N°06
Septembre 2025

La SupInfo

Les infos du Groupe de Chimie Supramoléculaire

SOMMAIRE

LE MOT DE LA PRÉSIDENTE

Chères adhérentes et chers adhérents,

Le début d'année 2025 a été marqué par le renouvellement du bureau. Le nombre de candidats ainsi que la participation au vote témoignent de la dynamique de notre groupe thématique. Au nom du bureau, je voudrais vous remercier pour la confiance que vous nous avez accordée.

En mai dernier, nous nous sommes retrouvés aux journées de chimie supramoléculaire qui se sont déroulées à Strasbourg. Cet événement, dont l'organisation a été magnifiquement orchestrée par Iwona Nierengarten, a connu un succès important, rassemblant non seulement la communauté française de chimie supramoléculaire mais aussi des collègues européens. Cette manifestation, qui a attiré de nombreux étudiants, doctorants et post-doctorants, s'ancre définitivement comme un événement majeur qui assure la visibilité de notre groupe. Nous vous donnons d'ores et déjà rendez-vous pour la prochaine édition à Marseille du 28 au 29 Mai 2026 !

Cette année aura été aussi synonyme de nouveauté avec la création d'un prix de thèse pour récompenser les travaux de nos jeunes docteurs, prix qui vient compléter les prix bisannuels remis aux chercheurs à différents stades de leur carrière. Cette année, le prix de thèse Supr@SCF a été décerné à Vivien Andrieux, qui a soutenu sa thèse en 2024 sous la direction de Christophe Bucher au laboratoire de chimie de l'ENS de Lyon. Félicitations à lui pour cette distinction qui couronne un travail collaboratif et pluridisciplinaire. Vous trouverez aussi dans ce numéro un article synthétique, rédigé par Anthony Kermagoret, qui retrace l'évolution des molécules mécaniquement entrelacées de type rotaxanes vers des systèmes hors équilibre de type pompes.

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 une belle rentrée universitaire !

Bien cordialement,

Émilie Moulin, Présidente du Groupe Supr@SCF

T0105-713- F: 0,00 €
9 111033 130485

SOCIÉTÉ CHIMIQUE DE France, Siège social : 250, rue Saint-Jacques, F-75005 Paris
Direction générale : 28, rue Saint-Dominique, F-75007 Paris / Tél. +33 (0)1 40 46 71 62 (63 Fax)
secretariat@societechimiquedefrance.fr - www.societechimiquedefrance.fr

Association Loi 1901 reconnue d'utilité publique – n° SIRET 329 714 216 000 10 code APE 9499Z

ACTUALITÉS RÉCENTES

Nouveau bureau du Groupe Thématique Supr@SCF

Émilie Moulin
Présidente, ICS Strasbourg

Laurent Vial
Vice-Président, ENS Lyon

David Canevet
Secrétaire, MOLTECH-Anjou, Angers

Sébastien Ulrich
Trésorier, IBMM Montpellier

Claire Fave
Trésorière adjointe, IPCM Paris

Guillaume Vives
Représentant DCO, IPCM Paris

Nathan D. McClenaghan
Chargé de Communication, Représentant DCP, ISM Bordeaux

Henri-Pierre Jacquot de Rouville
Chargé de Communication,
Représentant DCC, Institut de Chimie de Strasbourg

David Bardelang
Représentant Groupe Chimie des Origines, ICR Marseille

Olivier Galangau
Chargé de Mission Pédagogie / Enseignement, ISC Rennes

Anne-Marie Caminade
Chargé de Communication, LCC Toulouse

Jean-Pierre Dutasta
Chargé de Communication, ENS Lyon

Mathieu Sollogoub
Membre associé, IPCM Paris

Le Groupe Thématique de Chimie Supramoléculaire de la Société Chimique de France (Supr@SCF) a été créé en 2020. Après 5 années entièrement dédiées à la communauté française de chimie supramoléculaire, 2025 a vu le renouvellement de son bureau. Pour rappel, les activités initiées par le groupe ont été nombreuses et génératrices de rencontres et collaborations scientifiques *via* un travail de diffusion d'informations au sein de notre communauté, qui compte à ce jour plus de 500 adhérentes et adhérents, et l'organisation de manifestations scientifiques et remises de prix. La pérennisation du congrès international triennal Supr@Ville, dont le premier s'est tenu à Lyon en 2018, suivi de Supr@Stasbourg (2021), Supr@Paris (2024) et prochainement Supr@Angers en 2027, est devenu un évènement international incontournable dédié à la chimie supramoléculaire. Le groupe Supr@SCF organise également tous les ans des *Journées de Chimie Supramoléculaire* (JCS). Les JCS sont des symposiums dont le programme est largement dédié à l'intervention de jeunes chercheuses et jeunes chercheurs français. Cet évènement, gratuit pour les étudiants, doctorants et post-doctorants qui sont membres de la SCF, a pris place à Lyon en 2022, à Montpellier en 2023, à Strasbourg en 2025 et sera organisé à Marseille en 2026.

La reconnaissance de la qualité des travaux français en chimie supramoléculaire se fait au travers de la remise des trois Prix bisannuels du groupe : Prix Christiane Dietrich-Buchecker (jeune), Prix Henry Le Chatelier (confirmé) et Prix André Collet (senior), et du Prix de thèse décerné pour la première fois cette année. Vous pouvez retrouver la liste de tous les récipiendaires sur notre site web. Le groupe Supr@SCF joue un rôle important dans l'échange d'informations au sein de la communauté française au travers de son site web (https://new.societechimiquedefrance.fr/groupes/chimie-supramoleculaire/), de son compte Bluesky (@supraSCF), et de sa liste de diffusion par courrier électronique. Enfin, n'oublions pas la diffusion de cette gazette semestrielle « *La SupInfo* ». Vous pouvez retrouver tous les numéros sur notre site web. En raison du caractère fortement interdisciplinaire de la chimie supramoléculaire, le groupe Supr@SCF est associé aux Divisions de Chimie Organique, de Chimie de Coordination et de Chimie Physique de la Société Chimique de France.
Bienvenue au nouveau bureau, certain que dynamisme et passion perpétueront les actions et projets qui ont fait le groupe Supr@SCF depuis 2020. Ces initiatives renforcent les liens entre les équipes nationales engagées dans la recherche en chimie supramoléculaire et contribuent à son rayonnement. N'hésitez pas à rejoindre notre communauté grandissante en adhérant au groupe Supr@SCF !

Les Journées de Chimie Supramoléculaire 2025

Les 22 et 23 mai 2025 s'est déroulée la troisième édition des "*Journées de Chimie Supramoléculaire*" (JCS2025), réunissant 172 chimistes partageant un intérêt pour les différents aspects de la chimie supramoléculaire. Cet événement s'inscrit dans le cadre des activités scientifiques du groupe thématique de Chimie Supramoléculaire (SUPR@SCF) de la Société Chimique de France (SCF). Cette année, les JCS2025 se sont tenues dans les locaux de l'École Européenne de Chimie, Polymères et Matériaux (ECPM) à Strasbourg, berceau de la chimie supramoléculaire avec les prix Nobel de Jean-Marie Lehn (1987) et Jean-Pierre Sauvage (2016).

Quatre chimistes strasbourgeois : Iwona Nierengarten (LIMA), Henri-Pierre Jacquot de Rouville (Institut de Chimie), Giulio Ragazzon (ISIS) et Aline Nonat (IPHC), avec le partenariat de la Fondation Jean-Marie Lehn de l'Université de Strasbourg, étaient en charge de l'organisation de cet événement.
Le programme scientifique de ces deux demi-journées était très riche avec quatre conférences plénières, 12 communications orales et 15 communications flash.

Nous avons eu l'honneur d'accueillir deux lauréats des prix décernés par le groupe SUPR@SCF : Ling PENG (Aix-Marseille Université, CNRS, CINaM) qui a reçu le prix André Collet récompensant ses recherches dans le domaine des dendrimères supramoléculaires pour des applications biomédicales, et Clément FALAISE (Institut Lavoisier de Versailles) qui s'est vu remettre le prix Christiane Dietrich-Buchecker pour ses travaux novateurs sur la nature chaotropique des polyanions inorganiques.

La troisième conférence plénière donnée par Andrey KLYMCHENKO (Faculté de Pharmacie, Université de Strasbourg) nous a permis de découvrir l'univers des sondes supramoléculaires fluorescentes hautement sensibles pour des applications dans le domaine de la biologie. Enfin, la participation d'Anne NIJS, éditrice en chef des journaux scientifiques de Chemistry Europe, était une opportunité unique pour les jeunes

chercheurs et étudiants de mieux connaître les enjeux de la publication scientifique et d'échanger avec un des acteurs majeurs de l'édition scientifique dans le domaine de la chimie.

Par ailleurs, de nombreuses communications orales ont été offertes aux jeunes chimistes et étudiants pour leur donner l'opportunité de présenter leurs travaux à la communauté des chimistes supramoléculaires.

Les discussions et le partage scientifique se sont poursuivis pendant une session de posters en fin d'après-midi. Ce moment très convivial a été accompagné d'une dégustation de vins locaux et d'une spécialité alsacienne, la tarte flambée.

Le point fort des "*Journées de Chimie Supramoléculaire*" est la diversité thématique présentée par tous les intervenants montrant que la chimie des interactions non-covalentes peut être utilisée pour construire des matériaux de nouvelle génération et pour répondre aux besoins de la société dans des domaines aussi variés que la médecine, l'énergie et la durabilité. Cela confirme que la chimie supramoléculaire est extrêmement dynamique et ouverte à tous.

Quatre posters, choisis par les conférenciers pléniers, ont reçu les prix des meilleurs posters généreusement sponsorisés par *ChemistryEurope*. Ces prix ont été décernés à Camille Duranteau (Université de Lorraine, Nancy), Lucrezia Trevisan (Université de Rennes), Arnaud Tillet (Institut Lavoisier de Versailles, UVSQ, Paris) et Jakub Ossowski (Université de Strasbourg). De plus, les membres du comité d'organisation ont également récompensé Angelina Jocic (Heidelberg University, Allemagne) et Ioan Stroia (Institut Européen des Membranes, Montpellier) pour les meilleures communications orales.

Félicitations à tous !

Cet événement a été aussi marqué par une très grande participation d'étudiants et de jeunes chimistes venus de toute la France mais aussi de l'étranger. Nous avons été très heureux d'accueillir de jeunes collègues venus d'Allemagne, de Suisse, d'Espagne et d'Angleterre, ce qui, nous l'espérons, contribuera à promouvoir les activités scientifiques de la SCF et plus particulièrement de Supr@SCF à l'international.

Le comité d'organisation tient à remercier chaleureusement les étudiants qui ont contribué à l'organisation, les sponsors et les institutions académiques pour leur soutien financier et enfin tous les participants pour ces moments d'échanges scientifiques et humains qui renforcent des liens entre chimistes de toutes générations. Votre présence et votre enthousiasme ont clairement montré que la Chimie Supramoléculaire est un domaine de recherche hautement interdisciplinaire et dynamique, vos contributions sont une source d'inspiration pour l'ensemble de la communauté, merci à tous pour avoir fait des JCS 2025 un moment aussi convivial.

Prochain rendez-vous pour la quatrième édition des "*Journées de Chimie Supramoléculaire*" à Marseille en 2026 !

Iwona Nierengarten (au nom du comité d'organisation).

Kyoto 2025: International Symposium on Macrocyclic and Supramolecular Chemistry

L'*International Symposium on Macrocyclic and Supramolecular Chemistry* - ISMSC, conférence annuelle phare dans notre domaine, s'est tenue dans la ville historique de Kyoto, au Japon, du 25 au 30 mai 2025, avec un nombre record de 969 participants. Cette prouesse organisationnelle réalisée par Tomoki Ogoshi (Université de Kyoto / Université de Kanazawa), Shigehisa Akine (Université de Kanazawa) et Shiki Yagai (Université de Chiba) a permis à 80 intervenants de donner des présentations orales. Plus de 700 posters ont également été présentés sur tous les aspects de la chimie supramoléculaire.

Outre une participation japonaise impressionnante, une délégation française importante était également présente, avec des participants venus de Paris, Bordeaux, Rennes, Montpellier et Angers.

ISMSC 2026 à Bordeaux

Nous attendons avec impatience la 20ème édition de cette série de conférences, qui ont lieu alternativement en Europe, Asie et Amérique du Nord, et qui reviendra en France en 2026 après Strasbourg en 2015. Cette conférence mono-session se tiendra à Bordeaux du 5 au 10 juillet 2026, avec 7 conférences plénières, 22 conférenciers invités, circa 25 contributions orales courtes et des sessions de posters.

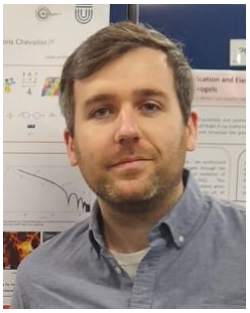
De plus amples informations sur la conférence sont données dans notre rubrique "À VOS AGENDAS".

Website : www.ismsc2026.com
Bluesky : @ismsc2026.bsky.social
E-mail : contact@ismsc2026.com

Nathan McClenaghan & Yann Ferrand
Co-chairs ISMSC 2026

PRIX DE THÈSE Supr@SCF 2025

Cette année nous avons décerné notre premier prix de thèse Supr@SCF au **Dr Vivien Andrieux**.



Vivien Andrieux est actuellement chercheur postdoctoral au sein du groupe du Pr. Birgit Esser à l'Université d'Ulm (Allemagne). Il a intégré l'École Normale Supérieure de Lyon en 2017, où il a obtenu une licence de chimie (parcours Sciences de la matière). Il a ensuite poursuivi sa formation dans le cadre d'un double cursus entre le master de chimie de l'ENS de Lyon et le master "Ingénierie des matériaux et nanotechnologies" du Politecnico di Milano. De 2021 à 2024, il a effectué son doctorat au sein du Laboratoire de chimie de l'ENS de Lyon (financement CDSN, Contrat Doctoral Spécifique Normalien). Ses travaux de thèse portaient sur la synthèse, la caractérisation et la stimulation par transfert d'électrons de matériaux mous supramoléculaires formés par auto-assemblage de viologènes. Ils ont permis de développer de nouveaux gels conducteurs, dont le réseau supramoléculaire peut être réversiblement désassemblé et réassemblé par stimulation électrochimique. Une nouvelle voie de synthèse permettant l'obtention de composés bipyridium π-étendus a également été développée dans le cadre du doctorat. Ces nouveaux composés ont permis la première observation, en solution et en l'absence de contrainte conformationnelle, d'un complexe à valence mixte (pimère) d'un dérivé bis-viologène.
Ses recherches actuelles se concentrent sur le développement de nouveaux matériaux auto-assemblés pour l'électronique organique et le stockage d'énergie.

À VOS AGENDAS

Les Journées de Chimie Supramoléculaire 2026 à Marseille

Le Groupe de Chimie Supramoléculaire (Supr@SCF) de la Société Chimique de France (SCF) organise les prochaines *Journées de Chimie Supramoléculaire* JCS2026 à Marseille les **28 et 29 Mai 2026**. Au programme trois conférences plénières, des communications orales et une session de présentation de posters.

Le programme et de plus amples informations sur ces journées vous seront communiqués prochainement par le comité d'organisation via notre site web et nos outils de communications habituels (liste de diffusion par courrier électronique, compte Bluesky (@supraSCF), SupInfo, l'Actualité Chimique…).

Nous vous attendons nombreux à Marseille en 2026 !

Pour le comité d'organisation :

David Bardelang, Cedric Colomban, Yoann Cotelle, Anthony Kermagoret, Anne-Doriane Manick, Maylis Orio.

2026 : Bordeaux au cœur des évènements SCF et Supr@SCF

CONGRÈS SCF 2026

Le comité d'organisation du congrès SCF 2026 est heureux de vous accueillir à Bordeaux, sur le campus universitaire à Matmeca (Campus Universitaire ENSEIRB – MATMECA, 33400 Talence), pour cet événement qui se tiendra **du 22 au 24 juin 2026**.

Placé sous le thème « Les défis de la chimie de demain », ce congrès a pour ambition de réunir la communauté des chimistes, qu'ils soient français ou internationaux, afin de partager les avancées les plus récentes dans tous les domaines de la chimie.

Ce rendez-vous incontournable pour notre communauté scientifique proposera un programme varié comprenant des conférences invitées, des présentations scientifiques et des sessions de posters pour mettre en lumière les recherches les plus prometteuses qui construiront la chimie de demain.
La remise des Grand Prix nationaux et des prix binationaux de la SCF, temps fort et emblématique de l'événement, mettra également à l'honneur des chercheurs de renom.

Nous souhaitons que le SCF 2026 soit un espace d'échanges et de rencontres, favorisant le dialogue entre scientifiques de toutes générations et de tous horizons, qu'ils viennent du monde académique ou industriel. Ces trois journées seront, nous l'espérons, une occasion de réfléchir ensemble aux défis et aux opportunités de la chimie de demain.

À très bientôt au congrès SCF 2026 !
https://premc.org/fr/scf2026-fr/

Contact et informations : Comité d'organisation SCF 2026, Email : scf2026@premc.org

Weekend Grand Public 20-21 juin 2026, Cap-Sciences, Bordeaux, France

ISMSC Bordeaux 2026

Comme annoncé ci-dessus, la 20ème édition de l'*International Symposium on Macrocyclic and Supramolecular Chemistry* se tiendra à Bordeaux **du 5 au 10 juillet 2026**, organisée par Nathan McClenaghan et Yann Ferrand, Co-chairs ISMSC 2026. Vous serez régulièrement informés via le site web et le compte Bluesky de la conférence. Nous vous encourageons à les consulter régulièrement.
Venez nombreux à Bordeaux en 2026 !

Les inscriptions et la soumission des résumés ouvriront à l'automne 2025.

Website : www.ismsc2026.com
Bluesky : @ismsc2026.bsky.social
E-mail : contact@ismsc2026.com

Nathan McClenaghan & Yann Ferrand
Co-chairs ISMSC 2026

Supr@Angers 2027

Après Lyon (2018), Strasbourg (2021) et Paris (2024), la quatrième édition des Supr@Ville, congrès dédié à tous les domaines de la chimie supramoléculaire, aura lieu à Angers.

Vous pouvez dès à présent noter dans vos agendas que **Supr@Angers** se tiendra durant la **première quinzaine de Juin 2027**.

De plus amples informations sur cet événement vous seront communiquées régulièrement via notre site web (https://new.societechimiquedefrance.fr/groupes/chimie-supramoleculaire/), notre compte Bluesky (@supraSCF), et la gazette *SupInfo* semestrielle.

Supr@Angers

Nous vous attendons nombreuses et nombreux à cet événement devenu incontournable pour notre communauté. Nous pourrons ainsi partager un moment scientifique unique dans la capitale de l'Anjou !

Pour le comité d'organisation de Supr@Angers 2027,
David Canevet & Sébastien Goeb (Laboratoire MOLTECH-Anjou, Université d'Angers, CNRS)

UN POINT SUR... ROTAXANES, NAVETTES ET POMPES MOLÉCULAIRES

Définitions. Le journal officiel du 19/09/2023 a actualisé la définition de « rotaxane » en le décrivant comme « *Assemblage supramoléculaire constitué d'au moins un macrocycle et d'une entité moléculaire en forme d'haltère qui le traverse, sans lui être liée de façon covalente, et qui ne peut s'en dégager en raison de la forme et de la dimension de ses extrémités* » (Figure 1).[1] Le macrocycle et l'haltère sont piégés cinétiquement et condamnés à rester unis à température ambiante tant qu'il n'y a pas de ruptures de liaisons chimiques.

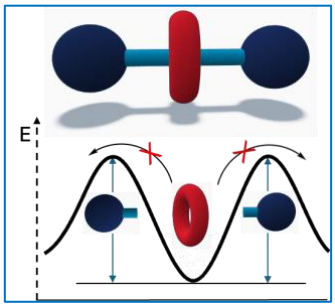


Figure 1. Profil énergétique du [2]rotaxane

Le premier rotaxane a été proposé en 1958 par A. Lüttringhaus et coll. comme espèce intermédiaire pour synthétiser le premier caténane.[2] Mais la topologie des rotaxanes a été définie véritablement par L. Frisch et E. Wasserman en 1961,[3] bien que la première synthèse d'un rotaxane ait été réalisée par I. T. Harrison et S. Harrison en 1967 avec un rendement modeste de 6%.[4] L'idée d'exploiter un polymère comme axe pour le revêtir de macrocycles et former des polyrotaxanes a été proposée dès l'année 1975,[5] ouvrant des perspectives innovantes pour l'organisation polymérique des macrocycles. Contrôler le nombre de macrocycles autour de l'axe devient un défi que J. F. Stoddart releva en enfilant deux éther-couronnes sur un axe comportant deux sites ammoniums et terminé par deux bouchons.[6] Ce nouvel assemblage supramoléculaire à trois éléments (1 axe et 2 macrocycles) fut baptisé [3]rotaxane (Figure 2, type 1.2).

L'émergence de ces nouveaux types de rotaxanes a incité F. Vögtle et coll. à proposer une nomenclature précise pour définir toutes les structures possibles de rotaxanes, caténanes et structures mixtes.[7] Cet article influencera le comité IUPAC, et un rapport détaillé sera édité en 2008 pour harmoniser la classification des rotaxanes.[8] Le nombre [*w*] d'axes et le nombre [*x*] de macrocycles indépendants (non liés par des liaisons covalentes) définissent le nombre [*v*] (v = w + x) de composants, et le type de rotaxane (*w.x*). Cette nomenclature intègre les rotaxanes branchés où des axes ou des macrocycles sont liés (Figure 2).[9]

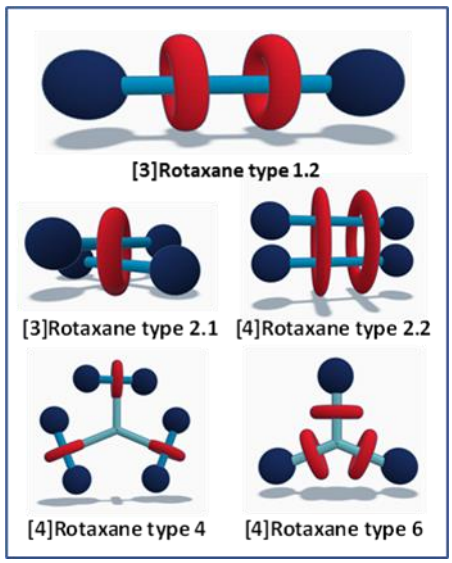


Figure 2. Exemples de diférents types de rotaxanes suivant les recommandations IUPAC.[8]

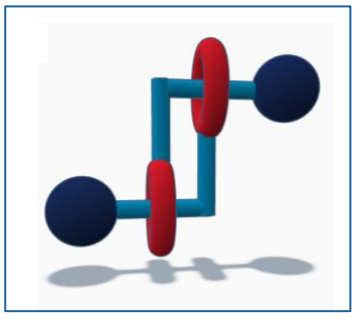


Figure 3. Rotaxane "daisy chain"

La famille des rotaxanes sera complétée dès la fin des années 90 par les rotaxanes « daisy chain », famille à la croisée des rotaxanes et des caténanes.[10] Le cycle et l'axe étant liés de façon covalente, les assemblages « daisy chain » à « n » molécules sont donc des [n]rotaxanes (Figure 3). Si l'assemblage s'organise en cycle supramoléculaire, le préfixe « *cyclo* » peut être ajouté au nom.[2] Pionnier de la synthèse des catenanes,[11] J.-P. Sauvage et son équipe ont démontré l'intérêt des rotaxanes comme précurseurs de la synthèse dirigée par complexation métallique des caténanes.[12] En fonctionnalisant l'axe avec deux sites de coordination (phénanthroline vs terpyridine) et en le liant à un cycle portant un site phénanthroline, ils ont mis en évidence l'extension/ contraction du cycle d'un *cyclo*-[2]rotaxane daisy chain contrôlée par la complexation rivale de centres Cu(I) et de centres Zn(II),[13] créant le premier *muscle moléculaire*, un des graals des machines moléculaires.[14]

Rotaxanes : "navettes, interrupteurs et pompes". Le potentiel des rotaxanes pour former des machines moléculaires a été exploré dès 1991 par le groupe de J. F. Stoddart.[15] La compétition de deux sites sur l'axe moléculaire ayant les mêmes affinités pour le macrocycle entraine un mouvement de navette du macrocycle le long de l'axe de la molécule invitée.[16] Inversement un rotaxane, offrant le contrôle de l'affinité des sites de l'axe par stimulation, génère un basculement commandé du macrocycle sur l'axe,[17] et sera ensuite défini comme un interrupteur moléculaire par A. E. Kaifer.[18]

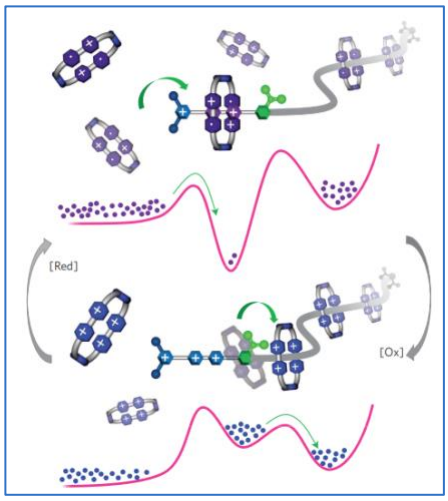


Figure 4. Pompe moléculaire conçue par Stoddart et coll.[19]

Récemment, l'équipe de J. F. Stoddart a conçu une pompe moléculaire artificielle constituée d'un long axe moléculaire à deux bouchons terminaux et deux sites d'accueil différents pour le macrocycle "*blue box*" (cyclobis(paraquat-*p*-phenylene)) séparés par un cliquet antiretour (Figure 4).[19] Un mécanisme d'oxydation-réduction de la *blue box* permet le déplacement de celle-ci. Le premier bouchon, à une extrémité de l'axe, autorise le franchissement de la *blue box* réduite pour rejoindre le premier site de complexation. Oxydée, la *blue box* doit changer de site. Mais ne pouvant énergétiquement franchir le premier bouchon, le macrocycle migre sur le second site en traversant le cliquet positionné entre les deux sites de complexation. Le processus est répété avec une seconde *blue box* réduite, qui après oxydation rejoint la première *blue box* sur le second site. L'ajustement ultime des barrières d'activation des bouchons par stimulation a permis de concevoir cette pompe moléculaire, dont l'accumulation de macrocycles sur l'axe est le travail de cette machine moléculaire. La construction d'un axe moléculaire possédant des bouchons stimulables pour contrôler la barrière d'énergie du pseudo-rotaxane, tels que les cliquets d'énergie,[20] ouvre des perspectives fascinantes pour les machines moléculaires. Les rotaxanes sont maintenant parmi les systèmes les plus inspirants de la chimie supramoléculaire. Balzani,[21] Wasserman, Harrison, Schill, Zollenkopf, Sauvage et Stoddart resteront des pionniers pour la synthèse et l'exploration des propriétés des rotaxanes comme jouets moléculaires. Ces travaux séminaux ont déjà un impact significatif sur la science des machines moléculaires et sont incontournables pour les technologies du futur.

(1) Rotaxane. *Journal Officiel de la République Française*, https://www.legifrance.gouv.fr/jorf/id/JORFTEXT000048086378.
(2) Lüttringhaus, A.; Cramer, F.; Prinzbach, H.; Hengle, F. M. *Liebigs Ann. Chem.* **1958,** *613*, 185-198.
(3) Frisch, H. L.; Wasserman, E. *J. Am. Chem. Soc.* **1961,** *83*, 3789-3795.
(4) Harrison, I. T.; Harrison, S. *J. Am. Chem. Soc.* **1967,** *89* (22), 5723-5724.
(5) Maciejewski, M.; Smets, G. *Pr. Nauk. Inst. Technol. Org. Tworzyw Sztucznych Politech. Wroclaw.* **1975,** *16*, 57-69.
(6) Aston, P. R.; Glink, P. T.; Stoddart, J. F.; Tasker, P. A.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1996,** *2* (6), 729-736.
(7) Safarowsky, O.; Windisch, B.; Mohry, A.; Vögtle, F. *J. Prakt. Chem.* **2000,** *342* (5), 437-444.
(8) Yerin, A.; Wilks, E. S.; Moss, G. P.; Harada, A. *Pure Appl. Chem.* **2008,** *80* (9), 2041-2068.
(9) a) Amabilino, D. B.; Ashton, P. R.; Bělohradský, M.; Raymo, F. M.; Stoddart, J. F. *J. Chem. Soc., Chem. Commun.* **1995,** (7), 751-753. b) Elizarov, A. M.; Chiu, S.-H.; Glink, P. T.; Stoddart, J. F., *Org. Lett.* **2002,** *4* (5), 679-682.
(10) a) Ashton, P. R.; Parsons, I. W.; Raymo, F. M.; Stoddart, J. F.; White, A. J. P.; Williams, D. J.; Wolf, R. *Angew. Chem. Int. Ed.* **1998,** *37* (13-14), 1913-1916. b) Rotzler, J.; Mayor, M. *Chem. Soc. Rev.* **2013,** *42* (1), 44-62.
(11) Dietrich-Buchecker, C. O.; Sauvage, J. P.; Kintzinger, J. P. *Tetrahedron Lett.* **1983,** *24* (46), 5095-5098.
(12) a) Chambrom, J.-C.; Heitz, V.; Sauvage, J.-P. *Bull. Soc. Chim. Fr.* **1995,** *132* (3), 340-347. b) Cárdenas, D. J.; Gaviña, P.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1997,** *119* (11), 2656-2664.
(13) Jiménez, M. C.; Dietrich-Buchecker, C.; Sauvage, J.-P. *Angew. Chem. Int. Ed.* **2000,** *39* (18), 3284-3287.
(14) Bruns, C. J.; Stoddart, J. F. *Acc. Chem. Res.* **2014,** *47* (7), 2186-2199.
(15) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007,** *46* (1+2), 72-191.
(16) Anelli, P. L.; Spencer, N.; Stoddart, J. F. *J. Am. Chem. Soc.* **1991,** *113* (13), 5131-5133.
(17) Ashton, P. R.; Bissell, R. A.; Spencer, N.; Stoddart, F.; Tolley, M. S. *Synlett* **1992,** (11), 914-918.
(18) Cordova, E.; Bissell, R. A.; Kaifer, A. E. in *From rotaxanes to molecular switches*, 210th ACS National Meeting, Chicago, IL; August 20-24, 1995.
(19) Cheng, C.; McGonigal, P. R.; Schneebeli, S. T.; Li, H.; Vermeulen, N. A.; Ke, C.; Stoddart, J. F. *Nat. Nanotechnol.* **2015,** *10* (6), 547-553.
(20) Yang, X.; Cheng, Q.; Monnier, V.; Charles, L.; Karoui, H.; Ouari, O.; Gigmes, D.; Wang, R.; Kermagoret, A.; Bardelang, D. *Angew. Chem. Int. Ed.* **2021,** *60* (12), 6617-6623.
(21) Ballardini, R.; Ceroni, P.; Credi, A.; Gandolfi, M. T.; Maestri, M.; Semararo, M.; Venturi, M.; Balzani, V. *Adv. Funct. Mater.* **2007**, 17, 740–750.

Cet article a été rédigé par **Anthony Kermagoret**, Maitre de Conférence à Aix-Marseille Université
Anthony.kermagoret@univ-amu.fr

À LA RENCONTRE DE… STÉPHANIE DUROT

Carrière :

2010- Maître de conférences, LSAMM (Dir. V. Heitz), Université de Strasbourg
2005-2010 Maître de conférences, LCOM (Dir. J.-P. Sauvage), Université Louis Pasteur/de Strasbourg
2003-2005 Post-doctorante, LEDSS (Pr. J.-L. Pierre), Université Joseph Fourier, Grenoble.

Formation :

2000-2003 Doctorat de Chimie Bioinorganique, modèles de Mn-SOD, Dr. C. Policar, Pr. J.-P. Mahy, LCBB, Université Paris XI
1999-2000 DEA des Systèmes Bioinorganiques, Magistère de Physico-Chimie Moléculaire, Université Paris XI, Orsay
1999 Agrégation de Sciences Physiques, option Chimie
1996-2000 Élève de l'ENS Cachan

Ma première expérience au laboratoire a été si diversifiée, passionnante et enrichissante que j'ai souhaité continuer la recherche.

Les jeunes devraient s'intéresser à la chimie supramoléculaire car elle intervient partout, dans le vivant, les matériaux...La formation de complexes d'inclusion, d'auto-assemblages, la catalyse supramoléculaire sont des phénomènes fascinants, pouvant s'accompagner de changement de propriétés, de couleur ou d'émission de lumière.

À mes heures perdues, je fais du sport, de préférence en milieu naturel : escalade, course à pied, randonnée. Passer du temps avec ma famille, mes amis, un bon livre ou un bon film est aussi essentiel à mon équilibre.

Mes molécules préférées sont complexes, colorées, entrelacées, dynamiques, chirales ou tout à la fois !

La chose la plus importante que j'ai apprise de mes étudiants est d'être disponible pour rester à l'écoute et mieux les comprendre, ceci pour les aider à progresser.

Si je n'avais pas fait carrière dans la chimie, je serais professeur de mathématiques ou médecin. Aider les autres est ma principale motivation.

Je célèbre le succès en faisant la fête et en partageant du champagne, origine rémoise oblige !

Intérêts de recherche : Cages moléculaires et molécules entrelacées

Chimie supramoléculaire, reconnaissance moléculaire, cages moléculaires, rotaxanes et navettes moléculaires, porphyrines, chimie de coordination, catalyse homogène, luminescence, photocatalyse, chiralité, chimie bioinorganique.

Quelques prix et distinctions :

Chercheuse invitée à l'Université de Nagoya (2024).
Accueil en délégation au CNRS et CRCT (2011, 2021).
Porteur de projets ANR PRC (2023) et JCJC (2014).

Cinq références significatives :

R. Djemili, S. Adrouche, S. Durot, V. Heitz. Allosterically Driven Assembly of a Multisite Cage-Based [2]Semirotaxane. *J. Org. Chem.* **2023**, *88*, 14760.

L. Schoepff, L. Monnereau, S.Durot, S. Jenni, C. Gourlaouen, V. Heitz. A flexible bis-Co(III) porphyrin cage as a bimetallic catalyst for the conversion of CO_2 and epoxides into cyclic carbonates. *ChemCatChem* **2020**, *12*, 5826.

R. Djemili, L. Kocher, S. Durot, A. Peuronen, K. Rissanen, V. Heitz. Positive allosteric control of guests encapsulation by metal binding to covalent porphyrin cages. *Chem. Eur. J.* **2019**, *25*, 1481.

S. Durot, J. Taesch, V. Heitz. Multiporphyrinic cages: architectures and functions. *Chem. Rev.* **2014**, *114*, 8542.

J.-P. Collin, S. Durot*, M. Keller, J.-P. Sauvage, Y. Trolez, M. Cetina, K. Rissanen. Synthesis of [5]rotaxanes containing bi- and tridentate coordination sites in the axis. *Chem. Eur. J.* **2011**, 17, (3), 947.

NOTRE SÉLECTION D'ARTICLES

Le bureau du Groupe Supr@SCF 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 février 2025 - juillet 2025 dans les journaux suivants :
- *Nature, Science, Nat. Nanotechnol., Nat. Chem., Chem, Nat. Comm., J. Am. Chem. Soc., Angew. Chem. Int. Ed., Chem. Sci., Chem. Comm., Chem. Eur. J.*

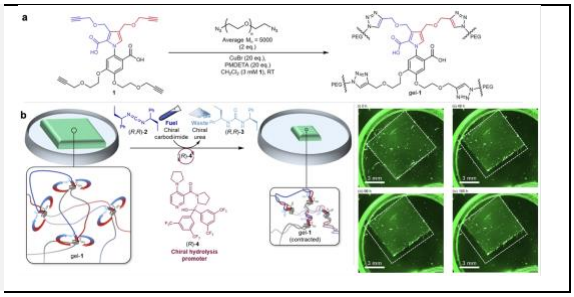
Cette sélection est évidemment non exhaustive, et nous invitons les membres du groupe à nous faire part de leurs récentes publications.

Transducing chemical energy through catalysis by an artificial molecular motor

Wang, P. L.; Borsley, S.; Power, M. J.; Cavasso, A.; Giuseppone, N.; Leigh, D. A.

Nature **2025**, *637*, 594–600

DOI: 10.1038/s41586-024-08288-x



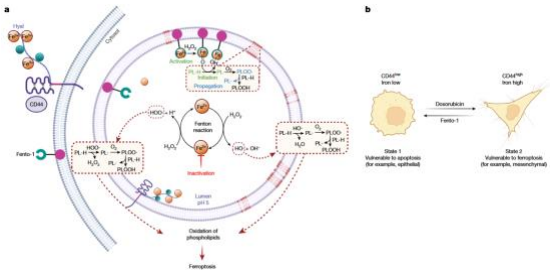
***Abstract*:** Cells display a range of mechanical activities generated by motor proteins powered through catalysis1. This raises the fundamental question of how the acceleration of a chemical reaction can enable the energy released from that reaction to be transduced (and, consequently, work to be done) by a molecular catalyst2,3,4,5,6,7. Here we demonstrate the molecular-level transduction of chemical energy to mechanical force8 in the form of the powered contraction and powered re-expansion of a cross-linked polymer gel driven by the directional rotation of artificial catalysis-driven9 molecular motors. Continuous 360° rotation of the rotor about the stator of the catalysis-driven motor-molecules incorporated in the polymeric framework of the gel twists the polymer chains of the cross-linked network around one another. This progressively increases writhe and tightens entanglements, causing a macroscopic contraction of the gel to approximately 70% of its original volume. The subsequent addition of the opposite enantiomer fuelling system powers the rotation of the motor-molecules in the reverse direction, unwinding the entanglements and causing the gel to re-expand. Continued powered twisting of the strands in the new direction causes the gel to re-contract. In addition to actuation, motor-molecule rotation in the gel produces other chemical and physical outcomes, including changes in the Young modulus and storage modulus—the latter is proportional to the increase in strand crossings resulting from motor rotation. The experimental demonstration of work against a load by a synthetic organocatalyst, and its mechanism of energy transduction6, informs both the debate3,5,7 surrounding the mechanism of force generation by biological motors and the design principles6,10,11,12,13,14 for artificial molecular nanotechnology.

Activation of lysosomal iron triggers ferroptosis in cancer

Cañeque, T.; Baron, L.; Müller, S.; Carmona, A.; Colombeau, L.; Versini, A.; Solier, S.; Gaillet, C.; Sindikubwabo, F.; Sampaio, J. L.; Sabatier, M.; Mishima, E.; Picard-Bernes, A.; Syx, L.; Servant, N.; Lombard, B.; Loew, D.; Zheng, J. S.; Proneth, B.; Thoidingjam, L. K.; Grimaud, L.; Fraser, C. S.; Szylo, K. J.; Kazarian, E. D.; Bonnet, C.; Charafe-Jauffret, E.; Ginestier, C.; Santofimia-Castaño, P.; Estaras, M.; Dusetti, N.; Iovanna, J. L.; Cunha, A. S.; Pittau, G.; Hammel, P.; Tzanis, D.; Bonvalot, S.; Watson, S.; Gandon, V.; Upadhyay, A.; Pratt, D. A.; Freitas, F. P.; Angeli, J. P. F.; Stockwell, B. R.; Conrad, M., Ubellacker, J. M.; Rodriguez, R.

Nature **2025**, *642*, 14067–14078

DOI: 10.1038/s41586-025-08974-4



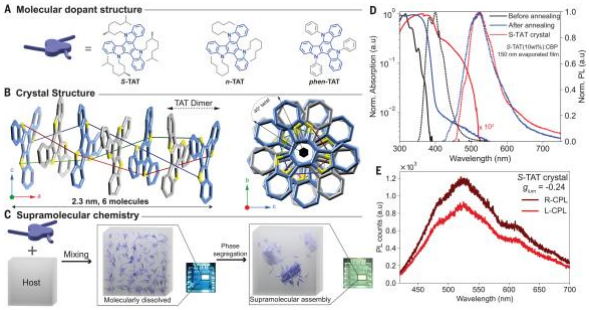
***Abstract*:** Iron catalyses the oxidation of lipids in biological membranes and promotes a form of cell death called ferroptosis1. Defining where this chemistry occurs in the cell can inform the design of drugs capable of inducing or inhibiting ferroptosis in various disease-relevant settings. Genetic approaches have revealed suppressors of ferroptosis2,3,4; by contrast, small molecules can provide spatiotemporal control of the chemistry at work5. Here we show that the ferroptosis inhibitor liproxstatin-1 exerts cytoprotective effects by inactivating iron in lysosomes. We also show that the ferroptosis inducer RSL3 initiates membrane lipid oxidation in lysosomes. We designed a small-molecule activator of lysosomal iron—fentomycin-1—to induce the oxidative degradation of phospholipids and ultimately ferroptosis. Fentomycin-1 is able to kill iron-rich CD44high primary sarcoma and pancreatic ductal adenocarcinoma cells, which can promote metastasis and fuel drug tolerance. In such cells, iron regulates cell adaptation6,7 while conferring vulnerability to ferroptosis8,9. Sarcoma cells exposed to sublethal doses of fentomycin-1 acquire a ferroptosis-resistant cell state characterized by the downregulation of mesenchymal markers and the activation of a membrane-damage response. This phospholipid degrader can eradicate drug-tolerant persister cancer cells in vitro and reduces intranodal tumour growth in a mouse model of breast cancer metastasis. Together, these results show that control of iron reactivity confers therapeutic benefits, establish lysosomal iron as a druggable target and highlight the value of targeting cell states10.

Circularly polarized electroluminescence from chiral supramolecular semiconductor thin films

Chowdhury, R.; Preuss, M. D.; Cho, H.-H.; Thompson, J. J. P.; Sen, S.; Baikie, T. K.; Ghosh, P.; Boeije, Y.; Chua, X. W.; Chang, K. W.; Guo, E. R.; van der Tol, J.; van den Bersselaar, B. W. L.; Taddeucci, A.; Daub, N.; Dekker, D. M.; Keene, S. T.; Vantomme, G.; Ehrler, B.; Meskers, S. C. J.; Rao, A. K.; Monserrat, B.; Meijer, E. W.; Friend, R. H.

Science **2025**, *146*, 13580–13587

DOI: 10.1126/science.adt3011



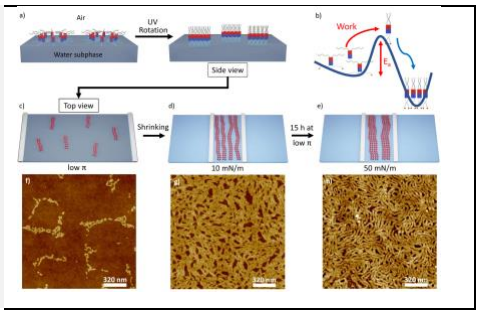
***Abstract*:** Current organic light-emitting diode (OLED) technology uses light-emitting molecules in a molecular host. We report green circularly polarized luminescence (CPL) in a chirally ordered supramolecular assembly, with 24% dissymmetry in a triazatruxene (TAT) system. We found that TAT assembled into helices with a pitch of six molecules, associating angular momentum to the valence and conduction bands and obtaining the observed CPL. Cosublimation of TAT as the "guest" in a structurally mismatched "host" enabled fabrication of thin films in which chiral crystallization was achieved in situ by thermally triggered nanophase segregation of dopant and host while preserving film integrity. The OLEDs showed external quantum efficiencies of up to 16% and electroluminescence dissymmetries >= 10%. Vacuum deposition of chiral superstructures opens new opportunities to explore chiral-driven optical and transport phenomena.

Supramolecular polymerization through rotation of light-driven molecular motors

Schiel, P.; Maaloum, M.; Moulin, E.; Nyrkova, I.; Semenov, A.; Dattler, D.; Accou, L. A.; Christoulaki, A.; Buhler, E.; Plamont, R.; Lehn, J. M.; Giuseppone, N.

Nat. Nanotechnol **2025**, *20*, 1052–1061

DOI: 10.1038/s41565-025-01933-0



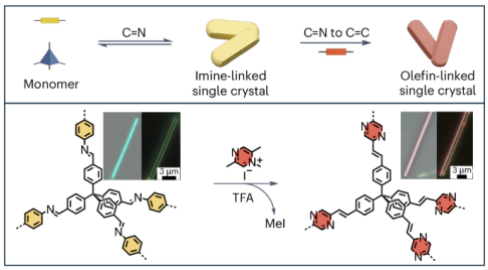
***Abstract*:** Molecular motors can act on their environment through their unique ability to generate non-reciprocal autonomous motions at the nanoscale. Although their operating principles are now understood, artificial molecular motors have yet to demonstrate their general capacity to confer novel properties on (supra)molecular systems and materials. Here we show that amphiphilic light-driven molecular motors can adsorb onto an air–water interface and form Langmuir monolayers upon compression. By irradiation with ultraviolet light, the surface pressure isotherms of these films reveal a drastic shift toward a smaller molecular area as a consequence of motor activation. We explain this counterintuitive phenomenon by the rotation-induced supramolecular polymerization of amphiphilic motors through a non-thermal annealing process to escape a kinetically trapped amorphous state. The effect is limited by the maximum torque the molecular motor can deliver (~10 pN nm) and leads to the formation of highly organized patterns. This serendipitous discovery highlights the opportunities offered by molecular motors to control supramolecular polymerization for the design of innovative materials.

Synthesis of single-crystalline sp2-carbon-linked covalent organic frameworks through imine-to-olefin transformation

Li, S. X.; Xu, S. Q.; Lin, E.; Wang, T. H.; Yang, H. Y.; Han, J. Y.; Zhao, Y. X.; Xue, Q. J.; Samori, P.; Zhang, Z. J.; Zhang, T.

Nat. Chem. **2025**, *17*, 226–232

DOI: 10.1038/s41557-024-01690-y



***Abstract*:** sp2-carbon-linked covalent organic frameworks (sp2c-COFs) are crystalline porous polymers with repeat organic units linked by sp2 carbons, and have attracted increasing interest due to their robust skeleton and tunable semiconducting properties. Single-crystalline sp2c-COFs with well-defined structures can represent an ideal platform for investigating fundamental physics properties and device performance. However, the robust olefin bonds inhibit the reversible-reaction-based crystal self-correction, thus yielding polycrystalline or amorphous polymers. Here we report an imine-to-olefin transformation strategy to form single-crystal sp2c-COFs. The isolated single crystals display rectangular nanotube-like domains with sizes up to approximately 24 mu m x 0.8 mu m x 0.8 mu m, and permanent pore distribution around 1.1 nm. The highly conjugated olefin linkage endows the crystals with enhanced electronic connectivity which determines a remarkable room-temperature metal-free ferromagnetism (8.6 x 10-3 emu g-1). Our protocol is robust and generally applicable for the synthesis of single-crystalline sp2c-COFs for future spin-electron devices.

Not going back: Unidirectional movement by intramolecular one-way ratcheting of functionalized cyclodextrin

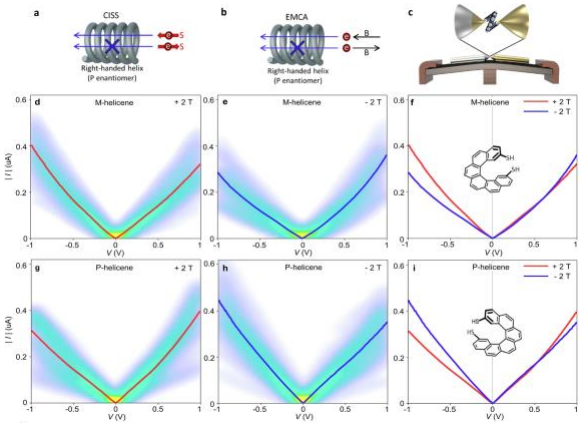
Liu, E.; Daou, D.; Hasenknopf, B.; Vives, G.; Sollogoub, M.

Chem **2025**, *11*, 102623

DOI: 10.1016/j.chempr.2025.102623

***Abstract*:** The achievement of unidirectional molecular movement is a significant challenge due to competition by Brownian motion. Nature can overcome this problem by employing chemically fueled Brownian ratcheting mechanisms to power biomolecular motors, the understanding of which has, in turn, inspired chemists to design artificial molecular systems with similar functionality. Here, we demonstrate that a selectively functionalized cyclodextrin threaded onto an axle with three segments undergoes unidirectional movement. The cyclodextrin's unique 3D structure enables both rim-selective functionalization and a regioselective deprotection reaction of temporary stoppers on the rotaxane axle. In this system, the cyclodextrin can actively open stoppering gates in one direction only. Its forward movement is further favored by a gate-closing reaction, which occurs faster when the cyclodextrin has crossed the gate, which is also caused by its cone shape. We have thus delineated a synergistic double-gated one-way ratchet thanks to the specific 3D structure of the cyclodextrin.

Single-molecule junctions map the interplay between electrons and chirality



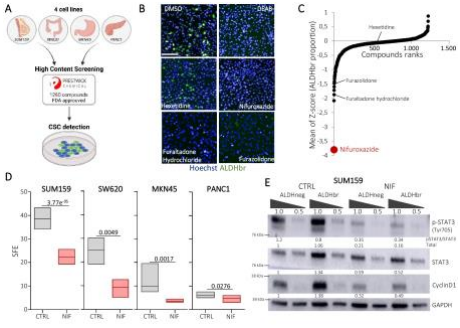
Singh, A. K.; Martin, K.; Talamo, M. M.; Houssin, A.; Vanthuyne, N.; Avarvari, N.; Tal, O.

Nat. Comm. **2025**, *16*, 1759

DOI: 10.1038/s41467-025-56718-9

***Abstract*:** The interplay of electrons with a chiral medium has a diverse impact across science and technology, influencing drug separation, chemical reactions, and electronic transport1-30. In particular, electron-chirality interactions can significantly affect charge and spin transport in chiral conductors, making them highly appealing for spintronics. However, an atomistic mapping of different electron-chirality interactions remains elusive. Here, we find that helicene-based single-molecule junctions behave as a combined magnetic-diode and spin-valve device. This dual-functionality enables the identification of an atomic-scale coexistence of different electron-chirality interactions: the magnetic-diode behavior is attributed to an interaction between electron's angular momentum in a chiral medium and magnetic fields, whereas the spin-valve functionality is ascribed to an interaction between the electron's spin and a chiral medium. This work uncovers the coexistence of electron-chirality interactions at the atomic-scale, identifies their distinct properties, and demonstrates how integrating their functionalities can broaden of the available methods for spintronics.

Inhibition of the STAT3/Fanconi anemia axis is synthetic lethal with PARP inhibition in breast cancer



Rouault, C. D.; Bansard, L.; Martínez-Balsalobre, E.; Bonnet, C.; Wicinski, J.; Lin, S. H.; Colombeau, L.; Debieu, S.; Pinna, G.; Vandamme, M.; Machu, M.; Rosnet, O.; Chevrier, V.; Popovici, C.; Sobol, H.; Castellano, R.; Pasquier, E.; Guasch, G.; Rodríguez, R.; Pannequin, J.; Pascussi, J. M.; Lachaud, C.; Charafe-Jauffret, E.; Ginestier, C.

Nat. Comm. **2025**, *16*, 2159

DOI: 10.1038/s41467-025-57476-4

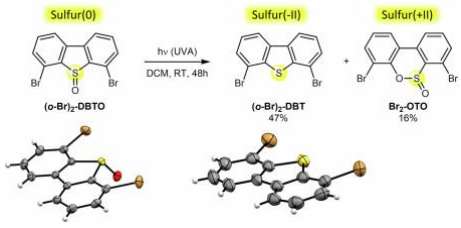
***Abstract*:** The targeting of cancer stem cells (CSCs) has proven to be an effective approach for limiting tumor progression, thus necessitating the identification of new drugs with anti-CSC activity. Through a high-throughput drug repositioning screen, we identify the antibiotic Nifuroxazide (NIF) as a potent anti-CSC compound. Utilizing a click chemistry strategy, we demonstrate that NIF is a prodrug that is specifically bioactivated in breast CSCs. Mechanistically, NIF-induced CSC death is a result of a synergistic action that combines the generation of DNA interstrand crosslinks with the inhibition of the Fanconi anemia (FA) pathway activity. NIF treatment mimics FA-deficiency through the inhibition of STAT3, which we identify as a non-canonical transcription factor of FA-related genes. NIF induces a chemical HRDness (Homologous Recombination Deficiency) in CSCs that (re)sensitizes breast cancers with innate or acquired resistance to PARP inhibitor (PARPi) in patient-derived xenograft models. Our results suggest that NIF may be useful in combination with PARPi for the treatment of breast tumors, regardless of their HRD status.

Photoinduced modulation of the oxidation state of dibenzothiophene S-oxide molecules on an insulating substrate

Hankache, M.; Magné, V.; Geagea, E.; Marques, P. S.; Clair, S.; Giovanelli, L.; Loppacher, C.; Fodeke, E.; Mallet-Ladeira, S.; Maerten, E.; Kammerer, C.; Madec, D.; Nony, L.

Nat. Comm. **2025**, *16*, 4841

DOI: 10.1038/s41467-025-60075-y



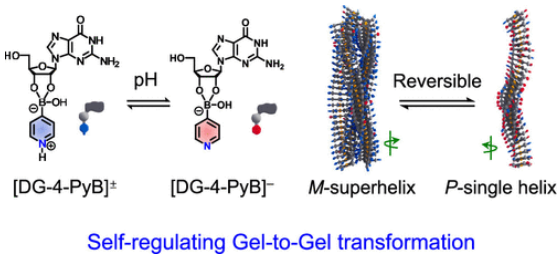
***Abstract*:** On-surface chemistry aims to overcome the limitations of conventional in-solution synthesis by taking advantage of the confinement in two dimensions to master highly ordered covalent structures with tailored properties. So far, most of the reported work is conducted on metal substrates and relies on unconventional mechanisms, thereby precluding a direct transposition of well-established organic reactions from solutions to surfaces. In addition, the intrinsic properties and reactivity of metal substrates often limit the activation methods available to trigger on-surface reactions, and photoinduced processes are especially difficult to handle due to quenching of the adsorbed precursor molecules. Herein, the photoinduced deoxygenation of dibenzothiophene S-oxide (DBTO) derivatives is transposed from solutions to insulating alkali halide surfaces in ultra-high vacuum. By combining in-solution and on-surface investigations by means of scanning tunneling microscopy, non-contact atomic force microscopy, as well as bias spectroscopy measurements, we provide evidence of the successful on-surface deoxygenation of individual DBTO derivatives under UV irradiation. The photoinduced deoxygenation is conducted at low temperature (<25 K) on a NaCl thin film formed on a Au(111) substrate to yield the reduced dibenzothiophene (DBT) product with excellent chemoselectivity. This work thus opens the way to in-situ photocontrolled charge state manipulation in purely organic compounds.

Self-Regulating Hydrogel with Reversible Optical Activity in Its Gel-to-Gel Transformation

Li, J. J.; Yin, F.; Wang, J. H.; Du, H. C.; Xu, F.; Meskers, S.; Li, Y. D.; Wijker, S.; Peng, Y.; Bellan, R.; Vantomme, G.; Song, J.; Liu, C. S.; Meijer, E. W.

J. Am. Chem. Soc. **2025**, *147*, 17361–17371

DOI: 10.1021/jacs.5c03844



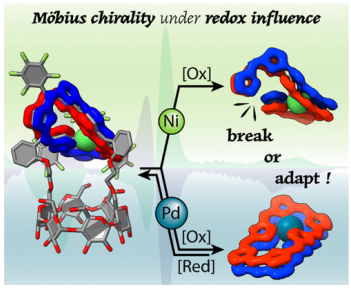
***Abstract*:** This study reports a supramolecular gel system capable of dynamic gel-to-gel transformations and reversible inversion of optical activity between superhelical and single-helical structures without passing through a sol phase. Inspired by collagen-like adaptability, the system utilizes 4-pyridinylboronic acid and guanosine as building blocks. Hierarchical assembly is achieved through pH-responsive boronic ester formation and guanosine-mediated G-quadruplex stacking, enabling transitions between superhelices and single helices with opposite optical activity. The system employs three regulatory pathways: bidirectional pH modulation, monotonic pH increase, and monotonic pH decrease, demonstrating programmable and reversible control over chirality, morphology, and mechanical properties. In the autonomous pH regulation, we have created an out-of-equilibrium hydrogel system with controlled switching of optical activity. Unlike traditional gel-sol-gel systems, this gel maintains macroscopic stability during transformations. Our remarkable finding bridges the gap between static supramolecular assemblies and dynamic soft materials, offering a platform for designing functional, biomimetic systems. The combination of hierarchical organization, dynamic chirality control, and robust programmability positions this gel for applications in adaptive optics, responsive biomaterials, and programmable soft matter.

Encoding and Expressing the Handedness of a Möbius π System in a Totemic Architecture

Dash, S.; Fihey, A.; Favereau, L.; Lagrost, C.; Benchouaia, R.; Blanchard, S.; Ménand, M.; Le Gac, S.

J. Am. Chem. Soc. **2025**, *147*, 15242–15252

DOI: 10.1021/jacs.5c00524



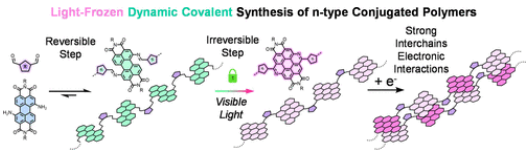
***Abstract*:** The efficient control of the chirality of Möbius π systems remains a challenging task that hinders the development of such molecules into information processing systems. Achieving such control through a redox process would thus open new opportunities. In this context, redox behaviors of Ni(II) and Pd(II) complexes of a Möbius aromatic [28]hexaphyrin doubly linked to an α-cyclodextrin have been investigated. This totemic architecture embedding three types of chirality elements generates two pseudoenantiomers after coordination with either metal. These isomeric pairs possess marked and opposite chiroptical signatures resulting from the P and M configurations of the Möbius π systems. Chemical oxidation to 26-π systems led to behaviors reminiscent to The Oak and the Reeds fable, due to a N3C coordination sphere of Ni(II) being more robust than that of Pd(II). Oxidized Ni(II) complexes (the Oak) maintain a Möbius-type conformation at the expense of the π-systems, which undergo an interruption due to inevitable water insertion. In contrast, oxidation of Pd(II) complexes (the Reeds) converts the Möbius aromatic systems into Hückel (rectangular) aromatic ones that are maintained in the chiral environment provided by the linking pattern with the cyclodextrin. This constitutes an effective chiral instructing site, as reduction back to their original Möbius configuration occurs with high stereoselectivity. Such a reversible shape-shifting process corresponds to a chiral memory phenomenon where the handedness of a cyclic π system is encoded in a scaffold and expressed upon changing an electronic state. For both metals, spectroelectrochemical studies ultimately revealed robust ON-OFF chiroptical switches, which is unprecedented with Möbius π-systems.

Synthesis of Electron-Deficient BisAzaCoroneneDiimide-Conjugated Polymers by Light-Locking Dynamic Covalent Bonds

Gapin, A.; Chatir, E.; Aléveque, O.; Pasgrimaud, C.; David, A. H. G.; De Maria, A.; Legros, M.; Le Bras, L.; Levillain, E.; Goujon, A.

J. Am. Chem. Soc. **2025**, *147*, 12218–12227

DOI: 10.1021/jacs.5c01351



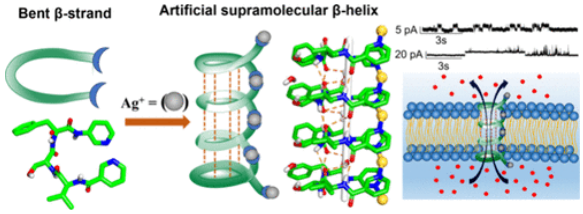
***Abstract*:** We present a novel light-locked dynamic covalent polymerization methodology to synthesize conjugated polymers based on BisAzaCoroneneDiimides (BACDs). This metal-free process converts reversible poly imines into kinetically locked conjugated polymers using visible light, generating minimal side products. By incorporating aldehyde-functionalized comonomers, the approach enables the creation of diverse n-type semiconducting polymers with tunable optical band gaps and low LUMO levels. The polymers exhibit exceptional thermal, electrochemical, and photostability with strong interchain interactions upon electrochemical reduction observed in solution, attributed to the BACD core. Broad absorption from the visible to the near-infrared range underscores their potential in charge and energy transport applications for organic electronics. This scalable, sustainable strategy unlocks access to a versatile class of n-type diimide polymers..

Metal-Directed Self-Assembly of Minimal Heterochiral Peptides into Metallo-Supramolecular β-Helical Tubules for Artificial Transmembrane Water Channels

Pophali, S.; Su, D. D.; Ata, R.; Vijayakanth, T.; Nandi, S.; Jain, R.; Shimon, L. J. W.; Misra, R.; Barboiu, M.

J. Am. Chem. Soc. **2025**, *147*, 17404–17415

DOI: 10.1021/jacs.5c03970



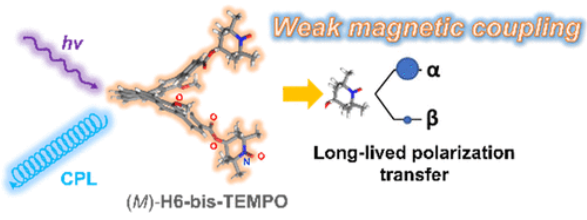
***Abstract*:** Transmembrane selective transport of metabolites controls essential biological functions. During the last two decades, artificial channels have been developed and cyclic peptides have emerged as ideal platforms for efficient ion, sugar, and nucleic acid channel translocation. Despite these tremendous developments, cyclic peptides have eluded selective water transport. Herein, we report the formation of narrow artificial β-helical tubules with diameters ranging from 2.80 to 3.25 Å that selectively control the water translocation, akin to natural aquaporin channels. The tubular assemblies resulted from the metal-driven folding and assembly of minimal heterochiral metal-binding 3-pyridyl-terminated peptides. The bent ultrashort peptide ligand coordinates with Ag+ metal ions in a head-to-tail manner, which undergoes subsequent polymerization into a β-helical tubular structure stabilized by interstrand hydrogen bonds (H-bonds) between the β-strands and π–π staking interactions between terminal pyridyl moieties. Furthermore, sequence engineering of the heterochiral peptide and subsequent Ag+ ion coordination of the tailored peptides enabled the formation of distinct synthetic double β-barrel and artificial β-helical tubular assemblies, with water molecules encapsulated in the hydrophilic core of the tubes. These water-encapsulated tubes were further explored as artificial water channels in lipid bilayers. Our findings suggest that such β-helical tubular channels achieve a single-channel permeability of 106 water molecules/second/channel, which is within 1-2 orders of magnitude lower than that of aquaporins, with a rather good ability to sterically reject ions and prevent proton transport. These assemblies present significant potential for engineering efficient membranes for water purification and separation sciences.

Circularly Polarized Luminescence and Photoinduced Spin Polarization in Helicene-Bis-TEMPO Diradicals

Cadeddu, S.; Chowdhury, R.; Cordeiro, C. D.; Parmar, S.; Kramer, A.; Cordier, M.; Pensel, A.; Vanthuyne, N.; Sessoli, R.; Chiesa, M.; Liao, Y. K.; Friend, R. H.; Salvadori, E.; Autschbach, J.; Crassous, J.

J. Am. Chem. Soc. **2025**, *147*, 23643–23653

DOI: 10.1021/jacs.5c04887



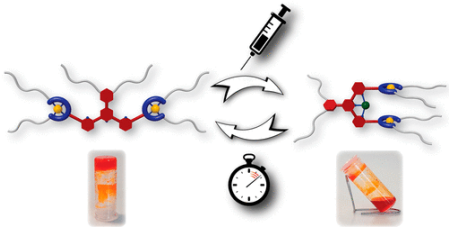
***Abstract*:** Readily accessible high spin excited states are highly coveted due to their potential use in spintronic and quantum sensing applications. Adding a chiral twist to this problem potentially allows for control of the emergent spin polarization through the helicity of the system. Herein we report the realization of a novel, chiral, diradical system, H6-bis-TEMPO, consisting of two TEMPO radicals bridged by a chiral carbo[6]helicene, which after photoexcitation of the helicene core generates a weakly coupled three-spin system comprising the helicene triplet (S = 1) and the two TEMPO radicals (S = 1/2). Time-resolved absorption and theoretical calculations help explain the specific photophysics of this system, while time-resolved EPR shows that the TEMPO radicals become spin polarized once the photoexcited spin intermediate has decayed. Comparison with a nonradical bis-dibenzoate capped helicene H6-bis-BENZ experimentally validates the results. This work constitutes a first step toward the realization of molecular systems able to generate spin polarization through helical chirality at the single-molecule level. Moreover, the helically chiral TEMPO persistent radical shows circularly polarized luminescence.

Sequential and Time-Controlled Sol–Gel Transitions by Mechanical Switching of Molecular Tweezers

Msellem, P.; Groslambert, G.; Miton, L.; Pomes-Hadda, M.; Van Zee, N. J.; Guibert, C.; Vives, G.

J. Am. Chem. Soc. **2025**, *147*, 5360–5367

DOI: 10.1021/jacs.4c17146



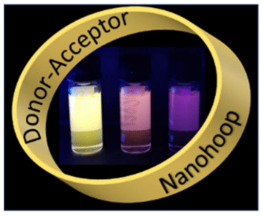
***Abstract*:** Controlling the motion of molecular machines to influence higher-order structures is well-established in biological systems but remains a significant challenge for synthetic analogs. Herein, we aim to harness the mechanical switching of switchable molecular tweezers to modulate their self-assembly and produce stimuli-responsive organogels. We report a series of terpy(Pt-salphen)2 molecular tweezers functionalized with alkyl chains that act as low-molecular-weight gelators (LMWGs) in their open conformation. The resulting organogels were thoroughly characterized by SEM, cryo-TEM, SAXS, and rheology. The macroscopic transition from gel to solution was achieved by the cation-induced closing of the tweezers, which triggers their substantial structural reorganization. Reversible sol–gel transitions were achieved through the sequential addition of chemical stimuli or by a decomposable acid in a time-controlled operation. Such transient disassembly process regulated by a chemical fuel enables multiple gelation cycles with minimal waste while maintaining stable rheological properties. These results underscore the potential of switchable molecular tweezers in creating advanced stimuli-responsive materials.

Donor–Acceptor Nanohoops: Impact of the Ratio and Arrangement of the Fluorenone and Carbazole Moieties

Brouillac, C.; Dureau, E.; Jeannin, O.; Rault-Berthelot, J.; Poriel, C.; Quinton, C.

J. Am. Chem. Soc. **2025**, *147*, 11267–11276

DOI: 10.1021/jacs.4c18293



***Abstract*:** We report herein the synthesis and characterization of four donor–acceptor nanohoops incorporating fluorenone and carbazole as electron-poor and electron-rich units, respectively. The well-known platinum-mediated cyclization reaction here provides, in high yields, a mixture of four nanohoops possessing different and unexpected molecular arrangements. The four nanohoops have been isolated and characterized, and the impact of the number and arrangement of the carbazole and fluorenone moieties has been studied by spectroscopic and electrochemical analyses. Thanks to the intramolecular charge transfer resulting from the interaction between the carbazole and fluorenone units, their fluorescence was significantly red-shifted by 100 nm compared with a cyclic 2,7-tetracarbazole. This work highlights the singularity of the platinum-mediated cyclization reaction to construct donor–acceptor nanohoops with molecular arrangements, which are challenging to reach by other synthetic methods.

Upconversion Luminescence with Bis-pyclen Yb(III) Chelates: Crown vs. Linear Polyether Linkers in Discrete Heteropolynuclear Architectures

Hamon, N.; Godec, L.; Sanchez, S.; Beyler, M.; Charbonnière, L. J.; Tripier, R.

Angew Chem. Int. Ed. **2025**, *64*, e202414608

DOI: 10.1002/anie.202414608

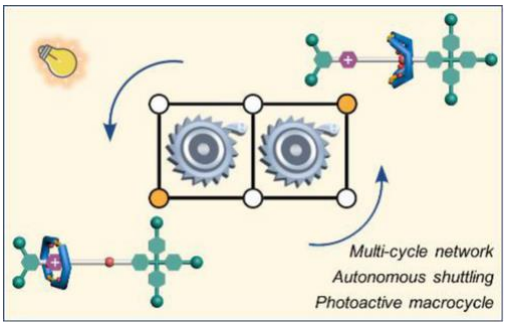
***Abstract*:** Ligands combining two lateral bis-pyridyl-phosphonated-pyclens were synthesized, using a flexible linear pegylated linker (L2) or a bulkier K22 crown-ether (L3). A functionalized pyridyl-phosphonated-pyclen (L1) was also prepared as a mononuclear analogue. Coordination behavior of lanthanide cations was studied via NMR titration with Lu for L1, and UV/Vis and luminescence spectroscopy with Yb for L2/L3. Strong coordination of two Yb atoms enabled isolation and spectroscopic characterization of dinuclear complexes in H2O and D2O. Excited state lifetime analysis at 980 nm revealed strong protection of Yb cations, with no coordinated water molecule. Upon titration of the isolated dinuclear Yb complexes with Tb cations, cooperative upconversion (UC) sensitization of Tb in the visible was observed upon excitation of Yb at 980 nm in D2O. In the absence of Tb, the Yb complexes also exhibited cooperative luminescence with a weak emission band around 500 nm upon NIR Yb excitation. Efficient UC with Tb was only observed after thermal treatment, suggesting a slow kinetic of formation of the UC species. [Yb2TbL3] showed weak Tb centered UC emission, while the dinuclear complex of L2 displayed more intense UC emission up to two equivalents of Tb, forming [(Yb2L2)Tbx] (x=1–2), with the tetranuclear heterometallic complex being the most intense emitter. Log-Log plot analysis confirmed the two-photon nature of the UC process.

Beyond Single-Cycle Autonomous Molecular Machines: Light-Powered Shuttling in a Multi-Cycle Reaction Network

Yang, Z.; Wang, X.; Penocchio, E.; Ragazzon, G.; Chen, X.; Lu, S.; Zhou, Y.; Fu, K.; Liu, Z.; Cai, Y.; Yu, X.; Li, X.; Li, X.; Feng, W.; Yuan, L.

Angew Chem. Int. Ed. **2025**, *64*, e202414072

DOI: 10.1002/anie.202414072

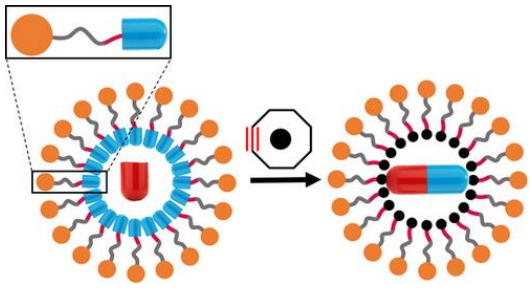


Abstract: Biomolecular machines autonomously convert energy into functions, driving systems away from thermodynamic equilibrium. This energy conversion is achieved by leveraging complex, kinetically asymmetric chemical reaction networks that are challenging to characterize precisely. In contrast, all known synthetic molecular systems in which kinetic asymmetry has been quantified are well described by simple single-cycle networks. Here, we report on a unique light-driven [2]rotaxane that enables the autonomous operation of a synthetic molecular machine with a multi-cycle chemical reaction network. Unlike all prior systems, the present one exploits a photoactive macrocycle, which features a different photoreactivity depending on the binding sites at which it resides. Furthermore, E to Z isomerization reverses the relative affinity of the macrocycle for two binding sites on the axle, resulting in a multi-cycle network. Building on the most recent theoretical advancements, this work quantifies kinetic asymmetry in a multi-cycle network for the first time. Our findings represent the simplest rotaxane capable of autonomous shuttling developed so far and offer a general strategy to generate and quantify kinetic asymmetry beyond single-cycle systems.

Click-and-Release Formation of Urea Bonds in Living Cells Enabled by Micelle Nanoreactors

Madegard, L.; Girard, M.; Blochouse, E.; Yaw, B. R.; Palazzolo, A.; Laquembe, M.; Audisio, D.; Poinot, P.; Papot, S.; Taran, F.

DOI: 10.1002/anie.202422627



Abstract: The development of innovative strategies enabling chemical reactions in living systems is of great interest for exploring and manipulating biological processes. Herein, we present a pioneering approach based on both bioorthogonal and confined chemistry for intracellular drug synthesis. Exploiting a click-to-release reaction, we engineered nanoparticles capable of synthesizing drugs within cellular environments through bioorthogonal reactions with cyclooctynes. Proof of concept experiments showed that this new approach could be successfully applied to the synthesis of the FDA-approved Sorafenib within cancer cells. The integration of bioorthogonal and confined chemistry not only offers exciting prospects for advancing therapeutic strategies but also opens up new avenues for exploring non-natural reactions within living systems. This innovative approach represents a fundamental extension of the biorthogonal chemistry concept and holds great promise for pioneering developments in therapeutic applications.

Metastable Macrocyclic Bis-Meisenheimer Adduct

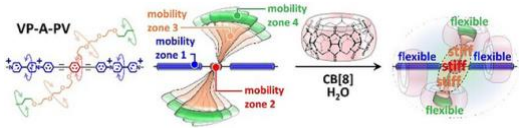
Pascal, S.; Ruiz, A. T.; Baker, A. E.; Vander Griend, D. A.; Giorgi, M.; Planchat, A.; Jacquemin, D.; Siri, O.

Angew Chem. Int. Ed. **2025**, e202511037

DOI: 10.1002/anie.202511037

Abstract: An electron-deficient tetranitroazacalixarene is shown to undergo reversible cyanide capture via nucleophilic aromatic substitution, yielding an unprecedented class of metastable dianionic macrocycle incorporating two Meisenheimer units, fully characterized by single-crystal X-ray diffraction, NMR, and electronic absorption spectroscopies. Acting as a chemical fuel, cyanide transiently drives the formation of this adduct, which can spontaneously regenerate the parent macrocycle under mild conditions, representing a rare demonstration of metastability in a Meisenheimer complex. The dynamic behavior of this system, reminiscent of out-of-equilibrium assemblies, is finely tunable through macrocycle concentration, counterion nature, solvent, and temperature. Detailed crystallographic, spectroscopic, and computational analyses reveal that intramolecular hydrogen bonding plays a key role in stabilizing the adduct. Comparative studies with simpler analogues further highlight the importance of macrocyclic preorganization and non-covalent interactions in governing this reversible reactivity.

Molecular Stiffening by Macrocycle Clustering



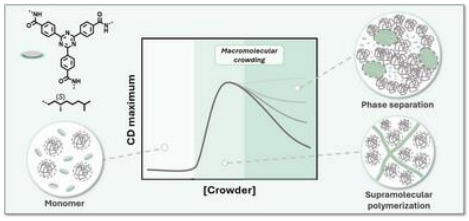
Yin, H.; Cheng, Q.; Rosas, R.; Viel, S.; Monnier, V.; Charles, L.; Siri, D.; Gigmes, D.; Yemloul, M.; Wang, R.; Kermagoret, A.; Bardelang, D.

Angew Chem. Int. Ed. **2025**, *64*, e202420880

DOI: 10.1002/anie.202420880

***Abstract*:** Allosteric stiffening of a portion of a protein surface is a strategy used in nature to regulate protein oligomerization and provide crucial functions for cells. However, a similar strategy to selectively control part of a compound dynamics remains elusive. Here we show that cucurbit[n]uril (CB[n]) macrocycles can bind almost all portions of a tetratopic guest molecule, stiffening the different parts of the guest to different extents. "Host–guest" interactions were found to be instrumental in selectively "freezing" guest molecular motions. The combination of 1H-NMR (1D, 2D), DOSY, VT-NMR, isothermal titration calorimetry (ITC), mass spectrometry and molecular modelling enabled to highlight the crucial role of cucurbit[8]uril (CB[8]) binding in the selective hardening of relevant portions of the guest molecule. Beyond implications for bioinspired systems mimicking control of a system dynamic to create a new function, this approach has relevance for improving room temperature phosphorescence, and could also be used to allosterically control organocatalysis in water.

Macromolecule-Driven Supramolecular Polymerization Induced by Crowding Effects



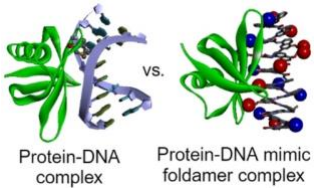
van der Tol, J. J. B.; Dekker, M. M. J.; Müller, A.; Springintveld, P.; Meijer, E. W.; Vantomme, G.

Angew Chem. Int. Ed. **2025**, *64*, e202512216

DOI: 10.1002/anie.202512216

***Abstract*:** Macromolecular crowding plays a crucial role in biological systems by regulating dynamic processes, yet its effects in fully synthetic environments remain largely unexplored. Here, we systematically investigate how excluded volume effects influence supramolecular polymerizations in organic media. We employ various discotic supramolecular monomers that assemble sequentially into polymers and kinetically-controlled higher-order aggregates (HOAs) only in the presence of macromolecular crowders. The phase diagram of the supramolecular assemblies reveals a strong dependence on the macromolecule concentration, size, and polarity, which can be tuned to control polymerization. Remarkably, at high crowder concentrations, large condensed and aligned assemblies were observed in dried samples, suggesting a transition to phase-separated states. By testing different monomers, macromolecules, and solvents, we establish the general applicability and versatility of macromolecular crowding in guiding supramolecular polymerization. This work provides fundamental insights into assembly processes in crowded environments and opens new avenues for applying macromolecular crowding beyond aqueous systems.

DNA Mimic Foldamer Recognition of a Chromosomal Protein



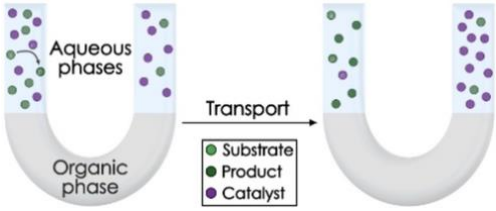
Deepak, D.; Wu, J.; Corvaglia, V.; Allmendinger, L.; Scheckenbach, M.; Tinnefeld, P.; Huc, I.

Angew Chem. Int. Ed. **2025**, *64*, e202422958

DOI: 10.1002/anie.202422958

***Abstract*:** Helical aromatic oligoamide foldamers bearing anionic side chains that mimic the overall shape and charge surface distribution of DNA were synthesized. Their interactions with chromosomal protein Sac7d, a non-sequence-selective DNA-binder that kinks DNA, were investigated by Surface Plasmon Resonance (SPR), Isothermal Titration Calorimetry (ITC), Circular Dichroism spectroscopy (CD), melting curve analysis, Atomic Force Microscopy (AFM), and Nuclear Magnetic Resonance (NMR), as well as by single crystal X-ray crystallography. The foldamers were shown to bind to Sac7d better than a DNA duplex of comparable length. The interaction is diastereoselective and takes place at the DNA binding site. Crystallography revealed that the DNA mimic foldamers have a binding mode of their own and that they can bind to Sac7d without being kinked.

Catalysis-driven Active Transport Across a Liquid Membrane



Liang, K.; Nicoli, F.; Shehimy, S. A.; Penocchio, E.; Di Noja, S.; Li, Y.; Bonfio, C.; Borsley, S.; Ragazzon, G.

Angew Chem. Int. Ed. **2025**, *64*, e202421234

DOI: 10.1002/anie.202421234

***Abstract*:** Biology has mastered energy transduction, converting energy between various forms, and employing it to drive its vital processes. Central to this is the ability to use chemical energy for the active transport of substances, pumping ions and molecules across hydrophobic lipid membranes between aqueous (sub)cellular compartments. Biology employs information ratchet mechanisms, where kinetic asymmetry in the fuel-to-waste (i. e., substrate-to-product) conversion results in catalysis-driven active transport. Here, we report an artificial system for catalysis-driven active transport across a hydrophobic phase, pumping a maleic acid cargo between aqueous compartments. We employ two strategies to differentiate the conditions in either compartment, showing that active transport can be driven either by adding fuel to a single compartment, or by differentiating the rates of activation and/or hydrolysis when fuel is present in both compartments. We characterize the

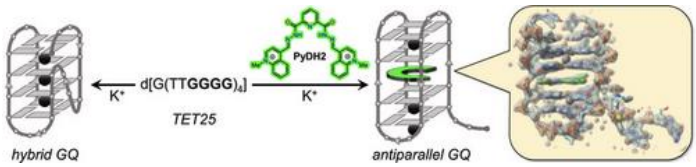
nonequilibrium system through complete kinetic analysis. Finally, we quantify the energy transduction achieved by the catalysis-driven active transport and establish the emergence of positive and negative feedback mechanisms within the system.

Conformational Change in a Four-Tetrad DNA G-Quadruplex upon Intercalation of a Small-Molecule Ligand PyDH2

Martin, K. N.; Lam, G.; Reznichenko, O.; Brunner, K. E.; Zdilla, M. J.; McCarthy, S. E.; Granzhan, A.; Yatsunyk, L. A.

Angew Chem. Int. Ed. **2025**, *64*, e202501443

DOI: 10.1002/anie.202501443



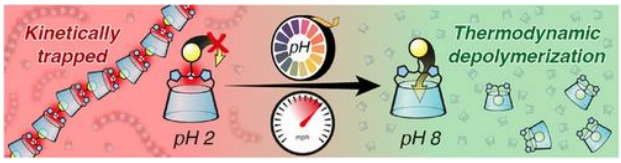
***Abstract*:** G-quadruplexes (G4s) are non-canonical DNA structures implicated in a number of biological processes. Small-molecule ligands can alter stability and folding of G4s, which can potentially be exploited for therapeutic purposes. In this work, we investigate the interaction of telomeric DNA fragment from Tetrahymena thermophila (TET25, 5′-G(TTGGGG)4-3′) with a G4 ligand PyDH2 belonging to the bisquinolinium family. When alone, TET25 adopts a mixture of three conformations, with the most abundant being a four-tetrad hybrid G4. In the presence of PyDH2, surprisingly, TET25 folds into an antiparallel chair G4, with PyDH2 intercalated between G-tetrads 2 and 3, according to our crystal structure. The structure represents the second example, and the first crystallographic evidence, of ligand intercalation into a G4. In solution, the interaction of PyDH2 and TET25 leads to a number of complexes differing by G4 topology and binding stoichiometry, strong stabilization of G4 (ΔTm = 12.4 °C in the presence of one equiv. of PyDH2) and large hysteresis of ~10 °C, suggesting that ligand binding and G4 folding processes are complex.

Transient Supramolecular Polymers by pH-Gated Conformational Control of a Self-Assembling Cyclodextrin

Hu, W.; Libérioux, V.; Rossignol, J.; Pembouong, G.; Derat, E.; Ménand, M.; Bouteiller, L.; Sollogoub, M.

Angew Chem. Int. Ed. **2025**, *64*, e202507069

DOI: 10.1002/anie.202507069



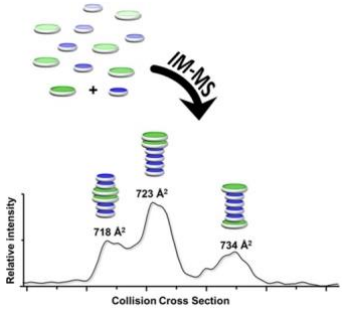
***Abstract*:** Linking a cyclodextrin (CD) host to a hydrophobic guest can result in two distinct conformations: an introverted form (in), in which the guest is self-included within the CD cavity, and an extraverted form (out), which enables intermolecular interactions and thus the formation of a supramolecular polymer. In this study, we demonstrate that a subtle variation of the linker enables interconversion between these two conformations, the in conformer being thermodynamically the most stable in water. At basic pH (>8) the out conformer is instantly converted into the in. In contrast, at acidic pH (<2), the out monomer can be kinetically trapped and can self-assemble into a supramolecular polymer. DFT calculations reveal that the interconversion mechanism is governed by a key hydrogen bond that locks the conformational states. Furthermore, we show that pH provides fine kinetic control over the interconversion rate and, consequently, the polymerization process. The system can then be reset toward the out conformation by using DMSO. This system stands in contrast to known transient supramolecular polymerization processes, which rely on metastable (non-assembled) monomers. Here, it is the kinetic trapping of the assembling monomer that allows control over the lifetime of the transient supramolecular polymer via a pH-responsive mechanism.

Ion Mobility Mass Spectrometry to Probe Sequences in Supramolecular Copolymers

Przybylski, C.; Brocorens, P.; Xerri, L. E.; Perennes, A.; Gontard, G.; Lazzaroni, R.; Raynal, M.; Bouteiller, L.

Angew Chem. Int. Ed. **2025**, *64*, e202421328

DOI: 10.1002/anie.202421328



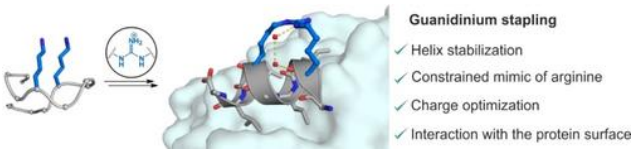
***Abstract*:** The analysis of the microstructure of supramolecular copolymers is difficult because of their dynamic character. Here, benzene-1,3,5-tricarboxamide (BTA) co-assemblies are analysed by ion mobility – mass spectrometry (IM–MS) to reveal the presence of various sequences. For example, the IM–MS mobilogram for hexamers composed of 4 units from a first monomer and 2 units from a second monomer is a broad distribution due to the presence of 9 possible isomeric sequences, which can be sorted out based on calculated collision cross-sections. This approach gives unprecedented information on supramolecular copolymer sequences.

Guanidinium-Stapled Helical Peptides for Targeting Protein-Protein Interactions

Perdriau, C.; Luton, A.; Zimmeter, K.; Neuville, M.; Saragaglia, C.; Peluso-Iltis, C.; Osz, J.; Kauffmann, B.; Collie, G. W.; Rochel, N.; Guichard, G.; Pasco, M.

Angew Chem. Int. Ed. **2025**, *64*, e202416348

DOI: 10.1002/anie.202416348



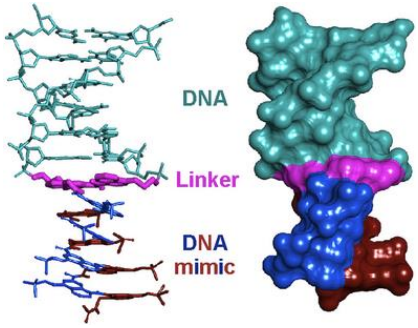
***Abstract*:** Peptide stapling has emerged as a versatile approach in drug discovery to reinforce secondary structure elements especially α-helices and improve properties of linear bioactive peptides. Inspired by the prevalence of arginine in protein-protein and protein-DNA interfaces, we investigated guanidinium-stapling as a means to constrain helical peptides. Guanidinium stapling was readily achieved on solid support, utilizing two orthogonally protected lysine or unatural α-amino acid residues with an amino function. This method allows for easy modulation of the nature and size of the staple as well as helix propensity. Evaluating a set of guanidinium-stapled peptides for their interaction with different protein targets identified several binders with increased target affinity. X-ray structure determination of four complexes revealed that all stapled peptides adopt a helical conformation upon protein binding. Notably, the disubstituted guanidinium generally exhibits a distinct cis/trans conformation and, in one instance, retains a conserved hydrogen bond with the protein surface. By identifying, for the first time, the guanidinium moiety as an effective helical peptide stapling group, this research significantly expands the repertoire of α-helix stapling techniques for the creation of useful protein mimics.

Interfacing B-DNA and DNA Mimic Foldamers

Loos, M.; Xu, F.; Mandal, P.; Chakrabortty, T.; Douat, C.; Konrad, D. B.; Cabbar, M.; Singer, J.; Corvaglia, V.; Carell, T.; Huc, I.

Angew Chem. Int. Ed. **2025**, *64*, e202505273

DOI: 10.1002/anie.202505273



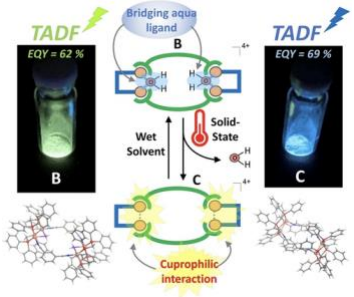
***Abstract*:** A linker unit was designed and synthesized that can serve both as a hairpin turn in a DNA duplex and anchor point for an aromatic helical foldamer mimicking the shape and surface properties of B-DNA. Methods were developed to synthesize natural/non-natural chimeric molecules combining foldamer and DNA segments. The ability of the linker to position the foldamer helix and the duplex DNA so that their rims and grooves are in register, despite their completely different chemical nature, was demonstrated using single crystal X-ray diffraction, circular dichroism and molecular models. Bio-layer interferometry confirmed that artificial hairpin DNA duplexes keep their ability to bind to DNA binding proteins. The chimeric molecules may pave the way to competitive inhibitors of protein-DNA interactions involving sequence-selective DNA-binding proteins.

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

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

Angew Chem. Int. Ed. **2025**, *64*, e202413151

DOI: 10.1002/anie.202413151



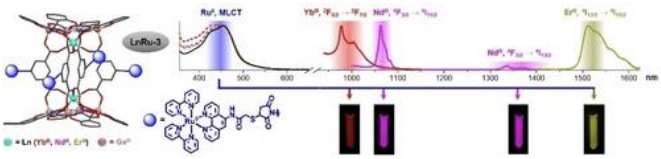
***Abstract*:** A new luminescent Cu(I) tetrametallic metallacycle B is reported that features very rare semi-bridging aqua ligands. When heated markedly above room temperature, this compound undergoes a post-synthetic transformation in the solid-state, affording the new luminescent metallacycle C. Thermogravimetric analysis, IR spectroscopy and single-crystal X-ray diffraction reveal that this alteration preserves the gross tetrametallic macrocycle structure, but is caused by the release of the coordinated water molecules with the concomitant formation of cuprophilic interactions. This transition induces a shift from eye-perceived green (B) to blue (C) room-temperature luminescence for these molecular solids. Photophysical measurements and time-dependent density-functional theory calculations have been conducted to identify the origins of the emission properties lying in these structurally related assemblies, and suggest that thermally activated delayed fluorescence dominates the radiative relaxation pathways. This study highlights the innovative feature of Cu(I) derivatives, offering access to stimuli-sensitive materials that can witness, a posteriori, the exceeding of critical temperatures in their environment.

Enabling Visible Light Sensitization of YbIII, NdIII and ErIII in Dimeric LnIII/GaIII Metallacrowns through Functionalization with RuII Complexes for NIR-II Multiplex Imaging

Badescu-Singureanu, C. C.; Nizovtsev, A. S.; Pecoraro, V. L.; Petoud, S.; Eliseeva, S. V.

Angew Chem. Int. Ed. **2025**, *64*, e202416101

DOI: 10.1002/anie.202416101



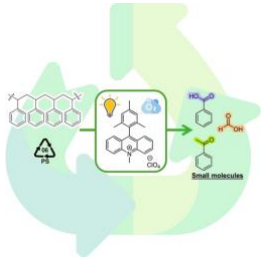
***Abstract*:** Multiplex imaging in the second near-infrared window (NIR-II, 1000–1700 nm) provides exciting opportunities for more precise understanding of biological processes and more accurate diagnosis of diseases by enabling real-time acquisition of images with improved contrast and spatial resolution in deeper tissues. Today, the number of imaging agents suitable for this modality remains very scarce. In this work, we have synthesized and fully characterized, including theoretical calculations, a series of dimeric LnIII/GaIII metallacrowns bearing RuII polypyridyl complexes, LnRu-3 (Ln=YIII, YbIII, NdIII, ErIII). Relaxed structures of YRu-3 in the ground and the excited electronic states have been calculated using dispersion-corrected density functional theory methods. Detailed photophysical studies of LnRu-3 have demonstrated that characteristic emission signals of YbIII, NdIII and ErIII in the NIR-II range can be sensitized upon excitation in the visible range through RuII-centered metal-to-ligand charge transfer (MLCT) states. We have also showed that these NIR-II signals are unambiguously detected in an imaging experiment using capillaries and biological tissue-mimicking phantoms. This work opens unprecedented perspectives for NIR-II multiplex imaging using LnIII-based molecular compounds.

Reassessing the Photochemical Upcycling of Polystyrene Using Acridinium Salts

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

Angew Chem. Int. Ed. **2025**, *64*, e202418680

DOI: 10.1002/anie.202418680



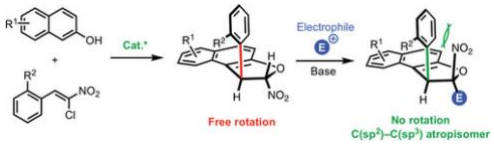
***Abstract*:** Polystyrene (PS) is a commodity plastic recalcitrant to chemical recycling or upcycling processes. Approaches aimed at deconstructing PS by photocatalytic means struggle to generate high-energy species capable of cleaving the robust C–H and C–C bonds of PS. We show that 9-mesityl-10-methylacridinium perchlorate (MA) is capable of upcycling various grades of PS substrates into up to 40 % benzoic acid (BAc), formic acid (FA) and small proportions of acetophenone (ACP), under visible light (456 nm) or through solar radiation. Time-resolved emission and absorption spectroscopy evidence that a reaction with oxygen is the primary photochemical step in oxygen-saturated solutions, accounting for 77 % of the photons absorbed vs. 1 % for the direct reaction with PS (0.303 M in repeating units). These results are in agreement with a mechanism in which MA-mediated photo upcycling of PS to BAc occurs through the abstraction of benzylic H atoms by reactive oxygen species generated by energy or electron transfer from the excited state of MA. Addition of triplet O2 to these radicals, followed by intra- or inter-molecular hydrogen atom transfer (HAT) generates C- or O-centered radicals then undergoing β-scission or hydroperoxide fragmentation. The formation of intermediate oligomers functionalized by terminal carbonyl groups is demonstrated by both infrared analysis and MALDI TOF mass spectrometry. These oligomers undergo further photoinduced conversion even in the absence of MA, as evidenced by size exclusion chromatography analysis of the irradiated samples.

Stereocontrol in Conformationally Stable C(sp2)–C(sp3) Atropisomers

Domain, A.; Bai, G.; Castillo, J. C.; Abdraman, H. M.; Humbel, S.; Giorgi, M.; Naubron, J. V.; Chentouf, S.; Rodriguez, J.; Bao, X.; Bonne, D.

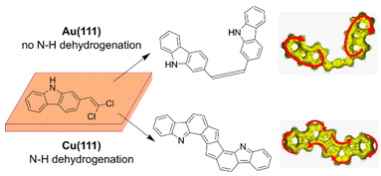
Angew Chem. Int. Ed. **2025**, *64*, e202506810

DOI: 10.1002/anie.202506810



***Abstract*:** We report a two-step sequence for the enantioselective construction of a rare family of stable C(sp2)–C(sp3) atropisomers featuring two additional stereogenic centers. The process begins with an organocatalyzed dihydrobenzofurannulation that establishes and controls the stereochemistry of two carbon centers, followed by a highly diastereoselective functionalization that significantly enhances the barrier to diastereomerization of the C(sp2)–C(sp3) bond, effectively locking and stabilizing its configuration.

Competing pathways to aromaticity governed by amine dehydrogenation and metal–organic complexation in on-surface synthesis



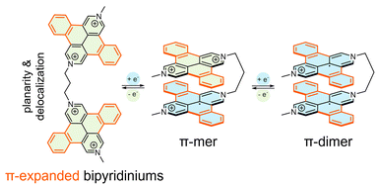
Lombana, A.; Chaunchaiyakul, S.; Chuzel, O.; Hagebaum-Reignier, D.; Parrain, J. L.; Bocquet, F.; Nony, L.; Loppacher, C.; Bondino, F.; Magnano, E.; Imada, H.; Kazuma, E.; Kim, Y.; Giovanelli, L.; Clair, S.

Chem. Sci. **2025**, *16*, 3198–3210

DOI: 10.1039/D4SC07550A

***Abstract*:** We investigated the reactivity of a gem-dichlorovinyl-carbazole precursor in the on-surface synthesis approach. Our findings reveal that, on the Au(111) surface, the thermally-induced dehalogenation reaction led to the formation of cumulene dimers. Contrastingly, the more reactive Cu(111) surface promoted the formation of a polyheterocyclic compound exhibiting extended aromaticity. The latter was found to be related to the dehydrogenation of the amine groups, which did not occur on Au(111), thus promoting the different reactivity observed. At higher annealing temperature, selective C–H activation led to the formation of well-defined organometallic chains. In addition, we found that the amine complexation with metal adatom on Cu(111) was an inhibiting factor for the dimerization reaction, a challenge that could be overcome through proper control of the deposition conditions.

π-Expansion as gateway to viologen-based pimers



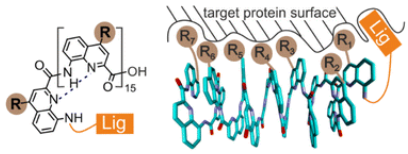
Groslambert, G.; Andrieux, V.; Duquesnoy, M.; Rullan, R.; Khrouz, L.; Denis-Quanquin, S.; Steinmann, S. N.; Le Bahers, T.; Chevallier, F.; Frath, D.; Bucher, C.

Chem. Sci. **2025**, *16*, 9320–9325

DOI: 10.1039/D5SC01361E

***Abstract*:** The present article reports on a new and efficient synthetic strategy towards tetracene-bipyridiniums. On the basis of extensive experimental analyses supported by DFT simulations, we report the first observation of a mixed valence complex formed in solution under standard conditions from an unconstrained bis-viologene derivative.

Structure-based design of an aromatic helical foldamer–protein interface



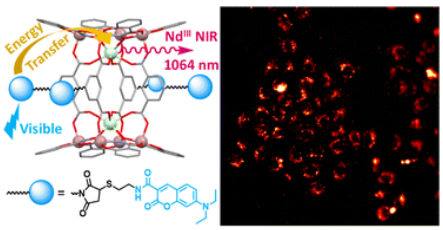
Wang, L. F.; Douat, C.; Sigl, J.; Reddy, P. S.; Fischer, L.; d'Estaintot, B. L.; Liu, Z. W.; Pophristic, V.; Yang, Y. W.; Zhang, Y. K.; Huc, I.

Chem. Sci. **2025**, *16*, 12385–12396

DOI: 10.1039/D5SC01826A

***Abstract*:** The starting point of this study is the solid state structure of a complex between human carbonic anhydrase II (HCAII) and a helically folded tetradecaamide aromatic foldamer with a nanomolar HCAII ligand appended at the N terminus of the helix. In this complex, the foldamer is achiral but its handedness is biased by diastereoselective interaction with the protein. Computational analysis of the HCAII surface and inspection of the initial solid state structure led to the suggestion of main chain and side chain modifications of the foldamer helix that would result in an extension of the foldamer protein interface as well as in absolute helix handedness control. Molecular dynamics simulations validated several of these suggested modifications as potentially resulting in favorable foldamer–protein contacts. Five new Fmoc-protected amino acid building blocks bearing new biogenic-like side chains were synthesized. Nine new tetradecaamide sequences with or without the appended HCAII ligand were synthesized on solid phase and purified by RP-HPLC. The solid state structures of four of these sequences in complex with HCAII were obtained and validated the main design principles: (i) side chains can be predictably introduced at precise positions of the foldamer surface to create new contacts with the protein; (ii) side chains modifications do not alter main chain behavior and can be implemented independent from each other; (iii) some main chain units derived from quinoline-, pyridine-, or benzene-based δ-amino acids are largely interchangeable without altering the overall helix curvature in the context of a complex with a protein. An assessment of the KD values required the adaptation of an existing fluorescence competition assay and suggested that the side chain and main chain modifications introduced in the new sequences did not result in significant improvement of the affinity of the foldamers to HCA.

Novel lanthanide(iii)/gallium(iii) metallacrowns with appended visible-absorbing organic sensitizers for molecular near-infrared imaging of living cells



Lathion, T.; Bourseguin, J.; Eliseeva, S. V.; Zeller, M.; Petoud, S.; Pecoraro, V. L.

Chem. Sci. **2025**, *16*, 12623–12634

DOI: 10.1039/D5SC01320H

***Abstract*:** Optical imaging of biological samples in the near-infrared (NIR) domain is of major interest for non-invasive experiments due to reduced light scattering, absorption and autofluorescence. Taking advantage of the maleimide moieties in the [Ln2Ga8(shi)8(mip)4]2− metallacrowns (MCs; shi3− = salicylhydroximate; mip2− = 5-maleimido-isophthalate; Ln = NdIII, GdIII, ErIII, YbIII and YIII), we appended visible-absorbing thiol-coumarin (C) sensitizers through a thiol-Michael addition click reaction, affording the functionalized [Ln2Ga8(shi)8(C-mip)4]2− MCs. By using this approach, the sensitization of NIR-emitting NdIII, ErIII and YbIII was achieved upon excitation in the visible range (λexc = 420 nm) through the appended coumarins. NIR epifluorescence microscopy of living HeLa cells incubated with the NdIII derivative confirmed unambiguous detection of the signal

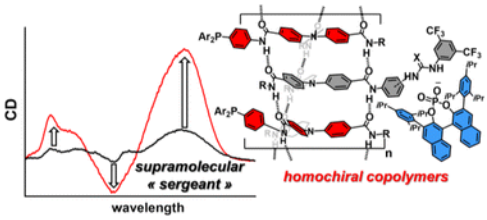
arising from the 4F3/2 → 4I11/2 electronic transition in the range of 1050–1080 nm in the cells. These results demonstrate that the [Ln2Ga8(shi)8(mip)4]2− MC can be used as a versatile molecule for tuning the chemical and photophysical properties of the [Ln2Ga8] MC family.

Supramolecular "sergeants": in situ and multi-level induction of chirality in helical assemblies of triarylamine trisamide monomers

Perennes, A.; Sallembien, Q.; Fang, W. W.; Grass, S.; Lacour, J.; Bouteiller, L.; Raynal, M.

Chem. Sci. **2025**, *16*, 14584–14594

DOI: 10.1039/D5SC02159F



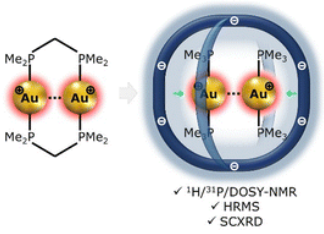
***Abstract*:** The induction and transmission of chirality across multiple length scales is fundamental to many (bio)chemical processes. For the majority of macromolecular and supramolecular structures adopting a helical configuration, this is harnessed by means of a monomer embedding a stereogenic element, also called a "sergeant" because of its ability to transfer its chirality preference to achiral monomers. Herein, we devise a triarylamine trisamide (TATA) monomer embedding a (thio)urea unit able to interact with a chiral phosphate anion through hydrogen bonding. Thanks to the orthogonal nature of the amide and (thio)urea functions, the anion specifically binds to the (thio)urea unit, thus yielding a supramolecular monomer acting as a "sergeant" i.e. allowing efficient chirality induction in amide-bonded TATA helical copolymers composed of various types of achiral TATA monomers. Unlike covalent "sergeants", chirality can be induced in situ by binding of the chiral anion to pre-formed coassemblies. In addition, the catalytic performance of TATA coassemblies embedding intrinsically achiral phosphine-functionalized TATA monomers has been evaluated: higher enantioselectivities are reached with the supramolecular versus covalent "sergeant". Our work may facilitate the design and development of supramolecular "sergeants" as a modular approach to induce chirality in supramolecular helical copolymers and catalysts.

Confinement-supported aurophilic interaction

Diack, Y.; Mallet-Ladeira, S.; Lesage, D.; Guerra, J. V. S.; Bourissou, D.; Szalóki, G.

Chem. Commun. **2025**, *61*, 8003–8006

DOI: 10.1039/D5CC01540E



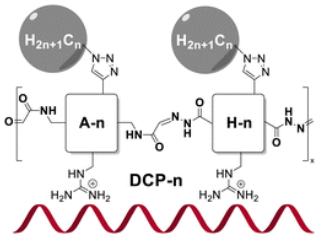
***Abstract*:** An anionic cyclotricatechylene cage (H) is shown (NMR, mass spectrometry and X-ray diffraction) to encapsulate cationic Au(I) complexes. As a result, an unprecedented bimetallic Au(I) complex (GG@H) has been characterized, in which confinement supports aurophilic interaction, even without bridging ligands.

mRNA delivery with templated dynamic covalent polymers

Coll, J. G.; Ali, L. M. A.; Montenegro, J.; Bettache, N.; Ulrich, S.

Chem. Commun. **2025**, *61*, 4050–4053

DOI: 10.1039/D4CC06518B



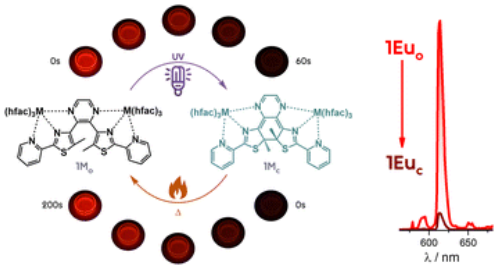
***Abstract*:** Messenger RNA is a novel therapeutic modality which was key in curbing the Covid-19 pandemic. However, the delivery of mRNA in cells requires the development of smart vectors. We here report on amphiphilic dynamic covalent polymers formed in situ through RNA templating, and show effective nanoparticle formation and delivery of EGFP mRNA in cells.

Photomodulation of dinuclear europium(iii) complex luminescence using thermally reversible photochromism of diarylethene

Freroux, Y.; Kiraev, S.; Galangau, O.; Phan, T. A.; Roisnel, T.; Maury, O.; Rigaut, S.; Norel, L.

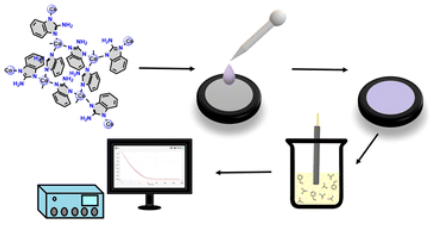
Chem. Commun. **2025**, *61*, 8051–8054

DOI: 10.1039/D5CC01334H



***Abstract*:** With the use of an original chelating T-type photochromic diarylethene unit, we describe the efficient switching of visible luminescence of a dinuclear europium(III) complex possessing a minute-scale thermal back reaction.

Systematic study of zeolitic imidazolate frameworks for enhanced electrochemical aldehyde sensing



Manka, M.; Kukulka, W.; Wlazlo, M.; Patroniak, V.; Ciesielski, A.; Montes-García, V.; Samorì, P.

Chem. Commun. **2025**, *61*, 1617–1620

DOI: 10.1039/D4CC05731G

***Abstract*:** Four distinct zeolitic imidazolate frameworks (ZIFs) are prepared using zinc and cobalt ions with 2-aminobenzimidazole and 2-methylimidazole as linkers to explore their electrochemical properties as platforms for aldehyde detection. The resulting ZIF-based sensors exhibit high sensitivity, low detection limits, and robust performance when applied to real-world samples.

Redox-Induced Structural Rearrangement in an M8L2 Self-Assembly

Zeid, J. B.; Dekhtiarenko, M.; Guechaichia, R.; Canevet, D.; Allain, M.; Freuze, I.; Sallé, M.; Goeb, S.

Chem. Eur. J. **2025**, *31*, e202501828

DOI: 10.1002/chem.202501828

***Abstract*:** Due to the reversible nature of the metal–ligand bond, coordination cages are inherently dynamic architectures which can undergo structural transformations upon appropriate external stimulations. This adaptability has been widely explored in various fields. Herein, we report the preparation of a redox-responsive discrete (Ru2)4L2 architecture through a coordination-driven self-assembly approach, where Ru2 is a bis(ruthenium(II)) complex and L a tetrapyridyl ligand. Importantly, ligand L is designed around the π-extended tetrathiafulvalene framework (exTTF), whose geometry is highly sensitive to its redox state. The resulting (Ru2)4L2 assembly was fully characterized, revealing a twisted configuration with two orthogonally oriented L units in close spatial proximity. Remarkably, this assembly undergoes an oxidation-induced transformation into a (Ru2)4Lox$_2$ structure, in which the two dicationic ligands are now spatially separated and aligned according to a face-to-face arrangement, affording a cage-like structure. This reorganization is driven by the redox-induced geometric and electronic changes of the exTTF cores and the resulting electrostatic repulsions occurring between both oxidized ligands. The process is fully reversible upon chemical reduction, restoring the original (Ru2)4L$_2$ structure.

Effective RNA Complexation by [2]Catenanes Confers Enhanced Resistance to Enzymatic Degradation

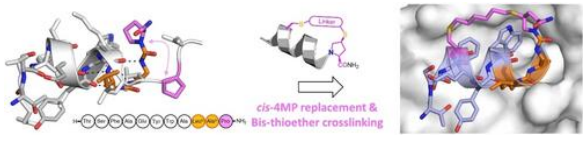
Delcourt, D.; Coll, J. G.; Cougnon, F. B. L.; Ulrich, S.

Chem. Eur. J. **2025**, *31*, e01631

DOI: 10.1002/chem.202501631

***Abstract*:** Cationic [2]catenanes bearing l-arginine residues were synthesized via dynamic covalent self-assembly in water. These peptide-based mechanically interlocked molecules (MIMs) exhibit proteolytic stability, efficiently complex small-interfering RNA (siRNA), and protect it from nuclease degradation. Their performance in siRNA binding is attributed to multivalency and preorganization enforced by the mechanical bond.

Optimal Stapling of a Helical Peptide-Foldamer Hybrid Using a C-Terminal 4-Mercaptoproline Enhances Protein Surface Recognition and Cellular Activity



Neuville, M.; Bourgeais, M.; Buratto, J.; Saragaglia, C.; Li, B.; Galeano-Otero, I.; Mauran, L.; Varajao, L.; Goudreau, S. R.; Kauffmann, B.; Thinon, E.; Pasco, M.; Khatib, A. M.; Guichard, G.

Chem. Eur. J. **2025**, *31*, e202403330

DOI: 10.1002/chem.202403330

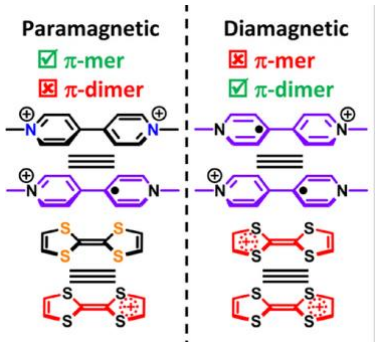
***Abstract*:** Structural analysis of a co-crystal of a helically-folded peptide-foldamer hybrid in complex with hDM2 E3 ubiquitin ligase, revealed a unique orientation for the C-terminal proline with the pyrrolidine ring pointing backwards in the sequence, and suggested new opportunities for macrocyclization. In particular, we found that the C-terminal prolyl residue could be replaced by its (2S,4S)-4-mercaptoprolyl analogue for optimal bisthioether crosslinking with a cysteine residue installed at position 4 in the sequence. The resulting i,i+7 stapled peptide-foldamer is a high-affinity binder to hDM2, is cell permeable and restores the p53 signalling pathway in p53wt cancer cells. The co-crystal structure of hDM2 and the stapled peptide-foldamer hybrid was determined at 1.84 Å, fully validating the original design and further highlighting the potential of cis-4-mercaptoproline in the context of peptide and foldamer stapling.

π-mers and π-dimers: Two Radical Supramolecular Interactions – A Tutorial Review

Joseph, J.; Berville, M.; Wytko, J.; Weiss, J.; Jacquot de Rouville, H. P.

Chem. Eur. J. **2025**, *31*, e202403115

DOI: 10.1002/chem.202403115



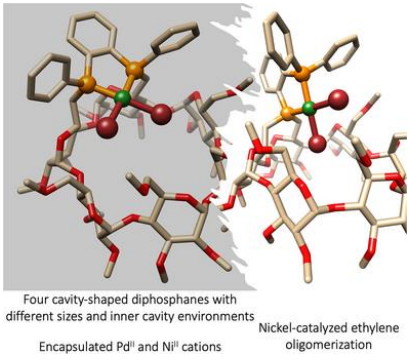
***Abstract*:** In this review, the difference between π-mers (pimers) and π-dimers (pi-dimers) will be discussed. Often interchanged or confused in the literature, these two radical interactions lead to different or even opposite physico-chemical behaviors. This review aims at clarifying the terms π-mers and π-dimers and at describing their main physico-chemical properties to address their differences. Finally, selected literature examples exhibiting the successive formation of π-mers and π-dimers within the same systems will be detailed to emphasize the physico-chemical changes occurring upon conversion.

Cis-Chelating Diphosphanes for Intracavity Nickel(II)-Catalyzed Ethylene Oligomerization

Li, Y.; Morais, S. F. A.; Han, M.; Phan, T. A.; Creste, G.; Jouffroy, M.; Matt, D.; Djukic, J. P.; Cornaton, Y.; Braunstein, P.; Pelzer, K.; Armspach, D.

Chem. Eur. J. **2025**, *31*, e202501188

DOI: 10.1002/chem.202501188



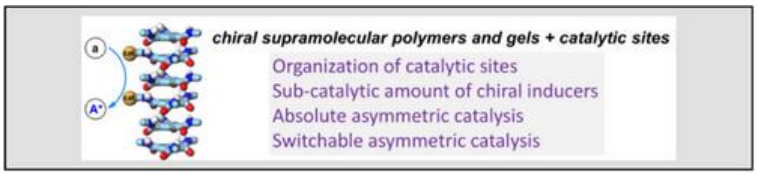
***Abstract*:** Four cis-chelating diphosphanes derived from cyclodextrins (CDs), each featuring a distinct intracavity environment, compel NiII or PdII metal centers to reside within α- or β-CD cavities. Nickel(II) complexes of these metal-confining ligands act as active catalysts in ethylene oligomerization upon activation with modified methylaluminoxane (MMAO). The size of the cavity and the position of the P2Ni fragment relative to the cavity affect both the activity and selectivity of the reaction. In all instances, 1-butene is the major product (up to 98% C4 products and 90% 1-butene within the C4 fraction). Extensive theoretical studies with state-of-the-art methods carried out on the most selective system suggest that the CD cavity restricts isomerization pathways by limiting the mobility of the coordinated olefin in this constrained supramolecular environment, thereby enhancing α-olefin formation.

The Ascent of Supramolecular Polymers and Gels in Asymmetric Catalysis

Chen, R.; Bouteiller, L.; Raynal, M.

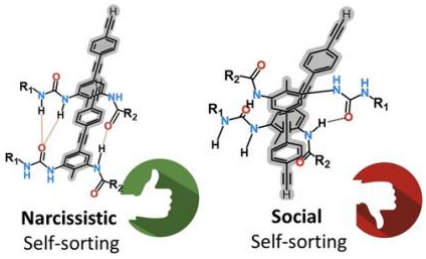
Chem. Eur. J. **2025**, *31*, e202501446

DOI: 10.1002/chem.202501446



***Abstract*:** Supramolecular polymers (SPs) and gels, formed by the spontaneous assembly of small molecules through various types of noncovalent interactions, are attractive materials for many applications. Their modularity also offers many opportunities in asymmetric catalysis that have been tackled in the last two decades and more intensively in the last one. In this review, strategies adopted to develop efficient asymmetric catalysts supported on SPs and gels are first categorized according to the chiral or achiral nature of the monomers used for their construction and second to their ability to be commuted into different states. Catalytic SPs have been described for which enantioselectivity stems mostly from the molecular chirality located next to the reactive group, or at opposite ends of the spectrum, exclusively from the chiral environment provided by the supramolecular helices. New paradigms revealed by these systems include (i) the organization of catalytic sites at the periphery of modular and well-structured 1D assemblies, (ii) the possibility to conduct asymmetric reactions with a sub-catalytic amount of chiral inducers and even in the absence of chiral monomers, and (iii) the development of a new class of switchable asymmetric catalysts.

Supramolecular Polymerization of Monomers Containing Both Urea and Amide Groups: Evidence for Narcissistic Hydrogen Bond Self-Sorting



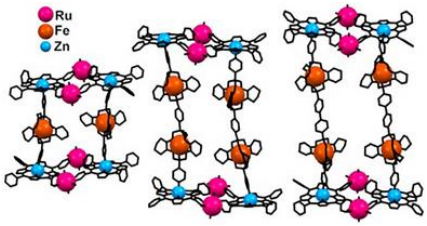
Gallonde, W. T.; Shekar, M.; Dorcet, V.; Rigaut, S.; Galangau, O.

Chem. Eur. J. **2025**, *31*, e202500443

DOI: 10.1002/chem.202500443

***Abstract*:** In this study, we unambiguously evidence, by mean of UV-Vis and NMR technics supported by theoretical calculations, that a narcissistic H-bond self-sorting takes place during supramolecular polymerization of a newly designed monomer equipped with mixed urea/amide H-bond donor/acceptor moieties.

Discrete Heterotrimetallic Assemblies Based on Rod-Shaped FeII-Metalloligands and a ZnII-Porphyrin/RuII-Metallacycle



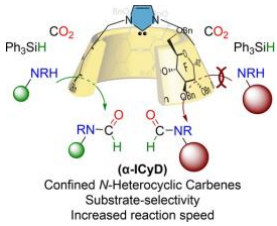
Amati, A.; Cecot, G.; Regeni, I.; Giraldi, E.; Severin, K.; Demitri, N.; Iengo, E.

Chem. Eur. J. **2025**, *31*, e202501811

DOI: 10.1002/chem.202501811

***Abstract*:** An efficient strategy for the preparation of heterometallic discrete porphyrin assemblies, tuned both in dimensions and number of metal centers, is described. Five rod-shaped di-pyridyl FeII-metalloligands, with varied length (1.5 – 3.2 nm), lateral substituents, and number of iron centers, were used to bridge two RuII-metallacycles, made of two coplanar ZnII-porphyrin each. The resulting architectures consist of four RuII complexes, four zinc-porphyrins, and either two or four FeII-clathrochelate units. Earlier, geometrically similar sandwich-like architectures were based on purely organic connectors. Among other novel characteristics, the use of metalloligands was found to be beneficial for the overall stability, thus allowing for a solution-based characterization of the assemblies. Single crystal X-ray structures were determined for the complete collection, highlighting additional key features: the two facing ZnII-porphyrin platforms are set wide apart according to the span of the two connecting metalloligands, while the latter are parallelly aligned by the anchoring ZnII-porphyrin/RuII-metallacycles, at fixed inter Fe··Fe distance(s). Mutual control over these geometrical parameters is very strict, as evidenced by self-sorting experiments. Useful implementation of these systems into functional systems may be envisaged by pairing the peripheral metalloporphyrin photosensitizers with photo/redox/catalytically active inner metal cores.

Cyclodextrin-Encapsulated NHCs: Increased Selectivity and Reactivity of CO2 in Amine Formylation



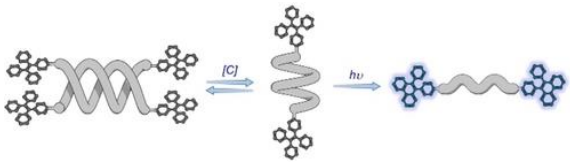
Bijouard, K.; Nicolas, E.; Anthore-Dalion, L.; Sollogoub, M.; Cantat, T.

Chem. Eur. J. **2025**, *31*, e202403955

DOI: 10.1002/chem.202403955

***Abstract*:** Herein, we describe the confinement of a N-Heterocyclic Carbene (NHC) organocatalyst in the cavity of cyclodextrins (CDs). These confined organocatalysts allow the formylation of amines through CO2 hydrosilylation. The presence of the cavity of the CDs leads to substrate-selectivity between amines in competition reactions. The use of the smallest α-CD induces the best selectivities but also increased reactivity compared to the bigger β-CD. A careful study conducted by NMR and DFT revealed that in α-CD, the complexed CO2 interacts with the cavity through hydrogen bonds. These H-bonds destabilize the NHC–CO2 adduct and are accountable for the higher reactivity observed using α-CD.

Photoresponsive Helical Foldamers: Conformational Control Through Double Helix Formation and Light-Induced Protonation



Hardoin, L.; Kdouh, R.; Aidibi, Y.; Azar, S.; Siegler, B.; Allain, M.; Goeb, S.; Levillain, E.; Bouit, P. A.; Galangau, O.; Sallé, M.; Canevet, D.

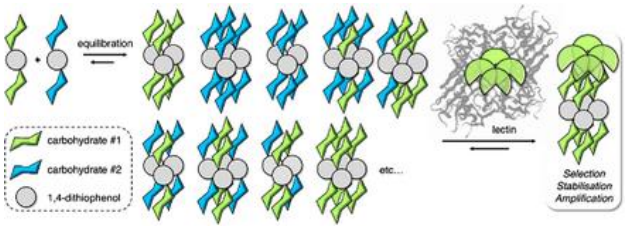
Chem. Eur. J. **2025**, *31*, e202403771

DOI: 10.1002/chem.202403771

***Abstract*:** Helical foldamers constitute particularly relevant targets in the field of host-guest chemistry, be that as hosts or substrates. In this context, the strategies reported so far to control the dimensions and shape of foldamers mainly involve modifications of the skeleton through covalent synthesis. Herein, we prepared an oligopyridine dicarboxamide foldamer substituted by photo-active tetraphenylethylene units (TPE). We demonstrate that it is possible to toggle the length of a helical foldamer by two means. First, the elongation of foldamers can be tuned by adjusting the concentration, as demonstrated by DOSY NMR spectroscopy and X-ray diffraction analyses on both the single and the double helix

structures. Secondly, and in a more original manner, a photo-induced protonation process triggered by TPE units promotes a novel pathway to unfold helical foldamers, leading to dramatic conformational and spectroscopic changes.

Dynamic Combinatorial Chemistry Generates Adaptative Libraries of Glyco-Dyn[n]Arenes That can Be Templated to Produce Anti-Adhesive Glycoconjugates Targeting Pseudomonas aeruginosa



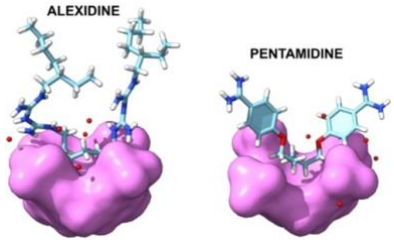
Demontrond, F.; Pascal, Y.; Donnier-Maréchal, M.; Raillon, C.; Luton, B.; de la Tramblais, C.; Vial, L.; Gueyrard, D.; Galia, W.; Berger, E.; Géloën, A.; Cournoyer, B.; Leclaire, J.; Vidal, S.

Chem. Eur. J. **2025**, *31*, e02161

DOI: 10.1002/chem.202502161

***Abstract*:** Carbohydrate-protein interactions are important in cell-cell communication, signal transduction, cancer, or infection. Chemists have designed glycosylated multivalent systems to mimic these recognition phenomena and produce potent ligands of lectins with therapeutic applications. Dynamic combinatorial chemistry (DCC) provides access to libraries of glycosylated macrocycles equilibrating through reversible covalent bonds. This strategy can be applied to the rapid and efficient identification of multivalent glycoclusters by introducing a protein into the equilibrating library. This strategy allowed the identification of the best ligands for more than one lectin in a single experimental set up by using two simple 1,4-dithiophenol building blocks. Selection of the best binder by each lectin (ConA, LecA, and LecB) was accompanied by the amplification of glyco-dyn[3]arenes and glyco-dyn[4]arenes. These macrocycles could be synthesized, isolated, and displayed nanomolar dissociation constants. Furthermore, while no toxicity could be detected against human cells or bacteria, their anti-adhesive properties against Pseudomonas aeruginosa were confirmed through a virulence assay on human cells. Altogether, extremely simple 1,4-dithiophenol building blocks provided access to a large diversity of glycoconjugates that could be selected by a lectin in a simple experimental set up to identify glycoconjugates with potential anti-infectious applications, thus speeding up the discovery of potential new antibacterial treatments.

Alexidine and Pentamidine Fold Inside the Bowl-shaped Cavity of p-Sulfonato-calix[4]arene



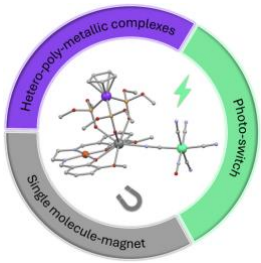
Kravets, K.; Kravets, M.; Sashuk, V.; Perret, F.; Maskani, W.; Albertini, D.; Lazar, A. N.; Zimnicka, M. M.; Danylyuk, O.

Chem. Eur. J. **2025**, *31*, e202404625

DOI: 10.1002/chem.202404625

***Abstract*:** We report on the U-shaped folding of flexible guest molecules of medicinal interest upon their inclusion into macrocyclic cavity of p-sulfonato-calix[4]arene in aqueous media. Alexidine and pentamidine are FDA-approved drug compounds currently rediscovered as potent membrane-targeting antibiotic adjuvants helping restore antibiotic activity against multidrug resistant bacteria pathogens. We have adopted host-guest and crystal engineering approach to study these drugs with a view of potential supramolecular formulations and/or crystal forms. We focus on the host-guest conformational and structural behaviour of alexidine and pentamidine under macrocyclic confinement conditions benefitting from single crystal X-ray diffraction analysis, self-assembly studies in solution by NMR spectroscopy, dynamic light scattering and atomic force microscopy, and ion mobility mass spectrometry (IM–MS) analysis complemented by theoretical calculations. Our findings show that the simple bowl-shaped host promotes conformational fixing and crystallization of these guest molecules of high conformational freedom that are otherwise challenging to crystallize. The IM–MS structural studies of p-sulfonato-calix[4]arene complexes with pentamidine and alexidine revealed significant guest reorganization in the solution/gas phase, compared to the binding modes observed in the crystal structures. Despite these changes, the host-guest complexation remained consistent, with new interactions highlighting the increased role of electrostatic forces in the gas phase.

Unlocking New Frontiers: Photo-Isomerism and Magnetic Properties in Multifunctional Hetero-Tetra-Metallic Complexes



Suzana, I.; Forté, J.; Pillet, S.; Bendeif, E.; Malischewski, M.; Marvaud, V.

Chem. Eur. J. **2025**, *31*, e202402601

DOI: 10.1002/chem.202402601

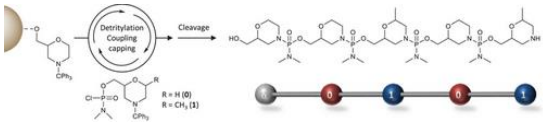
***Abstract*:** Hetero-tetra-metallic complexes, FeNOCuLnCo (Ln=Gd, Tb, Dy), combining magnetic properties and photo-isomerism, were obtained through the rational assembly of the photo-switching nitroprusside anion FeNO with new magnetic Schiff base CuLnCo precursors. Herein, we describe the synthesis and characterisation of these compounds followed by a demonstration of their multifunctional character. Particularly noteworthy is the FeNOCuTbCo complex which is one of the few examples of a photo-isomerisable SMM.

Conception and Synthesis of Sequence-Coded Morpholinos

Pousse, B.; Al Ouahabi, A.; Baxter, P. N. W.; Charles, L.; Lutz, J. F.

Chem. Eur. J. **2025**, *31*, e202501161

DOI: 10.1002/chem.202501161



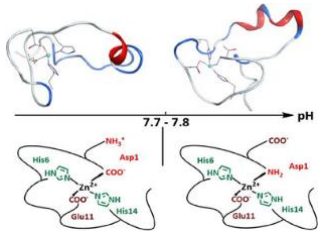
***Abstract*:** Solid-phase morpholino chemistry was explored as a new route to synthesize abiological sequence-defined oligomers. Two comonomers, 0 and 1 containing (i) a chlorophosphoramidate reactive function, (ii) a trityl-protected morpholine, and (iii) a coding substituent (H or CH3 for 0 and 1, respectively) on the morpholine ring were first synthesized and characterized. This binary alphabet was afterwards tested for the synthesis of digitally-encoded oligomers with different lengths and sequences. The oligomers were prepared on a modified polystyrene resin, cleaved, and characterized by liquid chromatography mass spectrometry. When using a repetitive cycle containing only morpholino coupling and trityl deprotection steps, the formed oligomers were not uniform. Thus, an additional capping step was added. In these conditions, uniform coded sequences were prepared in most cases. Furthermore, the oligomers were analyzed by tandem mass spectrometry. In the studied collision-induced dissociation conditions, the repeat units of the oligomers undergo two main-chain fragmentations and full sequence coverage was observed for all studied sequences. Therefore, the binary messages stored in the oligomers could be decoded and retrieved in all cases.

Constant pH Molecular Dynamics Simulation of pH Effects on Amyloid-β Structure, Dynamics, and Metal-Binding

Albrahadi, T.; Hureau, C.; Platts, J. A.

Chem. Eur. J. **2025**, *31*, e202500547

DOI: 10.1002/chem.202500547



***Abstract*:** We report the first molecular dynamics simulations to examine the effect of pH on the structure, dynamics, and metal-binding ability of amyloid-β, the peptide implicated in the onset of Alzheimer's disease. We show that in the pH range of 6 to 8 only histidine residues show variable protonation, that predicted pKa values are in agreement with experimental data, and that changes in pH affect the size, flexibility, and secondary structure of the peptide. The binding of Cu(II) or Zn(II) to the peptide induces a shift of 1 to 1.5 pKa units in unbound histidine residues, while metal binding modes associated with higher pH induce significant changes in peptide structure. We speculate on the significance of these findings on results showing pH dependence as well as on Cu(II) and Zn(II) modulation of aggregation of Amyloid-β.

Zinc Sensing with a Pyridine-Based Lanthanide Contrast Agent: Structural Analysis in Aqueous Solution

Martin, H.; Uguen, A.; Morfin, J. F.; Isaac, M.; Pallier, A.; Melchior, A.; Bonnet, C. S.

Chem. Eur. J. **2025**, *31*, e202403861

DOI: 10.1002/chem.202403861

***Abstract*:** Zinc is an important physiological cation, and its misregulation is implicated in various diseases. It is therefore important to be able to image zinc by non-invasive methods such as Magnetic Resonance Imaging (MRI). In this work, we have successfully synthesized a novel Gd3+-based complex specifically for Zn2+ sensing by MRI. Using a combination of NMR, luminescence, potentiometric, and relaxivity experiments, completed with DFT calculations, we demonstrate that incorporating a short linker between the Zn2+ sensing unit and the Gd3+ complex leads to unique behavior of the system in the absence of Zn2+. A significant increase in efficacy of the system is observed upon Zn2+ binding, and importantly, the complex is highly selective for Zn2+ relative to other physiological cations. A comprehensive structural study reliably determines the microscopic parameters at the origin of the Zn2+ response, primarily an increase in the number of water molecules directly coordinated to Gd3+ upon Zn2+ binding. Crucially, the system maintains a strong response to Zn2+ binding in the presence of Human Serum Albumin, highlighting its potential for biological applications.