by host-guest interactions. In addition, this supramolecular approach to CO₂ capture exhibits enhanced capture efficiency by increasing the state of protonation of complexed vs uncomplexed polyamines. Altogether, we report here that a templating approach can divert the outcome of two reversible covalent chemistries involving nucleophilic additions and acid-base reactions, challenging therefore the common knowledge that noncovalent and covalent bonds operate in separate energy frames.

Modulation of Deep-Red to Near-Infrared Room-Temperature Charge-Transfer Phosphorescence of Crystalline “Pyrene Box” Cages by Coupled Ion/Guest Structural Self-Assembly

W. Feng, D. Chen, Y. Zhao, B. Mu, H. Yan, M. Barboiu

J. Am. Chem. Soc. **2024**, *146*, 2484–2493

DOI: [10.1021/jacs.3c10206](https://doi.org/10.1021/jacs.3c10206)



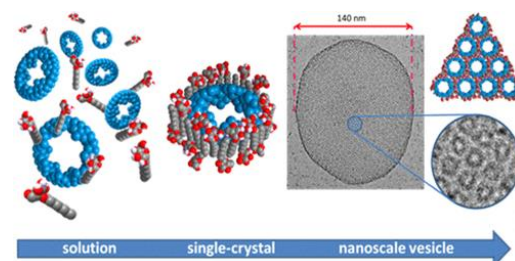
Abstract: Organic cocrystals obtained from multicomponent self-assembly have garnered considerable attention due to their distinct phosphorescence properties and broad applications. Yet, there have been limited reports on cocrystal systems that showcase efficient deep-red to near-infrared (NIR) charge-transfer (CT) phosphorescence. Furthermore, effective strategies to modulate the emission pathways of both fluorescence and phosphorescence remain underexplored. In this work, we dedicated our work to four distinct self-assembled cocrystals called “pyrene box” cages using 1,3,6,8-pyrenetetrasulfonate anions (PTS⁴⁻), 4-iodoaniline (**1**), guanidinium (G⁺), diaminoguanidinium (A₂G⁺), and hydrated K⁺ counteranions. The binding of such cations to PTS⁴⁻ platforms adaptively modulates their supramolecular stacking self-assembly with guest molecules **1**, allowing to steer the fluorescence and phosphorescence pathways. Notably, the confinement of guest molecule **1** within “pyrene box” PTSK**1** and PTSG**1** cages leads to an efficient deep-red to NIR CT phosphorescence emission. The addition of fuming gases like triethylamine and HCl allows reversible pH modulations of guest binding, which in turn induce a reversible transition of the “pyrene box” cage between fluorescence and phosphorescence states. This capability was further illustrated through a proof-of-concept demonstration in shrimp freshness detection. Our findings not only lay a foundation for future supramolecular designs leveraging weak intermolecular host–guest interactions to engineer excited states in interacting chromophores but also broaden the prospective applications of room-temperature phosphorescence materials in food safety detection.

Cooperative Self-Assembly Process Involving Giant Toroidal Polyoxometalate as a Membrane Building Block in Nanoscale Vesicles

C. Falaise, S. Khelifi, P. Bauduin, P. Schmid, J. Degrouard, A. Leforestier, W. Shepard, J. Marrot, M. Haouas, D. Landy, C. Mellot-Draznieks, E. Cadot

J. Am. Chem. Soc. **2024**, *146*, 1501–1511

DOI: [10.1021/jacs.3c11004](https://doi.org/10.1021/jacs.3c11004)



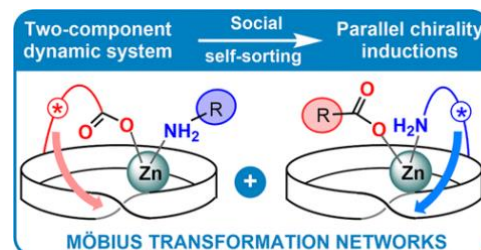
Abstract: The self-assembly of organic amphiphilic species into various aggregates such as spherical or elongated micelles and cylinders up to the formation of lyotropic hexagonal or lamellar phases results from cooperative processes orchestrated by the hydrophobic effect, while those involving ionic inorganic polynuclear entities and nonionic organic components are still intriguing. Herein, we report on the supramolecular behavior of giant toroidal molybdenum blue-type polyoxometalate, namely, the {Mo₁₅₄} species in the presence of n-octyl-β-glucoside (C8G1), widely used as a surfactant in biochemistry. Structural investigations were carried out using a set of complementary multiscale methods including single-crystal X-ray diffraction analysis supported by molecular modeling, small-angle X-ray scattering and cryo-TEM observations. In addition, liquid NMR, viscosimetry, surface tension measurement, and isothermal titration calorimetry provided further information to decipher the complex aggregation pathway. Elucidation of the assembly process reveals a rich scenario where the presence of the large {Mo₁₅₄} anion disrupts the self-assembly of the C8G1, well-known to produce micelles, and induces striking successive phase transitions from fluid-to-gel and from gel-to-fluid. Herein, intimate organic–inorganic primary interactions arising from the superchaotropic nature of the {Mo₁₅₄} lead to versatile nanoscopic hybrid C8G1–{Mo₁₅₄} aggregates including crystalline discrete assemblies, smectic lamellar liquid crystals, and large uni- or multilamellar vesicles where the large torus {Mo₁₅₄} acts a trans-membrane component.

Parallel Chirality Inductions in Möbius Zn(II) Hexaphyrin Transformation Networks

T. Nédellec, B. Boitrel, S. Le Gac

J. Am. Chem. Soc. **2023**, *145*, 27067–27079

DOI: [10.1021/jacs.3c10835](https://doi.org/10.1021/jacs.3c10835)



Abstract: Networked chemical transformations are key features of biological systems, in which complex multicomponent interactions enable the emergence of sophisticated functions. Being interested in chirality induction phenomena with dynamic Möbius π-systems, we have designed a pair of Möbius [28]hexaphyrin ligands in order to investigate mixtures rather than isolated molecules. Thus, a hexaphyrin bearing a chiral amino arm was first optimized and found to bind a ZnOAc moiety, triggering an impressive quasi-quantitative chirality induction over the Möbius π-system. Second, this amino-type hexaphyrin was mixed with a second hexaphyrin bearing a chiral carboxylate arm, affording at first ill-defined coordination assemblies in the presence of zinc. In contrast, a social self-sorting behavior occurred upon the addition of two exogenous achiral effectors (AcO⁻ and BuNH₂), leading to a well-defined 1:1 mixture of two Möbius complexes featuring a sole Möbius twist configuration (parallel chirality inductions). We next successfully achieved compartmentalized switching, i.e., a single-component transformation from such a complex

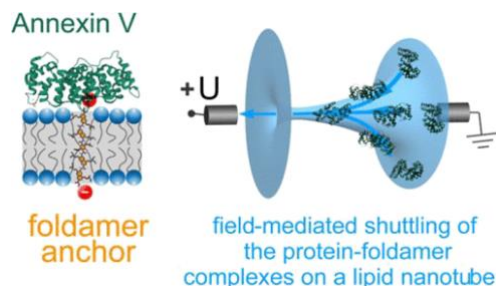
mixture. The BuNH₂ effector was selectively protected with Boc₂O, owing to a lower reactivity of the arm's NH₂ function intramolecularly bound to zinc, and subsequent addition of BuNH₂ restored the initial mixture, retaining parallel chirality inductions (five cycles). By changing the nature and twist configuration of only one of the two complexes, at initial state or by switching, this approach enables a "two-channel" tuning of the chiroptical properties of the ensemble. Such multiple dynamic chirality inductions, controlled by selective metal–ligand recognition and chemical reactivity, set down the basis for Möbius-type stereoselective transformation networks with new functions.

Molecular Sensing and Manipulation of Protein Oligomerization in Membrane Nanotubes with Bolaamphiphilic Foldamers

K. Aftahy, P. Arrasate, P. V. Bashkirov, P. I. Kuzmin, V. Maurizot, I. Huc, V. A. Frolov

J. Am. Chem. Soc. **2023**, *145*, 25150–25159

DOI: [10.1021/jacs.3c05753](https://doi.org/10.1021/jacs.3c05753)



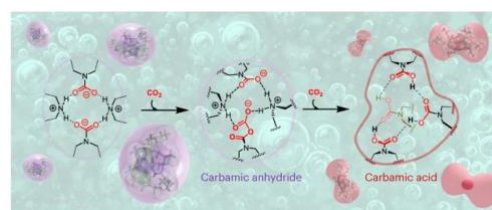
Abstract: Adaptive and reversible self-assembly of supramolecular protein structures is a fundamental characteristic of dynamic living matter. However, the quantitative detection and assessment of the emergence of mesoscale protein complexes from small and dynamic oligomeric precursors remains highly challenging. Here, we present a novel approach utilizing a short membrane nanotube (sNT) pulled from a planar membrane reservoir as nanotemplates for molecular reconstruction, manipulation, and sensing of protein oligomerization and self-assembly at the mesoscale. The sNT reports changes in membrane shape and rigidity caused by membrane-bound proteins as variations of the ionic conductivity of the sNT lumen. To confine oligomerization to the sNT, we have designed and synthesized rigid oligoamide foldamer tapes (ROFTs). Charged ROFTs incorporate into the planar and sNT membranes, mediate protein binding to the membranes, and, driven by the luminal electric field, shuttle the bound proteins between the sNT and planar membranes. Using Annexin-V (AnV) as a prototype, we show that the sNT detects AnV oligomers shuttled into the nanotube by ROFTs. Accumulation of AnV on the sNT induces its self-assembly into a curved lattice, restricting the sNT geometry and inhibiting the material uptake from the reservoir during the sNT extension, leading to the sNT fission. By comparing the spontaneous and ROFT-mediated entry of AnV into the sNT, we reveal how intricate membrane curvature sensing by small AnV oligomers controls the lattice self-assembly. These results establish sNT-ROFT as a powerful tool for molecular reconstruction and functional analyses of protein oligomerization and self-assembly, with broad application to various membrane processes.

Tetrameric self-assembly of water-lean solvents enables carbamate anhydride-based CO₂ capture chemistry

J. Leclaire, D. J. Heldebrant, K. Grubel, J. Septavaux, M. Hennebelle, E. Walter, Y. Chen, J. Leobardo Bañuelos, D. Zhang, M.-T. Nguyen, D. Ray, S. I. Allec, D. Malhotra, W. Joo, J. King

Nat. Chem. **2024**

DOI: [10.1038/s41557-024-01495-z](https://doi.org/10.1038/s41557-024-01495-z)



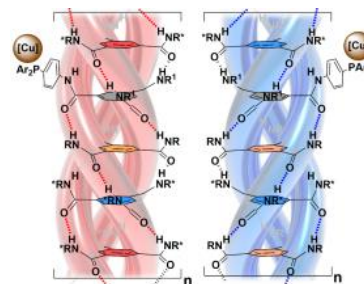
Abstract: Carbon capture, utilization and storage is a key yet cost-intensive technology for the fight against climate change. Single-component water-lean solvents have emerged as promising materials for post-combustion CO₂ capture, but little is known regarding their mechanism of action. Here we present a combined experimental and modelling study of single-component water-lean solvents, and we find that CO₂ capture is accompanied by the self-assembly of reverse-micelle-like tetrameric clusters in solution. This spontaneous aggregation leads to stepwise cooperative capture phenomena with highly contrasting mechanistic and thermodynamic features. The emergence of well-defined supramolecular architectures displaying a hydrogen-bonded internal core, reminiscent of enzymatic active sites, enables the formation of CO₂-containing molecular species such as carbamic acid, carbamic anhydride and alkoxy carbamic anhydrides. This system extends the scope of adducts and mechanisms observed during carbon capture. It opens the way to materials with a higher CO₂ storage capacity and provides a means for carbamates to potentially act as initiators for future oligomerization or polymerization of CO₂.

Switchable supramolecular helices for asymmetric stereodivergent catalysis

Ran Chen, Ahmad Hammoud, Paméla Aoun, Mayte A Martínez-Aguirre, Nicolas Vanthuyne, Régina Maruchenko, Patrick Brocorens, Laurent Bouteiller, Matthieu Raynal

Nat. Comm. **2024**, *15*, 4116

DOI: [10.1038/s41467-024-48412-z](https://doi.org/10.1038/s41467-024-48412-z)



Abstract: Despite recent developments on the design of dynamic catalysts, none of them have been exploited for the in-situ control of multiple stereogenic centers in a single molecular scaffold. We report herein that it is possible to obtain in majority any amongst the four possible stereoisomers of an amino alcohol by means of a switchable asymmetric catalyst built on supramolecular helices. Hydrogen-bonded assemblies between a benzene-1,3,5-tricarboxamide (BTA) achiral phosphine ligand coordinated to copper and a chiral BTA comonomer are engaged in a copper-hydride catalyzed hydrosilylation and hydroamination cascade process. The nature of the product stereoisomer is related to the handedness of the helices and can thus be directed in a predictable way by changing the nature of the major enantiomer of the BTA comonomer

present in the assemblies. The strategy allows all stereoisomers to be obtained one-pot with similar selectivities by conducting the cascade reaction in a concomitant manner, i.e. without inverting the handedness of the helices, or sequentially, i.e. by switching the handedness of the supramolecular helices between the hydrosilylation and hydroamination steps. Supramolecular helical catalysts appear as a unique and versatile platform to control the configuration of molecules or polymers embedding several stereogenic centers.

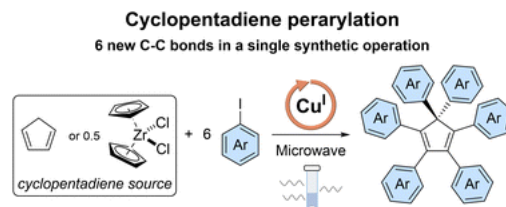
Copper-catalysed perarylation of cyclopentadiene: synthesis of hexaaryl cyclopentadienes

Y. Gisbert, P. S. Marqués, C. Baccini, S. Abid, N. Saffon-Merceron, G. Rapenne, C. Kammerer

Chem. Sci. **2024**, *15*, 9127-9137

DOI: [10.1039/D4SC02458C](https://doi.org/10.1039/D4SC02458C)

Abstract: While hexaphenylsilacyclopentadiene (hexaphenylsilole) is viewed as an archetypal Aggregation-Induced Emission (AIE) luminogen, its isostructural hydrocarbon surrogate hexaphenylcyclopentadiene has strikingly never been investigated in this context, most probably due to a lack of synthetic availability. Herein, we report a straightforward synthesis of hexaphenylcyclopentadiene, *via* the direct perarylation of cyclopentadiene upon copper(I) catalysis under microwave activation, with the formation of six new C–C bonds in a single synthetic operation. Using zirconocene dichloride as a convenient source of cyclopentadiene and a variety of aryl iodides as coupling partners, this copper-catalysed cross-coupling reaction gave rise to a series of unprecedented hexaaryl cyclopentadienes. The latter are direct precursors of extended π -conjugated polycyclic compounds, and their cyclodehydrogenation under Scholl reaction conditions yielded helicenic 17,17-diarylcyclopenta[*l,l'*]diphenanthrenes. These structurally complex polyannulated fluorene derivatives can now be prepared in only two synthetic steps from cyclopentadiene.



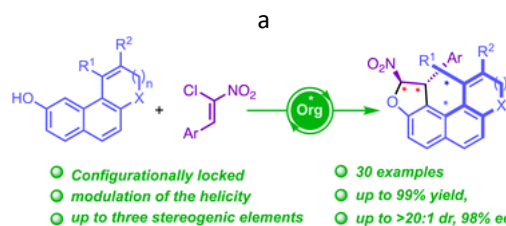
Padlocking dihydrofurannulation for the control of small degree of helicity built on a fused-tetracyclic core

A. Gaucherand, E. Yen-Pon, D. García-López, J.-V. Naubron, S. Chentouf, M. Giorgi, S. Humbel, M. Jean, J. Rodriguez, D. Bonne

Chem. Sci. **2024**, *7300-7307*

DOI: [10.1039/D4SC00745J](https://doi.org/10.1039/D4SC00745J)

Abstract: Enantioselective construction of small molecules displaying a configurationally stable helical shape built on a fused-tetracyclic core is a daunting synthetic challenge even more pronounced when five-membered rings are incorporated in the structure. The resulting higher configurational lability strongly hampers their access, and therefore the development of new efficient methodologies is timely and highly desirable. In this context, we describe a padlocking approach *via* the enantioselective organocatalytic domino furannulation of appropriately designed achiral fused-tricyclic precursors resulting in the synthesis of configurationally locked helically chiral tetracyclic scaffolds featuring one or two five-membered rings with the simultaneous control of central and helical chiralities.



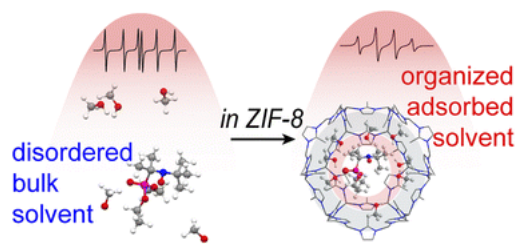
Nanoscale solvent organization in metal-organic framework ZIF-8 probed by EPR of flexible β -phosphorylated nitroxides

A. S. Poryvaev, A. A. Efremov, D. V. Alimov, K. A. Smirnova, D. M. Polyukhov, R. Z. Sagdeev, S. Jacoutot, S. R. A. Marque, M. V. Fedin

Chem. Sci. **2024**, *15*, 5268-5276

DOI: [10.1039/D3SC05724K](https://doi.org/10.1039/D3SC05724K)

Abstract: Metal-organic frameworks (MOFs) draw increasing attention as nanoenvironments for chemical reactions, especially in the field of catalysis. Knowing the specifics of MOF cavities is decisive in many of these cases; yet, obtaining them *in situ* remains very challenging. We report the first direct assessment of the apparent polarity and solvent organization inside MOF cavities using a dedicated structurally flexible spin probe. A stable β -phosphorylated nitroxide radical was incorporated into the cavities of a prospective MOF ZIF-8 in trace amounts. The spectroscopic properties of this probe depend on local polarity, structuredness, stiffness and cohesive pressure and can be precisely monitored by Electron Paramagnetic Resonance (EPR) spectroscopy. Using this approach, we have demonstrated experimentally that the cavities of bare ZIF-8 are sensed by guest molecules as highly non-polar inside. When various alcohols fill the cavities, remarkable self-organization of solvent molecules is observed leading to a higher apparent polarity in MOFs compared to the corresponding bulk alcohols. Accounting for such nanoorganization phenomena can be crucial for optimization of chemical reactions in MOFs, and the proposed methodology provides unique routes to study MOF cavities inside *in situ*, thus aiding in their various applications.



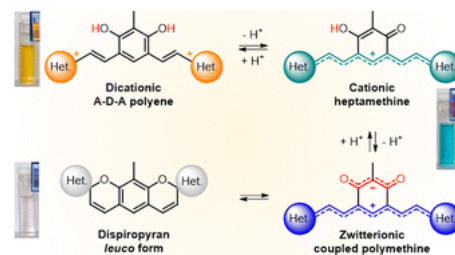
Insights into extended coupled polymethines through the investigation of dual UV-to-NIR acidochromic switches based on heptamethine–oxonol dyes

Benjamin Mourot, V. Mazan, M. Elhabiri, R. Sarkar, D. Jacquemin, O. Siri, S. Pascal

Chem. Sci. **2024**, *15*, 1248-1259

DOI: [10.1039/D3SC06126D](https://doi.org/10.1039/D3SC06126D)

Abstract: A series of heptamethine–oxonol dyes featuring different heterocyclic end groups were designed with the aim to explore structure–property relationships in π -extended coupled polymethines. These dyes can be stabilised under three different protonation states, affording dicationic derivatives with an aromatic core, cationic heptamethines, and zwitterionic bis-cyanine forms. The variation of the end groups directly impacts the absorption and emission properties and mostly controls reaching either a colourless neutral dispirocyclic species or near-infrared zwitterions. The acidochromic switching between the three states involves profound electronic rearrangements leading to notable shifts of their optical properties that were investigated using a parallel experiment–theory approach, providing a comprehensive description of these unique systems.



Dynamic covalent synthesis

F. B. L. Cougnon, A. R. Stefankiewicz, S. Ulrich

Chem. Sci. **2024**, *15*, 879-895

DOI: [10.1039/D3SC05343A](https://doi.org/10.1039/D3SC05343A)

Abstract: Dynamic covalent synthesis aims to precisely control the assembly of simple building blocks linked by reversible covalent bonds to generate a single, structurally complex, product. In recent years, considerable progress in the programmability of dynamic covalent systems has enabled easy access to a broad range of assemblies, including macrocycles, shape-persistent cages, unconventional foldamers and mechanically-interlocked species (catenanes, knots, etc.). The reversibility of the covalent linkages can be either switched off to yield stable, isolable products or activated by specific physico-chemical stimuli, allowing the assemblies to adapt and respond to environmental changes in a controlled manner. This activatable dynamic property makes dynamic covalent assemblies particularly attractive for the design of complex matter, smart chemical systems, out-of-equilibrium systems, and molecular devices.



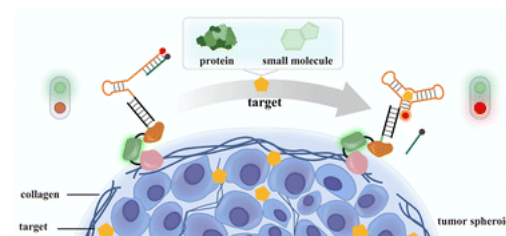
A collagen-immobilized nanodevice for *in situ* ratiometric imaging of cancer biomarkers in the tumor microenvironment

F. Tian, S. Zhou, S. Xie, Z. Zhang, L. Peng, L. Jiang, Z. Wang, Z. Nie, Y. Huang

Chem. Sci. **2023**, *14*, 12182-12193

DOI: [10.1039/D3SC03972B](https://doi.org/10.1039/D3SC03972B)

Abstract: Monitoring the spatiotemporal dynamics of cancer biomarkers within the tumor microenvironment (TME) is critical to understanding their roles in tumorigenesis. Here, we reported a multifunctional fusion protein (collagen-binding domain and duck circovirus tag fused to mCherry, CBD-mCherry-DCV) capable of binding collagen with high affinity and covalently binding specific nucleic acids with exceptional efficiency. We then constructed a chimeric protein–nucleic acid nanodevice (CPNN) using CBD-mCherry-DCV and an aptamer-based sensing module to enable spatially controlled ratiometric imaging of cancer biomarkers in the TME. The collagen-anchoring module CBD-mCherry-DCV allowed specific immobilization of CPNN on 3D multicellular tumor spheroids, enabling the sensing module to achieve “off–on” fluorescence imaging of cancer biomarkers upon specific target recognition by an aptamer. Taking advantage of the constant fluorescence signal of mCherry and the activatable fluorescence response of Cy5 to specific cancer biomarkers, the detection sensitivity and reliability of CPNN were improved by self-calibrating the signal intensity. Specifically, CPNN enabled ratiometric fluorescence imaging of varying concentrations of exogenous PDGF-BB and ATP in tumor spheroids with a high signal-to-background ratio. Furthermore, it allowed the visual monitoring of endogenous PDGF-BB and ATP released from cells. Overall, this study demonstrates the potential of the nanodevice as a versatile approach for the visualization and imaging of cancer biomarkers in the TME.

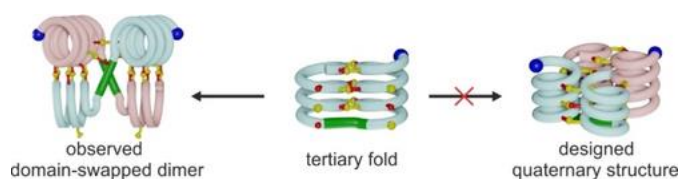


Domain Swapping in Abiotic Foldamers

S. Wang, B. Wicher, C. Douat, V. Maurizot, I. Huc

Angew Chem. Int. Ed. **2024**, *63*, e202405091

DOI: [10.1002/anie.202405091](https://doi.org/10.1002/anie.202405091)



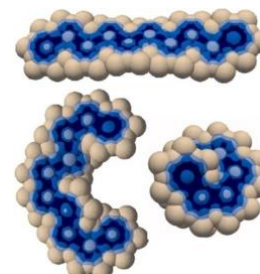
Abstract: Foldamer sequences that adopt tertiary helix-turn-helix folds mediated by helix-helix hydrogen bonding in organic solvents have been previously reported. In an attempt to create genuine abiotic quaternary structures, i.e. assemblies of tertiary structures, new sequences were prepared that possess additional hydrogen bond donors at positions that may promote an association between the tertiary folds. However, a solid state structure and extensive solution state investigations by Nuclear Magnetic Resonance (NMR) and Circular Dichroism (CD) show that, instead of forming a quaternary structure, the tertiary folds assemble into stable domain-swapped dimer motifs. Domain swapping entails a complete reorganization of the arrays of hydrogen bonds and changes in relative helix orientation and handedness that can all be rationalized.

Helicene Aromaticity Deviates from the Clar Rule—On the Electronic Dissimilarity of Large Isomeric Fibonacenes

L. Sturm, A. Artigas, Y. Coquerel, I. H. Bechtold, F. Durola, H. Bock

Angew Chem. Int. Ed. **2024**, *63*, e202403170

DOI: [10.1002/anie.202403170](https://doi.org/10.1002/anie.202403170)



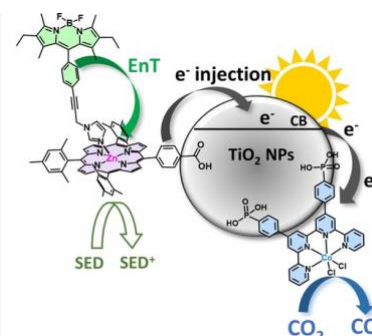
Abstract: This combined experimental and theoretical study illustrates the profound consequences of non-planarity on the electronic properties of polycyclic arenes. Three isomeric [10]fibonacene tetraesters were synthesized through a robust and regiocontrolled Perkin/Mallory approach: a nearly planar [10]phenacene derivative, a moderately twisted [10]semicircle derivative, and a 3D non-planar [10]helicene derivative. The photophysical properties of the 3D [10]helicene isomer were found to be dramatically different from the comparable ones of the [10]phenacene and [10]semicircle isomers. The aromatic properties of the [10]phenacene and [10]semicircle isomers conform well with their predictive Kekulé and Clar analyses, but the [10]helicene isomer deviates from these general topological rules, which appears to be a general phenomenon for [n]fibonacenes with $n \geq 9$.

Antenna Effect in Noble Metal-Free Dye-Sensitized Photocatalytic Systems Enhances CO₂-to-CO Conversion

V. Nikolaou, C. Govind, E. Balanikas, J. Bharti, S. Diring, E. Vauthey, M. Robert, F. Odobel

Angew Chem. Int. Ed. **2024**, *63*, e202318299

DOI: [10.1002/anie.202318299](https://doi.org/10.1002/anie.202318299)



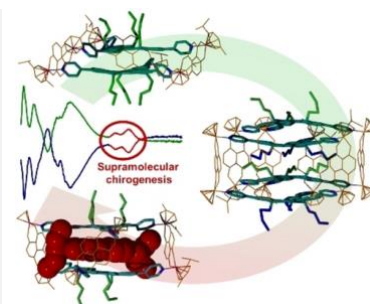
Abstract: Efficient CO₂-to-CO dye-sensitized photocatalytic systems are obtained by utilizing noble metal-free photosensitizer (zinc-porphyrin) and catalyst (cobalt-quaterpyridine) derivatives. Upon introducing an additional chromophore (Bodipy), an antenna effect enhanced the photoproduction leading to 42.1 mmol g⁻¹ h⁻¹ of CO and 759 turnover numbers.

Chiral Truxene-Based Self-Assembled Cages: Triple Interlocking and Supramolecular Chirogenesis

S. Séjourné, A. Labrunie, C. Dalinot, D. Canevet, R. Guechaichia, J. Bou Zeid, A. Benchohra, T. Cauchy, A. Brosseau, M. Allain, C. Chamignon, J. Viger-Gravel, G. Pintacuda, V. Carré, F. Aubriet, N. Vanthuyne, M. Sallé, S. Goeb

Angew Chem. Int. Ed. **2024**, *63*, e202400961

DOI: [10.1002/anie.202400961](https://doi.org/10.1002/anie.202400961)



Abstract: A chiral self-assembled cage constructed from the truxene framework dimerizes in solution thanks to favourable geometric and electronic parameters. The interlocked dimer can be dissociated upon forming a 1 : 1 host-guest complex in the presence of a guest. The chiral cavity induces chirality in the achiral guest molecule, as characterized by circular dichroism measurements.

Threading a Linear Molecule Through a Macrocycle Thanks to Boron: Optical Properties of the Threaded Species and Synthesis of a Rotaxane

M. Hicguet, L. Verrieux, O. Mongin, T. Roisnel, F. Berrée, A. Fihey, B. Le Guennic, Y. Trolez

Angew Chem. Int. Ed. **2024**, *63*, e202318297

DOI: [10.1002/anie.202318297](https://doi.org/10.1002/anie.202318297)

Abstract: Boron-containing species were threaded through macrocycles bearing a 2,2'-biphenol unit. The new threaded species exhibited interesting fluorescence features with quantum yields up to 91 % and an enhanced photostability. Their properties were rationalized with quantum chemistry to unravel the vibronic contributions. This methodology was used to synthesize a rotaxane.



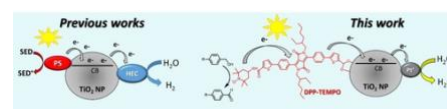
Dye-Sensitized Photocatalysis: Hydrogen Evolution and Alcohol-to-Aldehyde Oxidation without Sacrificial Electron Donor

D. Romito, C. Govind, V. Nikolaou, R. J. Fernández-Terán, A. Stoumpidi, E. Agapaki, G. Charalambidis, S. Diring, E. Vauthey, A. G. Coutsolelos, F. Odobel

Angew Chem. Int. Ed. **2024**, *63*, e202318868

DOI: [10.1002/anie.202318868](https://doi.org/10.1002/anie.202318868)

Abstract: This study shows that a two-hole oxidation process such as TEMPO catalyzed alcohol oxidation is a viable reaction to couple with reduction reaction to eliminate SED and generate two added-value chemicals in dye-sensitized photocatalytic systems.



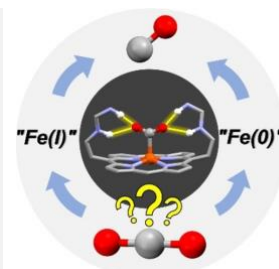
Second Coordination Sphere Effect Shifts CO₂ to CO Reduction by Iron Porphyrin from Fe⁰ to Fe^I

S. Amanullah, P. Gotico, M. Sircoglou, W. Leibl, M. J. Llansola-Portoles, T. Tibiletti, A. Quaranta, Z. Halime, A. Aukauloo

Angew Chem. Int. Ed. **2024**, *63*, e202314439

DOI: [10.1002/anie.202314439](https://doi.org/10.1002/anie.202314439)

Abstract: Bio-inspired second coordination sphere inducing a multipoint hydrogen bonding network triggers CO₂ activation at an earlier stage of the reaction mechanism in CO₂-to-CO electrocatalytic reduction by an iron porphyrin catalyst. Electrochemical and comprehensive spectroscopic investigations supported by DFT calculations revealed an unprecedented change in the active species' formal oxidation state from Fe(0) to Fe(I).



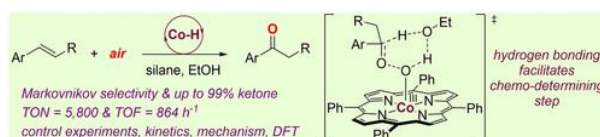
Markovnikov-Selective Cobalt-Catalyzed Wacker-Type Oxidation of Styrenes into Ketones under Ambient Conditions Enabled by Hydrogen Bonding

N. Abuhafez, A. W. Ehlers, B. de Bruin, R. Gramage-Doria

Angew Chem. Int. Ed. **2024**, *63*, e202316825

DOI: [10.1002/anie.202316825](https://doi.org/10.1002/anie.202316825)

Abstract: Cobalt-tetraphenylporphyrin complex was found to be a highly active and Markovnikov-selective catalyst for the Wacker-type oxidation of aromatic olefins into ketones under ambient conditions. Detailed mechanistic studies including kinetics, UV/Vis, control experiments and DFT calculations indicate a Mukaiyama-type mechanism with a change in the last fundamental step towards ketone formation via an unprecedented hydrogen bonding network thanks to the ethanol solvent.



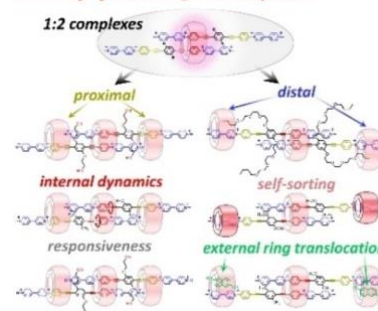
Internal Dynamics and Modular Peripheral Binding in Stimuli-Responsive 3 : 2 Host:Guest Complexes

H. Yin, R. Rosas, S. Viel, M. Giorgi, V. Monnier, L. Charles, D. Siri, D. Gimes, Y. Nassar, F. Chevallier, C. Bucher, R. Wang, A. Kermagoret, D. Bardelang

Angew Chem. Int. Ed. **2024**, *63*, e202315985

DOI: [10.1002/anie.202315985](https://doi.org/10.1002/anie.202315985)

Diversity of 3:2 host:guest complexes



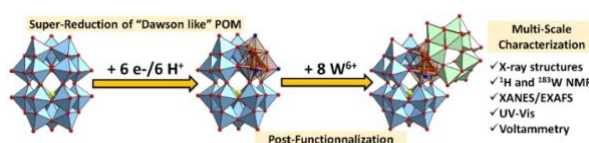
Abstract: A family of versatile 3 : 2 host/guest complexes has been prepared by combining cucurbit[*n*]urils with symmetric, linear diviologens. These assemblies have properties typical of 1 : 1 complexes, but also show a new type of supramolecular translational-rotational coupling, peripheral complexation amenable to proximal or distal binding, and controllable peripheral ring translocation.

Clustering Six Electrons within “Dawson-Like” Polyoxometalate: An Open Route toward Its Post-functionalization

G. Mpacko Priso, M. Haouas, N. Leclerc, C. Falaise, E. Cadot

Angew Chem. Int. Ed. **2023**, *62*, e202312457

DOI: [10.1002/anie.202312457](https://doi.org/10.1002/anie.202312457)



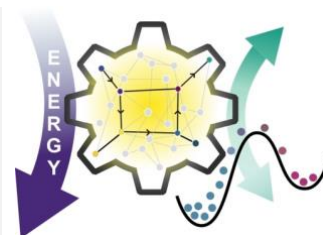
Abstract: The super-reduction of Dawson-like polyoxometalate (POM) $[H_2AsW_{18}O_{60}]^{7-}$ in water involves a disproportionation process generating POM with a metal-metal bonded triad as evidenced by single crystal X-ray diffraction and multi-nuclear magnetic resonance investigations. Then, the resulting six-electron reduced POM was used as a precursor to construct the largest POM containing W^{4+} reported to date.

Artificial Molecular Ratchets: Tools Enabling Endergonic Processes

T. Sangchai, S. Al Shehimi, E. Penocchio, G. Ragazzon

Angew Chem. Int. Ed. **2023**, *62*, e202309501

DOI: [10.1002/anie.202309501](https://doi.org/10.1002/anie.202309501)



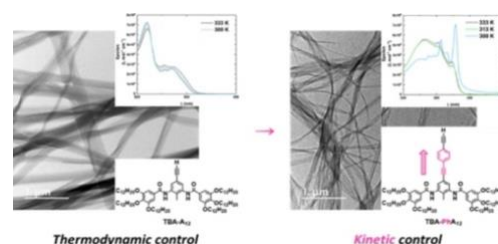
Abstract: How can we realize thermodynamically unfavored chemical processes? The operating principles of molecular machines—ratchet mechanisms—can help answer this. This tutorial Review provides an overview that balances experimental examples with rationalizations, while detaching from directional motion. A unifying picture is offered for chemical-, light-, and redox-driven systems, highlighting connections with active transport and bioenergetics, among others.

Kinetic Delay in Cooperative Supramolecular Polymerization by Redefining the Trade-Off Relationship between H-Bonds and Van der Waals/ π - π Stacking Interactions

W. T. Gallonde, C. Poidevin, F. Houard, E. Caytan, V. Dorcet, A. Fihey, K. Bernot, S. Rigaut, O. Galangau

Angew Chem. Int. Ed. **2023**, *62*, e202313696

DOI: [10.1002/anie.202313696](https://doi.org/10.1002/anie.202313696)



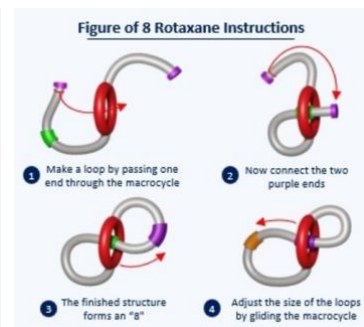
Abstract: Proper molecular engineering can open new opportunities to create kinetically metastable states in monomers undergoing cooperative supramolecular polymerizations. This occurs by favoring dispersive interactions over H-bonds and thereby rebalancing the interplay between π - π stacking, Van der Waals, and hydrogen-bonding interactions.

An Interlocked Figure-of-Eight Molecular Shuttle

M. Gauthier, K. Fournel-Marotte, C. Clavel, P. Waelès, P. Laurent, F. Coutrot

Angew Chem. Int. Ed. **2023**, *62*, e202310643

DOI: [10.1002/anie.202310643](https://doi.org/10.1002/anie.202310643)



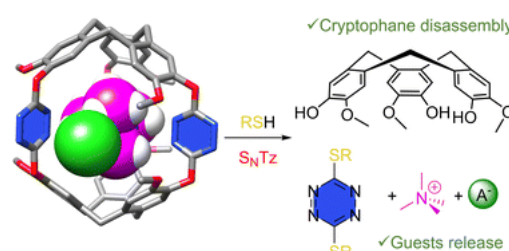
Abstract: A two-station figure of eight rotaxane molecular shuttle has been synthesized by making use of a template-driven intramolecular self-entanglement of a hermaphrodite disubstituted dibenzo-24-crown-8 derivative and the mechanical locking of the architecture. The shuttling of the macrocycle from the ammonium to the triazolium station results in an interdependent tightening/loosening of the two loops of the interlocked molecular architecture.

Self-assembled tetrazine cryptophane for ion pair recognition and guest release by cage disassembly

L. Miton, E. Antonetti, M. Poujade, J.-P. Dutasta, P. Nava, A. Martinez, Y. Cotellet

Chem. Commun. **2024**, *60*, 5217-5220

DOI: [10.1039/D4CC01421A](https://doi.org/10.1039/D4CC01421A)



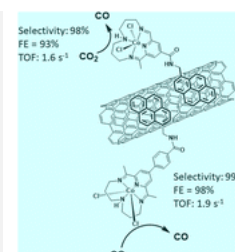
Abstract: Hereby, we describe the synthesis of a self-assembled syn-cryptophane using dynamic nucleophilic aromatic substitution of tetrazines. ¹H NMR cage titrations reveal that the tetramethylammonium cation binds under slow exchange conditions while counter-anions show a fast exchange regime. Finally, the cryptophane can be disassembled by the addition of thiols allowing guest release.

Carbon nanotube heterogenization improves cobalt pyridyldiimine complex CO₂ reduction activity in aqueous carbonate buffer

B. Andrin, P. J. M. Cordeiro Junior, D. Provost, S. Diring, Y. Pellegrin, M. Robert, F. Odobel

Chem. Commun. **2024**, *60*, 5022-5025

DOI: [10.1039/D4CC00629A](https://doi.org/10.1039/D4CC00629A)



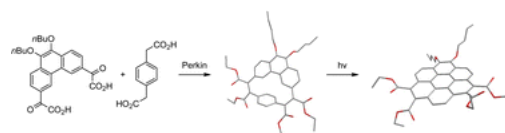
Abstract: We present two novel cobalt pyridyldiimine complexes functionalized with pyrene. Initially modest in homogeneous acetonitrile solution, their electrocatalytic CO₂ reduction performance significantly improves upon immobilization on MWCNTs in an aqueous carbonate buffer. The complexes exhibit outstanding stability, with CO selectivity exceeding 97%, and TON and TOF values reaching up to 10⁴ and above 1.2 s⁻¹, respectively.

Coronenes with push-pull geometries from macrocycle-forming Perkin condensations

L. Soliman, E. Ramassamy, K. Dujarric, G. Naulet, P. Dechambenoit, H. Bock, F. Durola

Chem. Commun. **2024**, *60*, 4439-4442

DOI: [10.1039/D4CC00935E](https://doi.org/10.1039/D4CC00935E)



Abstract: Although the Perkin reaction has been successful in producing ester-substituted conjugated macrocycles with four or six building blocks, macrocycles composed of only two elements remained elusive until now. Through the development of a building block derived from phenanthrene with two glyoxylic acid substituents in a pincer-like arrangement, formation of a two-block macrocycle was induced when paired with a complementary phenylenediacyclic acid unit. The addition of ether functions to the phenanthrene building block not only improved the yields, but led to macrocycles with push-pull geometries. Photocyclisation of the resulting cyclophanes efficiently yield tetra- and hexasubstituted coronenes.

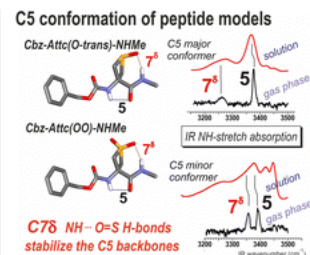
Effects of sulfoxide and sulfone sidechain–backbone hydrogen bonding on local conformations in peptide models

D. Liu, S. Robin, E. Gloaguen, V. Brenner, M. Mons, D. J. Aitken

Chem. Commun. **2024**, 60, 2074–2077

DOI: [10.1039/D3CC05933B](https://doi.org/10.1039/D3CC05933B)

Abstract: We examine peptide model systems designed to probe short-range N–H···O=S sidechain–backbone hydrogen bonding involving amino acid residues with sidechain sulfoxide or sulfone functional groups and its effects on local conformations. A strong 7-membered ring hydrogen bond of this type accompanies an intra-residue N–H···O=C interaction and stabilizes an extended backbone conformation in preference to classical folded structures.



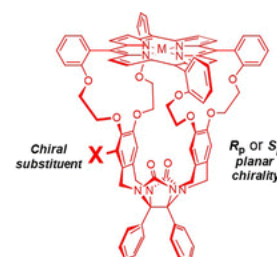
Kinetic enantio-recognition of chiral viologen guests by planar-chiral porphyrin cages

P. J. Gilissen, Q. Duez, G. L. Tripodi, M. M. J. Dekker, J. Ouyang, K. Dhbaibi, N. Vanthuyne, J. Crassous, J. Roithová, J. A. A. W. Elemans, R. J. M. Nolte

Chem. Commun. **2023**, 59, 13974–13977

DOI: [10.1039/D3CC04934E](https://doi.org/10.1039/D3CC04934E)

Abstract: The kinetic enantio-recognition of chiral viologen guests by planar-chiral porphyrin cage compounds, measured in terms of $\Delta\Delta G_{on}^\ddagger$, is determined by the planar-chirality of the host and influenced by the size, as measured by ion mobility-mass spectrometry, but not the chirality of its substituents.



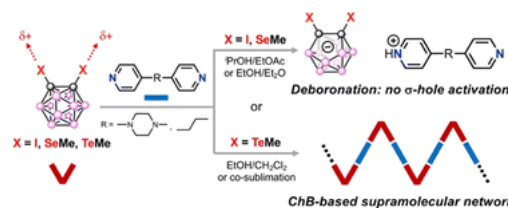
Carborane-based heteromolecular extended networks driven by directional C–Te···N chalcogen bonding interactions

M. Beau, O. Jeannin, M. Fourmigué, E. Aubert, E. Espinosa, S. Lee, W.-S. Han, I.-R. Jeon

Chem. Commun. **2023**, 59, 13727–13730

DOI: [10.1039/D3CC04338J](https://doi.org/10.1039/D3CC04338J)

Abstract: We demonstrate that *o-closo*-(TeMe)₂carborane directs, in the presence of linear ditopic neutral Lewis bases, the formation of co-crystals with 1D extended supramolecular networks. Specifically, the network formation is systematically stabilized by short and quasi-linear C–Te···N chalcogen-bonding (ChB) interactions. In sum, we report efficient carborane-based tectons to rationally design high-dimensional neutral heteromolecular networks.



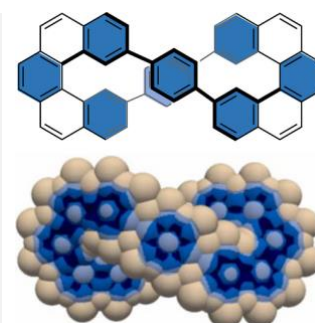
Aromaticity in Semi-Condensed Figure-Eight Molecules

A. Artigas, Y. Carissan, D. Hagebaum-Reignier, H. Bock, F. Durola, Y. Coquerel

Chem. Eur. J. **2024**, 30, e202401016

DOI: [10.1002/chem.202401016](https://doi.org/10.1002/chem.202401016)

Abstract: Aromaticity in the illustrated semi-condensed figure-eight molecule, a [5]helicene-bridged (1,4)cyclophane, is dominated by a (semi-)local character with some additional minor global character, as allowed by the small torsion angle along the single bonds.

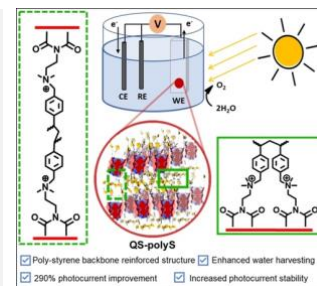


Combined Covalent and Supramolecular Polymerization to Reinforce Perylenebisimide Photosynthetic “Quantasomes”

A. Ranscht, F. Rigodanza, T. Gobatto, I. Crea, E. A. Quadrelli, J. Canivet, M. Bonchio

Chem. Eur. J. **2024**, *30*, e202303784

DOI: [10.1002/chem.202303784](https://doi.org/10.1002/chem.202303784)



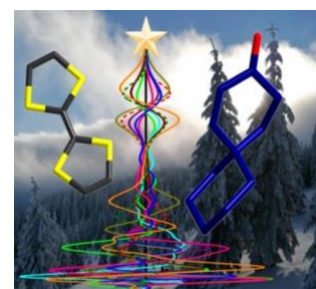
Abstract: Inspired by the paired function of Photosystem II (PSII) supercomplexes, artificial quantasomes (QS) are formed by encapsulating the deca-anionic oxygen-evolving catalyst Ru₄POM within a multichromophoric “corolla” of cationic perylenebisimides. Covalent fixation of the QS supramolecular network is obtained herein by photo-polymerization of styrene terminals installed on the PBI antennas (QS-PolyS), enhancing the oxygenic photocurrent and stability under high solar irradiance

Chiral Spiro-Tetrathiafulvalenes: Synthesis, Chiroptical Properties, Conformational Issues and Charge Transfer Complexes

A. Bogdan, I.-T. Moraru, N. Vanthuyne, P. Auban-Senzier, I. Grosu, N. Avarvari, F. Pop

Chem. Eur. J. **2024**, *30*, e202301301

DOI: [10.1002/chem.202400564](https://doi.org/10.1002/chem.202400564)



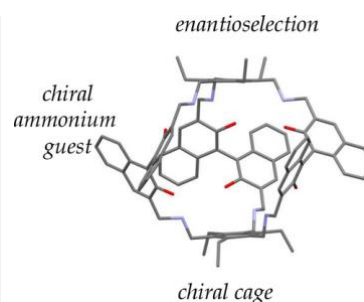
Abstract: Spiro-TTFs have been characterized experimentally and theoretically, and the formation of charge transfer complexes with TCNQF₂ and TCNQF₄ has been reported. The chiroptical investigation of the neutral systems revealed significant differences in chiroptical activity depending on the nature of chiral centres and between diastereomers.

A Chiral [2+3] Covalent Organic Cage Based on 1,1'-Bi-2-naphthol (BINOL) Units

M. Mohan, D.-J. Pham, A. Fluck, S. Chapuis, A. Chaumont, B. Kauffmann, L. Barloy, P. Mobian

Chem. Eur. J. **2024**, *30*, e202400458

DOI: [10.1002/chem.202400458](https://doi.org/10.1002/chem.202400458)



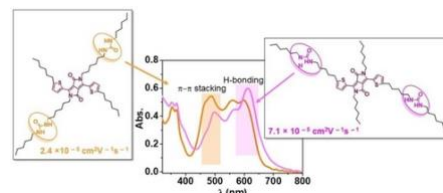
Abstract: A chiral cage formed with three 2,2'-BINOL units was prepared through a dynamic covalent chemistry approach. This architecture contains six OH functions pointing inside the cavity. Host-guest studies demonstrated enantioselectivity of the cage for a chiral ammonium cation.

Urea-Comprising Single Core Diketopyrrolopyrrole Derivatives: Exploring the Synthesis, Self-Assembly and Charge Transport Properties

G. Martinez, I. Id-boubrik, W. Matsuda, C. C. Carmona-Vargas, K.-I. Hong, C. Munuera, S. Seki, A. Ruiz-Carretero

Chem. Eur. J. **2024**, *30*, e202400392

DOI: [10.1002/chem.202400392](https://doi.org/10.1002/chem.202400392)



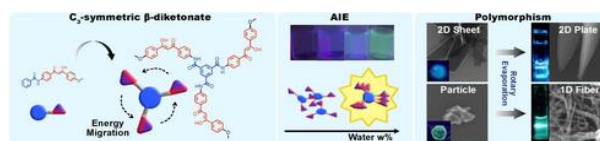
Abstract: We explore the synthesis, self-assembly and charge transport properties of two urea-containing single core thiophene-capped diketopyrrolopyrrole derivatives. The subtle differences in molecular design dictate the superior electronic properties of the lactam-functionalized analogue.

C_3 -Symmetric Luminescent Diketone with Amido-Linkage as a Polymorphic Fluorescence Emitter

S. Katsumi, Y. Kugai, M. Louis, T. Morimoto, M. Yamada, S. Maisonneuve, C. Goto, R. Métivier, T. Kawai, C. Allain

Chem. Eur. J. **2024**, *30*, e202304278

DOI: [10.1002/chem.202304278](https://doi.org/10.1002/chem.202304278)



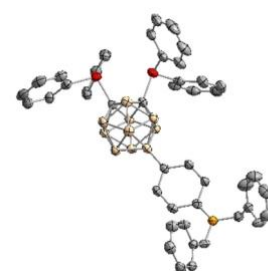
Abstract: The study presents BTA-D3, a novel C_3 -symmetric β -diketone compound, and its monomeric counterpart, D, focusing on synthesis, photophysical properties, theoretical calculation, and aggregation properties. BTA-D3 exhibits Aggregation-Induced Emission (AIE) with solvent-dependent fluorescence. The anisotropy fluorescence suggested the presence of energy migration in BTA-D3. Unique polymorphism and growth of self-organized aggregates offer insights into molecular alignment for diverse fluorescence in materials.

Carboranylphosphines: B9-Substituted Derivatives with Enhanced Reactivity for the Anchoring to Dendrimers

M. Milewski, A.-M. Caminade, S. Mallet-Ladeira, A. Lledós, P. Lönnecke, E. Hey-Hawkins

Chem. Eur. J. **2024**, *30*, e202303867

DOI: doi.org/10.1002/chem.202303867



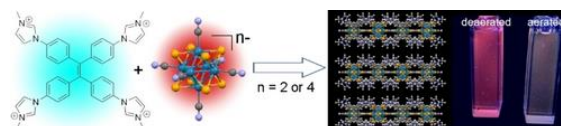
Abstract: Several *ortho*-carboranes functionalized in the B9 position were prepared and grafted to phosphorus dendritic compounds. 1- or 1,2-phosphanyl-substituted carboranes were also synthesized for eventual applications in catalysis or the medicinal sector.

Luminescent Supramolecular Ionic Frameworks based on Organic Fluorescent Polycations and Polyanionic Phosphorescent Metal Clusters

I. V. Kashnik, B. Yang, S. S. Yarovoi, T. S. Sukhikh, M. Cordier, G. Taupier, K. A. Brylev, P.-A. Bouit, Y. Molard

Chem. Eur. J. **2024**, *30*, e202400079

DOI: [10.1002/chem.202400079](https://doi.org/10.1002/chem.202400079)



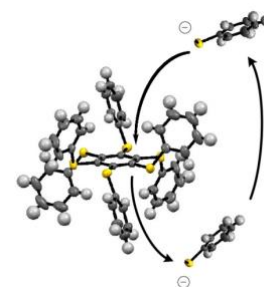
Abstract: Emissive ionic frameworks are designed by associating blue emissive tetraphenylethylene moieties functionalized with four imidazolium heads and red-NIR phosphorescent dianionic Mo or tetracationic Re-based octahedral clusters. Resulting hybrids show a porous structure in their crystalline state and their chemical and thermal stability depends on the charge of the metal cluster. Emission in the red-NIR by 1PA and 2PA were evidenced in both cases.

“The Sulfur Dance” Around Arenes and Heteroarenes - the Reversible Nature of Nucleophilic Aromatic Substitutions

S. Gahlot, J.-L. Schmitt, A. Chevalier, M. Villa, M. Roy, P. Ceroni, J.-M. Lehn, M. Gingras

Chem. Eur. J. **2024**, *30*, e202400231

DOI: [10.1002/chem.202400231](https://doi.org/10.1002/chem.202400231)



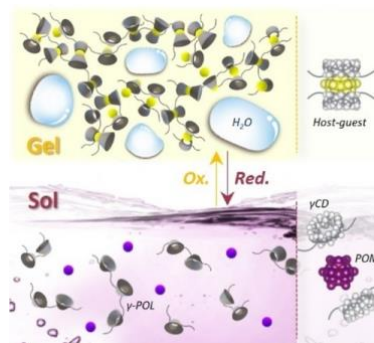
Abstract: The features of a category of reversible nucleophilic aromatic substitution reactions in view of their significance and wide scope in aromatic and heteroaromatic chemistry are presented. Exchange of sulfur components surrounding arenes and heteroarenes may occur at 25 °C, in a process that one may call a “sulfur dance”. A dynamic covalent system involving four components illustrates the thermodynamically-driven formation of a thiocalix[2]arene[2]pyrimidine. This work stimulates the implementation of reversible S_NAr reactions in organic, materials and covalent dynamic chemistry.

Switchable Redox and Thermo-Responsive Supramolecular Polymers Based on Cyclodextrin-Polyoxometalate Tandem

S. Khlifi, s. Yao, C. Falaise, P. Bauduin, V. Guérineau, N. Leclerc, M. Haouas, H. Salmi-Mani, P. Roger, E. Cadot

Chem. Eur. J. **2024**, *30*, e202303815

DOI: [10.1002/chem.202303815](https://doi.org/10.1002/chem.202303815)



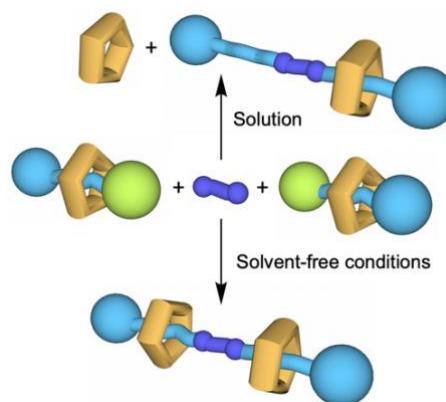
Abstract: The chaotropic behavior of polyoxometalates is exploited as an operating principle to promote a reversible and thermo-responsive sol-gel transition of cyclodextrin-based polymer where supramolecular networking results from the host-guest interactions between cyclodextrin-based oligomers and Keggin-type POMs acting as electro-active crosslinking agents. This study reveals that the chaotropic effect corresponds to an effective force able to induce responsiveness into supramolecular materials.

Solution and Solvent-Free Stopper Exchange Reactions for the Preparation of Pillar[5]arene-containing [2] and [3]Rotaxanes

N. Becharguia, I. Nierengarten, J.-M. Strub, S. Cianféroni, M. Rémy, E. Wasielewski, R. Abidi, J.-F. Nierengarten

Chem. Eur. J. **2024**, *30*, e202304131

DOI: [10.1002/chem.202304131](https://doi.org/10.1002/chem.202304131)



Abstract: Stopper exchange reactions between a rotaxane building block and diamine reagents gave dramatically different outcome in solution and in solvent-free conditions. Upon a first acylation, an intermediate host-guest complex with a terminal amine function is obtained. Dissociation of the intermediate occurs in solution but the inclusion complex is preserved under mechanochemical solvent-free conditions.

Enhancing the Features of DNA Mimic Foldamers for Structural Investigations

V. Corvaglia, J. Wu, D. Deepak, M. Loos, I. Huc

Chem. Eur. J. **2024**, *30*, e202303650

DOI: [10.1002/chem.202303650](https://doi.org/10.1002/chem.202303650)



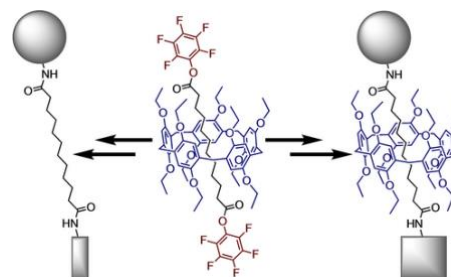
Abstract: DNA mimic aromatic oligoamide helical foldamers possess no nucleobase and no ribose-phosphate backbones. Nevertheless, their structure can be designed so as to reproduce typical features of nucleic acids such as palindromic-like C_2 symmetry, handedness control and extension by sticky ends to promote helix-helix associations.

Stepwise Functionalization of a Pillar[5]arene-Containing [2]Rotaxane with Pentafluorophenyl Ester Stoppers

N. Becharguia, E. Wasielewski, R. Abidi, I. Nierengarten, J.-F. Nierengarten

Chem. Eur. J. **2024**, *30*, e202303501

DOI: [10.1002/chem.202304131](https://doi.org/10.1002/chem.202304131)



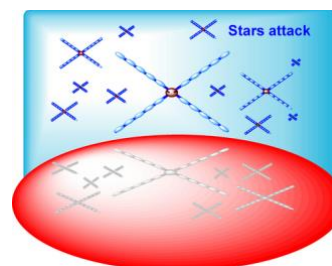
Abstract: The pillar[5]arene as a protecting group. Selective mono-functionalization of a rotaxane building block is very efficient owing to steric effects limiting the access of the nucleophilic reagents to the second reactive carbonyl group. Introduction of a second stopper is then possible to generate dissymmetrical rotaxanes or axles in high yields.

Giant Star-shaped *meso*-substituted Fluorescent Porphyrins with Fluorenyl-containing Arms Designed for Two-photon Oxygen Photosensitization

L. Shi, Z. Sun, N. Richy, M. Blanchard-Desce, O. Mongin, F. Paul, C. O. Paul-Roth

Chem. Eur. J. **2024**, *30*, e202303243

DOI: [10.1002/chem.202303243](https://doi.org/10.1002/chem.202303243)



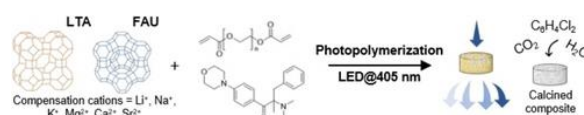
Abstract: New Starburst porphyrins possessing up to twenty conjugated fluorenyl units have been synthesized. Their detailed oxygen-photosensitizing ability, their fluorescence and their two-photon absorption properties are discussed

Zeolite/Polymer Composites Prepared by Photopolymerization: Effect of Compensation Cations on Opacity and Gas Adsorption Applications

Y. Gao, Y. Deniz Karatas, H. Nouali, J.-P. Salomon, J. Lalevée, A. Simon-Masseron

Chem. Eur. J. **2024**, *30*, e202302229

DOI: [10.1002/chem.202302229](https://doi.org/10.1002/chem.202302229)



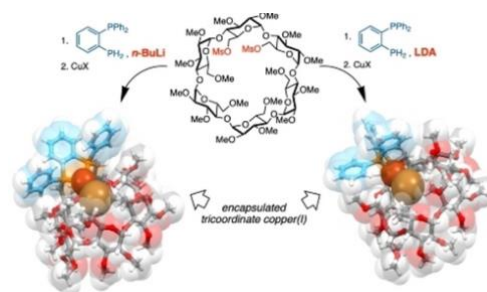
Abstract: Stopper exchange between a rotaxane building block and diamine reagents gave dramatically different outcome in solution and in solvent-free conditions. Upon a first acylation, an intermediate host-guest complex with a terminal amine function is obtained. Dissociation of the intermediate occurs in solution but the inclusion complex is preserved under mechanochemical solvent-free conditions.

Stabilization of Luminescent Mononuclear Three-Coordinate Cu^I Complexes by Two Distinct Cavity-Shaped Diphosphanes Obtained from a Single α -Cyclodextrin Precursor

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

Chem. Eur. J. **2024**, *30*, e202302750

DOI: [10.1002/chem.202302750](https://doi.org/10.1002/chem.202302750)



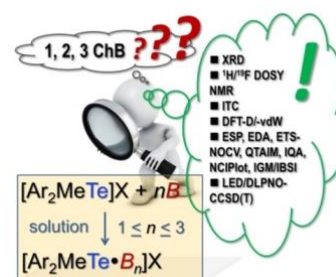
Abstract: Two for the price of one! Depending on the experimental conditions, two dramatically different diphosphanes can be obtained from diphenyl(2-phosphanylphenyl)phosphane and an α -cyclodextrin-derived dimesylate. The metal confining properties of the cavity-shaped ligands have been exploited to produce luminescent chelate [CuX(PP)] complexes (X=Cl, Br, I).

Affinity of Telluronium Chalcogen Bond Donors for Lewis Bases in Solution: A Critical Experimental-Theoretical Joint Study

L. Gros Lambert, Y. Cornaton, M. Ditte, E. Aubert, P. Pale, A. Tkatchenko, J.-P. Djukic, V. Mamane

Chem. Eur. J. **2024**, *30*, e202302933

DOI: [10.1002/chem.202302933](https://doi.org/10.1002/chem.202302933)



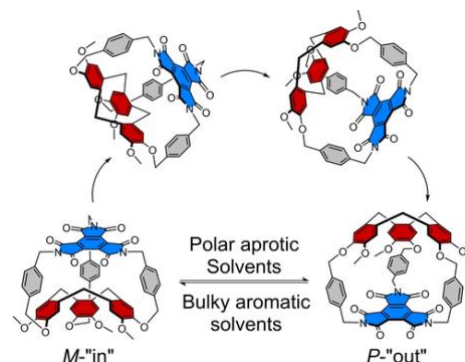
Abstract: Telluronium salts [Ar₂MeTe]X were synthesized, and their Lewis acidic properties towards a number of bases were addressed in solution by physical and theoretical means. DFT and ab-initio methods reveal the driving role of coulombic and dispersion interactions in the formation of [Ar₂MeTe · B_n]⁺ complexes in solution (B=Lewis base).

A Cyclotrimeratrylene Solvent-Dependent Chiral Switch

L. Miton, E. Antonetti, D. García-López, P. Nava, V. Robert, M. Albalat, N. Vanthuyne, A. Martinez, Y. Cotelle

Chem. Eur. J. **2024**, *30*, e202303294

DOI: [10.1002/chem.202303294](https://doi.org/10.1002/chem.202303294)



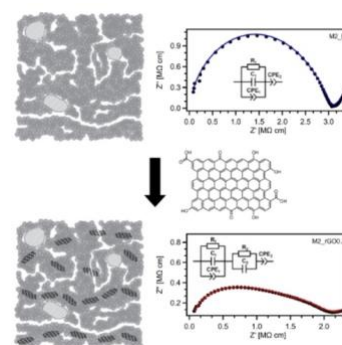
Abstract: In and out! The control of the cyclotrimeratrylene chirality by achiral solvents allow to switch from an open cage in polar aprotic solvents to an imploded one in bulky aromatic solvents. Interestingly, this controlled molecular motion of a cyclotrimeratrylene unit is described for the first time.

Controlling the Formation of Electroactive Graphene-Based Cementitious Composites: Towards Structural Health Monitoring of Civil Structures

M. Safuta, A. Ciesielski, P. Samori

Chem. Eur. J. **2023**, *29*, e202301816

DOI: [10.1002/chem.202301816](https://doi.org/10.1002/chem.202301816)



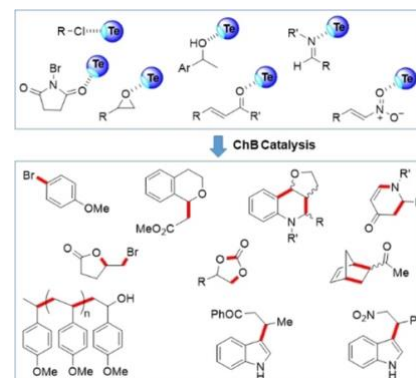
Abstract: Multifunctional rGO-based cement composite featuring remarkably enhanced electrical properties was developed. Simple and efficient method for obtaining homogeneous and stable rGO dispersion in cement composites was established. Electrochemical impedance spectroscopy was applied to investigate the conduction mechanisms within rGO-based cement mortar and new electrical equivalent circuit was proposed.

Chalcogen Bonding Catalysis: Tellurium, the Last Frontier?

P. Pale, V. Mamane

Chem. Eur. J. **2023**, *29*, e202302755

DOI: [10.1002/chem.202302755](https://doi.org/10.1002/chem.202302755)



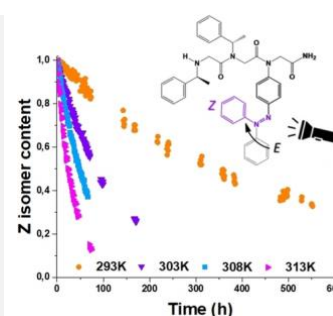
Abstract: This review highlights the importance of chalcogen bonding in organic synthesis through a compilation of tellurium derivatives used up-to-now in catalysis. These powerful chalcogen bond donors were shown to activate numerous kind of substrates by non-covalent interaction with functional groups such as chlorides, carbonyls, imines, epoxides, alcohols and nitro derivatives.

Site Selectivity of Peptoids as Azobenzene Scaffold for Molecular Solar Thermal Energy Storage

B. Tassignon, Z. Wang, A. Galanti, J. De Winter, P. Samori, J. Cornil, K. Moth-Poulsen, P. Gerbaux

Chem. Eur. J. **2023**, *29*, e202303168

DOI: [10.1002/chem.202303168](https://doi.org/10.1002/chem.202303168)



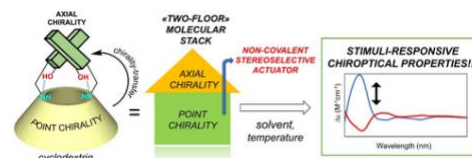
Abstract: Stopper exchange reactions between a rotaxane building block and diamine reagents gave dramatically different outcome in solution and in solvent-free conditions. Upon a first acylation, an intermediate host-guest complex with a terminal amine function is obtained. Dissociation of the intermediate occurs in solution but the inclusion complex is preserved under mechanochemical solvent-free conditions.

Enabling Stereochemical Communication and Stimuli-Responsive Chiroptical Properties in Biphenyl-Capped Cyclodextrins

G. Preda, S. Jung, G. Pescitelli, L. Cupellini, D. Armspach, D. Pasini

Chem. Eur. J. **2023**, *29*, e202302376

DOI: [10.1002/chem.202302376](https://doi.org/10.1002/chem.202302376)



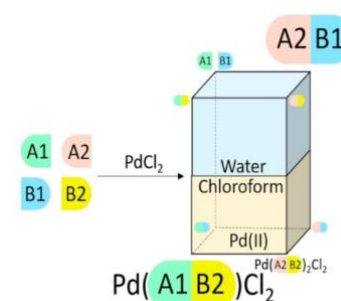
Abstract: The use of building blocks from the “chiral pool” is challenging for the construction of chiroptical materials, as they often lack chromophores suitable for significant chiroptical properties. A two-level molecular stack, which combines a point-chiral element (cyclodextrin) and an axially chiral element (biphenyl), is capable of effectively translating the overall stereochemical information contained in the cyclodextrin core into stimuli-responsive chiroptical properties.

Behavior of a Dynamic Covalent Library Driven by Combined Pd(II) and Biphasic Effectors for Metal Transport between Phases

R. Moneuse, D. Bourgeois, X. Le Goff, J.-M. Lehn, D. Meyer

Chem. Eur. J. **2023**, *29*, e202302188

DOI: [10.1002/chem.202302188](https://doi.org/10.1002/chem.202302188)



Abstract: Pd(II) acts as a chemical effector on an acylhydrazone-based dynamic covalent library (DCL) in a biphasic system. The introduction of Pd(II) leads to a significant increase in the constituent that is best suited for a transfer of Pd(II) into the organic phase. This study introduces a novel approach for liquid/liquid extraction and metal recovery by utilizing extractant species generated in situ by the DCL.