Société Chimique de France
Le réseau des chimistes

N°07
Mars 2026

La SupInfo

Les infos du Groupe de Chimie Supramoléculaire

SOMMAIRE

LE MOT DE LA PRÉSIDENTE

Chères adhérentes et chers adhérents,

Même si Janvier est déjà loin, au nom du bureau, je vous souhaite tout le meilleur pour cette année 2026 qui s'annonce riche en évènements pour notre communauté.

En effet, d'ici trois mois, nous aurons l'occasion de nous retrouver aux journées de chimie supramoléculaire qui se dérouleront à Marseille du 28 au 29 Mai 2026. Inscrivez-vous dès maintenant et encouragez vos étudiants, doctorants et post-doctorants, à présenter leurs travaux lors de cet évènement important pour notre groupe. Les mois de juin et juillet seront marqués, entre autres, par deux colloques internationaux organisés par des membres de notre groupe : ISMSC-2026 à Bordeaux du 5 au 10 Juillet et PEMM-2026 à Lyon du 13 au 16 Juillet, mais également par le congrès national de la SCF qui se tiendra à Bordeaux du 22 au 24 juin.

Dans cette gazette, vous retrouverez l'appel à candidatures pour les prix de notre groupe. Cette année, nous aurons l'honneur de décerner 4 prix dont les lauréats seront annoncés aux JCS de Marseille. N'hésitez pas à candidater et à encourager vos doctorants ayant soutenu en 2025 à postuler pour la seconde édition de notre prix de thèse.

Retrouvez également vos rubriques habituelles : « Un point sur… » où Jean Weiss nous propose un article synthétique sur les différences notables entre π-mères et π-dimères et « À la rencontre de… » qui dresse le portrait de Yoann Cotelle, maître de conférences depuis 2020 à l'université d'Aix-Marseille. Et ne manquez pas « Notre sélection d'articles » publiés au cours des 6 derniers mois par nos sociétaires.

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

Bien cordialement,

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

Supra60 : les 60 Ans du Laboratoire de Jean-Marie Lehn

Vous ne seriez sans doute pas en train de lire cette gazette sans sa contribution majeure à la chimie. Jean-Marie Lehn a célébré les 60 ans de son laboratoire lors d'un rassemblement à la fois scientifique et festif, organisé les 28 et 29 août 2025 à l'Institut de Science et d'Ingénierie Supramoléculaires (ISIS) de Strasbourg. À cette occasion, 126 anciens membres du laboratoire, âgés de 26 à 85 ans et venus des quatre coins du monde — d'Europe, du Japon, de Chine, des États-Unis, du Canada ou encore du Maroc — se sont réunis pour rendre hommage à une aventure scientifique hors du commun.
Maître de cérémonie, Jean-Marie Lehn a ouvert les journées en retraçant les grandes étapes de son parcours et l'évolution du laboratoire, devenu au fil des décennies une référence internationale. Le programme s'est ensuite articulé autour de 23 présentations orales et de 22 communications par posters, toutes réalisées par d'anciens membres. Ces contributions ont illustré la remarquable diversité des thématiques de la chimie supramoléculaire, ainsi que la richesse des parcours professionnels empruntés après le passage au laboratoire.

Au-delà des échanges scientifiques, ces journées ont été marquées par une atmosphère chaleureuse et conviviale. Les différentes générations réunies ont partagé le plaisir de se retrouver, dans des moments souvent empreints d'émotion, parfois ponctués de photographies d'archives…. Autant de témoignages de l'impact profond, scientifique mais aussi humain, qu'a représenté l'expérience au sein du laboratoire pour nombre de ses anciens. Deux figures marquantes ont par ailleurs été honorées à cette occasion : Peter Gölitz et Gérard Mathis, nommés membres honoraires du laboratoire.
En conclusion, Jean-Marie Lehn est revenu sur des faits marquants de cette épopée, en n'oubliant pas de dresser des perspectives pour l'avenir. La chimie supramoléculaire, riche de multiples voies encore inexplorées, s'inscrit résolument dans le futur. À l'évidence, ces 60 années ne constituent pas un aboutissement, mais bien le point de départ de nouvelles découvertes.

Notre groupe thématique Chimie Supramoléculaire de la Société Chimique de France (Supr@SCF) était également représenté. Sa présidente, Émilie Moulin, y a exposé nos activités, mettant en lumière la structuration et le dynamisme de la communauté nationale des chimistes supramoléculaires.
Les co-organisateurs de Supra60 : Annia Bertrand, Aline Chevalier, Mir Wais Hosseini, Philippe Reutenauer, Gaël Schaeffer, Jean-Louis Schmitt, Sébastien Ulrich.
Les représentants Supr@SCF : Émilie Moulin, Sébastien Ulrich.

Prix du Groupe Supr@SCF 2026 : Appel à candidatures.

Le Groupe Supr@SCF attribue chaque année différents prix récompensant des chercheur.euse.s remarquables dans notre discipline. Vous trouverez ci-dessous les appels à candidatures pour les prix de l'année 2026.

Prix bisannuels :

Prix André Collet. Attribué à un.e chimiste confirmé.e ayant effectué des travaux de recherche reconnus au niveau national et international, et membre de la SCF depuis au moins trois ans. Les candidatures doivent être accompagnées d'un CV détaillé incluant une liste complète des publications, d'un résumé de deux pages des travaux marquants, et être envoyées à Matthieu Sollogoub (matthieu.sollogoub@sorbonne-universite.fr) avant le 1er mai 2026.

Prix Henry Le Chatelier. Attribué à un.e chimiste confirmé.e de moins de 55 ans effectuant ses travaux en France et membre de la SCF depuis au moins trois ans. Les candidatures doivent être accompagnées d'un CV détaillé incluant une liste complète des publications, d'un résumé de deux pages des travaux marquants, et être envoyées à Laurent Vial (laurent.vial@ens-lyon.fr) avant le 1er mai 2026.

Prix Christiane Dietrich-Buchecker. Attribué à un.e chimiste de moins de 45 ans effectuant ses travaux en France et membre de la SCF depuis au moins trois ans. Les candidatures doivent être accompagnées d'un CV détaillé incluant une liste complète des publications, d'un résumé de deux pages des travaux marquants, et être envoyées à Émilie Moulin (emoulin@unistra.fr) avant le 1er mai 2026.

Prix de Thèse Supr@SCF 2026 :

Le Prix de Thèse du Groupe Thématique Chimie Supramoléculaire de la SCF est attribué à un.e candidat.e ayant soutenu sa thèse dans une université française au cours de l'année 2025. Le candidat ou la candidate doit être membre de la Société Chimique de France au moment du dépôt de candidature.

Les dossiers de candidature, rédigés en français ou en anglais, devront être adressés par courrier électronique à Olivier Galangau (olivier.galangau@univ-rennes.fr) avant le 1er Mai 2026 et comporter :

- Le CV du candidat (2 pages max. au format pdf) incluant la liste détaillée de la production scientifique avec les liens d'accès.
- Un résumé du manuscrit de thèse (3 pages max. au format pdf).
- L'avis du ou des directeurs de thèse.
- Les rapports autorisant la soutenance ainsi que celui de la soutenance de thèse.

Le ou la lauréate sera invité.e à donner une présentation orale de ses travaux lors des prochaines Journées du Groupe Thématique.

Découvrez les anciens lauréats sur notre site :
https://new.societechimiquedefrance.fr/groupes/chimie-supramoleculaire/prix-et-laureats-chimie-supramoleculaire/

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* JCS-2026 à Marseille les **28 et 29 Mai 2026**.

Lieu du Congrès : **Aix-Marseille Université – Jardin du Pharo**

Au programme quatre conférences invitées :

- Pr. Michaele Hardie, University of Leeds
- Dr. Hennie Valkennier-van Dijk, Université Libre de Bruxelles
- Dr. Mihail Barboiu, Institut Européen des Membranes (co-Récipiendaire du Prix André Collet 2024)
- Pr. Nicolas Giuseppone, Institut Charles Sadron (Récipiendaire du Prix Henry Le Chatelier 2024)

Des communications orales et plusieurs sessions de présentations de posters.

Vous trouverez de plus amples informations sur ces journées sur le site du congrès :
https://jcs2026.sciencesconf.org/?lang=fr

Inscriptions ouvertes depuis janvier 2026.
Date limite de soumission des abstracts : 15 Avril 2026.

Pour le comité d'organisation :
David Bardelang, Cedric Colomban, Yoann Cotelle, Anthony Kermagoret, Anne-Doriane Manick, Maylis Orio.

Congrès SCF 2026

La Société Chimique de France (SCF) a le plaisir d'annoncer la tenue de son prochain congrès national, **SCF 2026**, du **22 au 24 juin 2026 à Bordeaux**, sur le campus universitaire à Matmeca (Campus Universitaire ENSEIRB – MATMECA, 33400 Talence).

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.

Toutes les informations sur : https://premc.org/fr/scf2026-fr/
Comité d'organisation SCF 2026, Email : scf2026@premc.org
Les prochaines dates limites : Soumission des résumés avant le 27 février 2026.
Notification des auteurs - 17 mars 2026
Date limite d'inscription Early bird - 17 avril 2026
Date limite d'inscription - 15 mai 2026

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

ISMSC 2026 à Bordeaux

La 20ème édition de l'*International Symposium on Macrocyclic and Supramolecular Chemistry* se tiendra à Bordeaux **du 5 au 10 juillet 2026**. Cette conférence internationale a lieu alternativement en Europe, Asie et Amérique du Nord. Elle revient en France en 2026 après Strasbourg en 2015.
Au programme : 7 conférences plénières, 20 conférenciers invités, circa 25 contributions orales courtes et des sessions de posters.

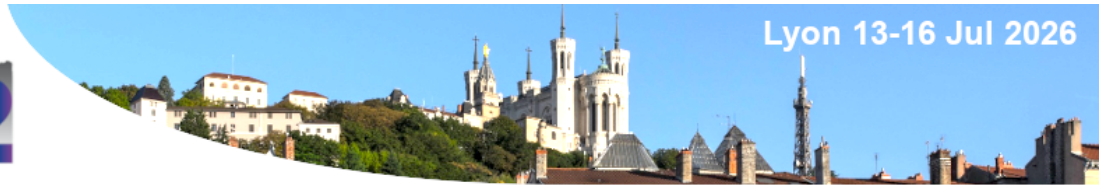
Call for Oral Communications closes : March 16, 2026
Call for Posters closes : April 30, 2026

Pour plus d'informations :

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

Nathan McClenaghan & Yann Ferrand
Co-chairs ISMSC 2026

PEMM - 2026



4th International Symposium on Photonic and Electronic Molecular Machines

The **4th International Symposium on Photonic and Electronic Molecular Machines (PEMM)** will take place at **ENS de Lyon** on **July 13-16, 2026**.

The conference covers several topics among which

- Molecular Motors, Rotors, Gears, Ratchets, Tweezers: Design & Properties
- Photochromic & Electrochromic Molecules or Materials
- Responsive Self-Assembly & Supramolecular Architectures
- Molecular Junctions, Memories & Switches
- Organic Electronics, Optoelectronics & Photonics: Materials & Devices
- Bioinspired Approaches & Biomimetic Devices
- 2D Materials, Nanotubes & Nanowires
- Scanning Probe Microscopies & Near Field Approaches
- Molecular Theoretical Modelling

This symposium will be organized in sessions bringing together senior speakers and young researchers full of potential. It will include sessions dedicated to **Molecular Electronics** jointly organized with GDR NEMO.

Call for Oral Communications closes: March 15, 2026
Call for Posters closes: May 30, 2026

Registration: Early bird: April 30, 2026
Contact: pemm-2026@sciencesconf.org

Dr. Denis Frath & Dr. Pascal Martin
Co-chairs PEMM – 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 du **25 au 28 mai 2027**.

De plus amples informations sur cet événement vous seront communiquées régulièrement via notre site web https://supra-angers-2027.cnrs.fr/, ainsi que les comptes Bluesky @SupraAngers et @supraSCF.

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… π-MÈRES ET π-DIMÈRES

La chimie conçoit et étudie les assemblages moléculaires interagissant par le biais d'interactions faibles intermoléculaires non covalentes et réversibles (empilement π, interactions hydrophobes, liaisons hydrogène, interactions de van der Waals, etc.). La formation de π-mères (pi-mères) et π-dimères (pi-dimères) impliquant des radicaux organiques conjugués identiques a été un ajout efficace à la boîte à outils supramoléculaire. Ces pages se proposent de décrypter les interactions présentes au sein de ces deux espèces « radicalement » différentes. Le premier exemple de π-dimère remonte aux années 1950.[1] Après avoir observé la disparition du paramagnétisme dans le spectre RPE d'un cation radical tétraméthyl-*p*-phénylène diamine, Hausser a attribué cette observation à l'association de deux espèces radicalaires et au couplage antiferromagnétique de leurs radicaux respectifs. Ces résultats ont été confirmés en 1972 par la résolution de la structure cristallographique à l'état solide du π-dimère correspondant.[2] Entre-temps, la première étude approfondie de la formation du π-dimère a été réalisée en 1964 par Kosower sur le noyau de 1,1'-diméthyl-4,4'-bipyridinium, également appelé méthyl-viologène (MV^{2+}) ou paraquat.[3] Au cours des décennies suivantes, ces interactions radical-radical ont fait l'objet d'une attention croissante car elles permettent d'accéder à des structures topologiques complexes et constituent un moyen d'induire un mouvement contrôlé par l'oxydoréduction dans des molécules ou des assemblages.[4] Ces interactions multi-centrées résultent d'un chevauchement des orbitales π à moitié vides des motifs radicaux.[5] Se répartissant généralement en trois catégories selon l'état de charge de l'espèce chimique (neutre, cationique, anionique),[6] ces interactions conduisent à des associations relativement faibles en solution avec des constantes d'équilibre (Ka) allant de 10 à 10^3 L mol^{-1}.[7] La stabilisation des π-mères et π-dimères est généralement favorisée par *i*) l'utilisation de forces supramoléculaires supplémentaires (y compris la solvophobie), *ii*) une faible température d'observation, *iii*) un environnement contraint tel que l'utilisation d'un espaceur covalent ou de liaisons mécaniques, ou *iv*) l'utilisation d'un environnement confiné (c'est-à-dire la formation de complexes d'inclusion et d'un environnement micellaire). Leurs propriétés sont généralement étudiées par des techniques analytiques comme la diffraction des rayons X, la spectroscopie UV/visible/NIR, l'électrochimie et les spectroscopies RMN et RPE.

1. Définition des π-mères et π-dimères

Les diagrammes orbitaux simplifiés des figures 1 et 2 présentent les notions de chevauchement stabilisateur π existant entre les radicaux π,[8] et permettent de souligner la différence entre les π-mères et les π-dimères. Cette description orbitalaire sommaire permet de rationaliser toutes les propriétés physico-chimiques observées dans ces systèmes. Même si les π-mères sont des intermédiaires - parfois de courte durée et/ou non observés - dans la formation des π-dimères, leur cas sera introduit en dernier.

1.1. π-dimères

Un π-dimère correspond à l'association de deux radicaux, provenant d'accepteurs $A^{\bullet -}$ ou de donneurs $D^{+\bullet}$, portant la même charge pour former un dimère diamagnétique $(A_2)^{2-}$ ou $(D_2)^{2+}$ (figure 1). La principale force motrice pour la formation de π-dimères est la combinaison des orbitales semi-occupées dégénérées (SOMO) pour générer une nouvelle HOMO stabilisée en énergie (ΔH_{Res})[8] (figure 1 en bas). Simultanément, une

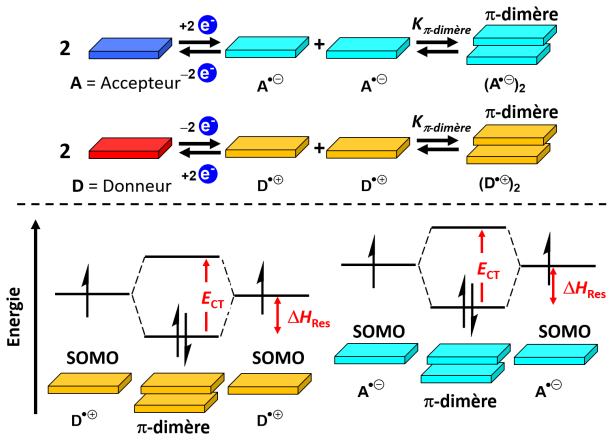


Figure 1. En haut : schéma réactionnel simplifié décrivant la formation de π-dimères et diagramme orbital simplifié. En bas à gauche : cas d'un cation radical généré à partir d'un donneur d'électrons. En bas à droite : cas d'un anion radical généré à partir d'un accepteur d'électrons.

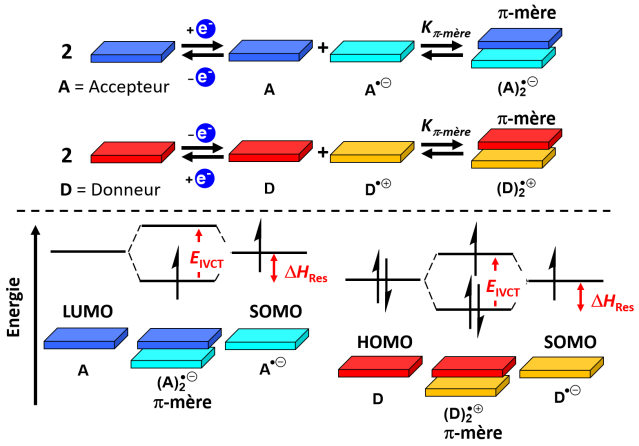


Figure 2. En haut : schéma réactionnel simplifié décrivant la formation des π-mères et diagramme orbital simplifié. En bas à gauche : cas d'un anion radical généré à partir d'un accepteur d'électrons. En bas à droite : cas d'un radical cationique généré à partir d'un donneur.

nouvelle LUMO naît de la combinaison anti-liante correspondante, conduisant ainsi à une nouvelle transition HOMO-LUMO (E_{CT}). Un paramètre essentiel est la grande π-délocalisation du radical sur chaque sous-unité. Par conséquent, l'interaction d'appariement se produit sur plusieurs atomes de chaque sous-unité et forme ainsi une liaison multi-centrée fréquemment appelée liaison « pancake », selon l'expression de Mulliken et Person.[9] L'interaction SOMO-SOMO confère un caractère covalent à la nouvelle liaison en raison de l'appariement des électrons dans les π-dimères.

1.2. π-mères

Un π-mère résulte de l'association d'un radical π-stabilisé avec son composé parent (figure 2) pour former un nouveau complexe donneur-accepteur dans lequel soit un cation radical joue le rôle d'accepteur pour le composé parent, soit un anion radical joue le rôle de donneur pour le composé parent.[10] Les π-mères sont associés par couplage électronique entre l'HOMO ou la LUMO du composé parent et la SOMO de l'espèce radicale (ΔH_{Res}) (figure 2, en bas). Également appelés complexes à charge résonnante, les π-mères diffèrent des complexes classiques à transfert de charge (CT).[11] Alors que dans les complexes CT classiques, seule une

fraction de la densité électronique est échangée entre les deux espèces, dans les π-mères, un électron contribue à la formation d'une nouvelle liaison. Ainsi, les π-mères peuvent être considérés comme un cas extrême de complexes CT. Malgré la formation de cette nouvelle liaison, un π-mère est toujours en équilibre avec les espèces séparées et non interactives, ce qui lui confère toutes les caractéristiques d'une espèce de classe II à valence mixte ou de classe III de Robin-Day. En effet, le donneur et l'accepteur sont suffisamment liés pour présenter des transitions d'intervalence électronique (EIVCT) dues à un mode de transfert de sphère interne. Par conséquent, les π-mères peuvent être décrits comme un continuum entre un complexe CT transitoire et une espèce de valence mixte.[11] Considérer les π-mères comme des composés de valence mixte justifie l'utilisation du terme dimère de valence mixte couramment utilisé dans la littérature.

Enfin, les configurations électroniques particulières des π-mères et π-dimères permettent leur étude et leur caractérisation au moyen d'un panel de techniques très variées indiqué dans la figure 3. Si les deux espèces fournissent toutes deux une réponse en spectrophotométrie d'absorption UV-visible, les deux espèces peuvent être caractérisées de manière univoque en RMN pour les π-dimères et RPE pour les π-mères sans laisser de doute sur la nature des espèces observées.

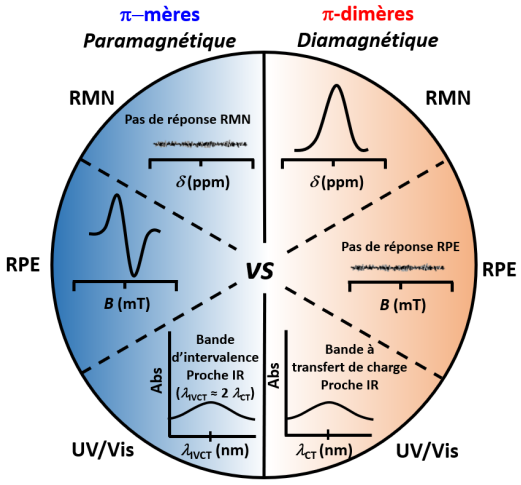


Figure 3. Caractérisation physique de la formation de π-mères et de π-dimères.

[1] K. H. Hausser, *Z. Naturforsch.* **1956**, *11a*, 20.
[2] M. J. Hove, B. M. Hoffman, J. A. Ibers, *J. Chem. Phys.* **1972**, *56*, 3490-3502.
[3] E. M. Kosower, J. L. Cotter, *J. Am. Chem. Soc.* **1964**, *86*, 5524–5527.
[4] K. Cai, L. Zhang, R. D. Astumian, J. F. Stoddart, *Nature Rev.* **2021**, *5*, 447–465.
[5] J. S. Miller, J. J. Novoa, *Acc. Chem. Res.* **2007**, *40*, 189–196.
[6] a) K. E. Preuss, *Polyhedron* **2014**, *79*, 1–15; b) J. M. Spruell, *Pure Appl. Chem.* **2010**, *82*, 2281–2294.
[7] D.-W. Zhang, J. Tian, L. Chen, L. Zhang, Z. T. Li, *Chem. Asian J.* **2015**, *10*, 56–68.
[8] a) T. Bally, K. Roth, R. Straub, *J. Am. Chem. Soc.* **1988**, *110*, 1639–1641; b) M. Kertesz, *Chem. Eur. J.* **2019**, *25*, 400–416.
[9] R. S. Mulliken, W. B. Person, *Molecular Complexes*, Wiley, Chichester, **1969**, Chap. 16, p. 259.
[10] J. K. Kochi, R. Rathore, P. Le Maguères, *J. Org. Chem.* **2000**, *65*, 6826–6836.
[11] S. V. Rosokha, J. K. Kochi, *J. Am. Chem. Soc.* **2007**, *129*, 3683–3697.

Cet article a été rédigé par **Jean Weiss**, Directeur de Recherche à l'Université de Strasbourg.
jweiss@unistra.fr

À LA RENCONTRE DE… YOANN COTELLE

Carrière :

2020- Maître de conférences, à Aix-Marseille Université, Institut des Sciences Moléculaires de Marseille (iSm2), équipe Chirosciences.

2017-2020 Post-doctorat à l'Université de Bâle dans le groupe du Pr. Thomas R. Ward.

2015-2017 Post-doctorat à l'Université de Genève dans le groupe du Pr. Stefan Matile.

Formation :

2011-2014 Doctorat en chimie organique, Laboratoire MOLTECH-Anjou, Université d'Angers.

2009-2011 Master Chimie Fine et Thérapeutique de l'Université de Nantes.

À mes heures perdues, j'écoute de la musique et, déformation professionnelle oblige, j'apprécie énormément de découvrir des morceaux qui sont atypiques que ce soit dans leurs structures, leurs rythmiques où dans les thèmes évoqués.

Les jeunes devraient s'intéresser à la chimie supramoléculaire car c'est un domaine qui permet d'aborder de nombreux phénomènes tels que la catalyse, l'étude des interactions protéines-ligands, ou les matériaux "intelligents" et ainsi de développer de nombreuses compétences. De plus, la chimie supramoléculaire permet le développement de molécules fonctionnelles dont l'étendue des possibilités me semble illimitée.

Je conseille à mes étudiants d'avoir l'esprit ouvert sur les résultats de leurs expériences. La recherche c'est avant tout s'intéresser à des résultats ou des phénomènes que l'on ne comprend pas ou que l'on ne peut pas expliquer immédiatement.

La chose la plus importante que j'ai apprise de mes étudiants est que l'on forme une équipe. Afin d'avancer le plus loin possible, il faut avant tout s'appuyer sur leurs compétences et leurs aspirations même si cela ne correspond pas tout à fait à l'idée de base que l'on avait pour ces travaux de recherches.

Le plus grand défi auquel est confrontée ma génération de scientifiques est de ramener la confiance du plus grand nombre envers la science et la méthode scientifique. Pour cela, il est important de rappeler la nécessité de débattre à partir d'arguments étayés et non seulement à partir d'opinions.

J'ai choisi mon orientation professionnelle actuelle parce qu'à l'origine je suis curieux et j'aime l'idée de pouvoir approfondir un sujet. Par la suite, si j'ai décidé de continuer, c'est que cette curiosité m'a permis de pouvoir exprimer une certaine créativité que ce soit dans les cibles que l'on synthétise ou dans les différentes applications visées.

Mes molécules préférées sont les polyimides aromatiques. Ces molécules possèdent des propriétés incroyables que ce soit pour la reconnaissance d'anions, pour la catalyse ou pour les machines moléculaires.

Intérêts scientifiques :

Chimie supramoléculaire, chimie organique, chiralité, cages moléculaires covalentes, interactions π-anioniques, catalyse en milieu confiné, études conformationnelles, mimes d'anhydrases carboniques.

Cinq références significatives :

Cotelle, Y.; Lebrun, V.; Sakai, N.; Ward, T. R.; Matile, S. "Anion-π Enzymes" *ACS Cent. Sci*. **2016**, *2*, 388-393.

Stein, A.; Chen, D.; Igareta, N.V.; Cotelle, Y.; Rebelein, J.G.; Ward, T.R. "A Dual Anchoring Strategy for the Directed Evolution of Improved Artificial Transfer Hydrogenases Based on Carbonic Anhydrase" *ACS Cent. Sci.* **2021**, *7*, 1874-1884.

Miton, L.; Antonetti, E.; Garcia-Lopez, D.; Nava, P.; Robert, V.; Albalat, M.; Vanthuyne, N.; Martinez, A.; Cotelle, Y. "A Cyclotriveratrylene Solvent-Dependent Chiral Switch" *Chem. Eur. J.* **2024**, *30*, e202303294.

Miton, L.; Antonetti, E.; Poujade, M.; Dutasta, J.-P.; Nava, P.; Martinez, A.; Cotelle, Y. "Self-assembled tetrazine cryptophane for ion pair recognition and guest release by cage disassembly" *Chem. Comm.* **2024**, *60*, 5217-5220.

Miton, L.; Dupin, P. A.; Antonetti, E.; Jean, M.; Nava, P.; Martinez, A.; Cotelle, Y. "Electron-deficient hemicryptophanes for the recognition of anions through anion–π interactions" *Org. Biomol. Chem.* **2025**, *23*, 4360-4364.

NOTRE SÉLECTION D'ARTICLES

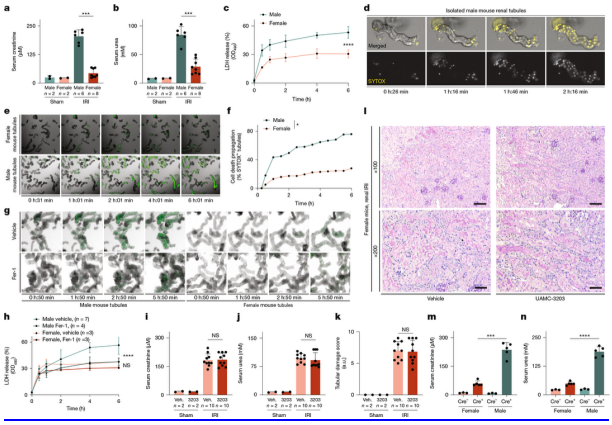
Le bureau du Groupe SupraSCF met en avant chaque semestre une sélection d'articles dont les auteur.rice.s sont membres de notre groupe thématique.
Vous trouverez ici un choix d'articles publiés sur la période août 2025 - décembre 2025 dans les journaux suivants :
- *Nature, Nat. Chem., Nat. Comm., Chem,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

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

Multiple oestradiol functions inhibit ferroptosis and acute kidney injury

Tonnus, W.; Maremonti, F.; Gavali, S.; Schlecht, M. N.; Gembardt, F.; Belavgeni, A.; Leinung, N.; Flade, K.; Bethe, N.; Traikov, S.; Haag, A.; Schilling, D.; Penkov, S.; Mallais, M.; Gaillet, C.; Meyer, C.; Katebi, M.; Ray, A.; Gerhardt, L. M. S.; Brucker, A.; Becker, J. N.; Tmava, M.; Schlicker, L.; Schulze, A.; Himmerkus, N.; Shevchenko, A.; Peitzsch, M .; Barayeu, U.; Nasi, S.; Putz, J.; Korach, K. S.; Neugarten, J.; Golestaneh, L.; Hugo, C.; Becker, J. U.; Weinberg, J. M.; Lorenz, S.; Proneth, B.; Conrad, M.; Wolf, E.; Plietker, B.; Rodriguez, R.; Pratt, D. A.; Dick, T. P.; Fedorova, M.; Bornstein, S. R.; Linkermann, A. *Nature* **2025**, *645*, 1011–1019

DOI: 10.1038/s41586-025-09389-x

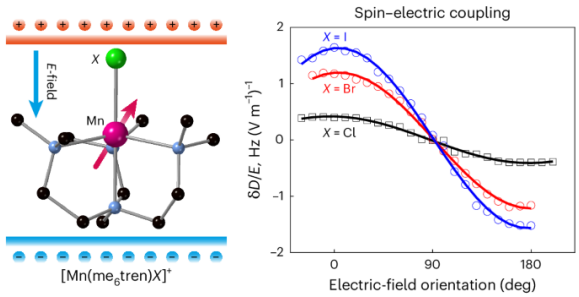


Abstract: Acute tubular necrosis mediates acute kidney injury (AKI) and nephron loss, the hallmark of end-stage renal disease. For decades, it has been known that female kidneys are less sensitive to AKI. Acute tubular necrosis involves dynamic cell death propagation by ferroptosis along the tubular compartment. Here we demonstrate abrogated ferroptotic cell death propagation in female kidney tubules. 17β-oestradiol establishes an anti-ferroptotic state through non-genomic and genomic mechanisms. These include the potent direct inhibition of ferroptosis by hydroxyoestradiol derivatives, which function as radical trapping antioxidants, are present at high concentrations in kidney tubules and, when exogenously applied, protect male mice from AKI. In cells, the oxidized hydroxyoestradiols are recycled by FSP1, but FSP1-deficient female mice were not sensitive to AKI. At the genomic level, female ESR1-deficient kidney tubules partially lose their anti-ferroptotic capacity, similar to ovariectomized mice. While ESR1 promotes the anti-ferroptotic hydropersulfide system, male tubules express pro-ferroptotic proteins of the ether lipid pathway which are suppressed by ESR1 in female tissues until menopause. In summary, we identified non-genomic and genomic mechanisms that collectively explain ferroptosis resistance in female tubules and may function as therapeutic targets for male and postmenopausal female individuals.

Chemical tuning of quantum spin–electric coupling in molecular magnets

Vaganov, M. V.; Suaud, N.; Lambert, F.; Cahier, B.; Herrero, C.; Guillot, R.; Barra, A. L.; Guihéry, N.; Mallah, T.; Ardavan, A.; Liu, J. J. *Nat. Chem.* **2025**, *17*, 1903–1909

DOI: 10.1038/s41557-025-01926-5

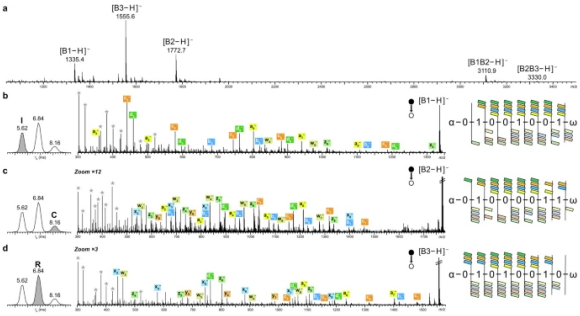


Abstract: Controlling quantum spins using electric rather than magnetic fields promises substantial architectural advantages for developing quantum technologies. In this context, spins in molecular magnets offer tunability of spin–electric couplings (SECs) by rational chemical design. Here we demonstrate systematic control of SECs in a family of Mn(II)-containing molecules by varying the coordination environment of the spin centre. The trigonal bipyramidal (tbp) molecular structure with C3 symmetry leads to a substantial molecular electric dipole moment that is directly connected to its magnetic anisotropy. The interplay between these two features gives rise to experimentally observed SECs, which can be rationalized by wavefunction theoretical calculations. Our findings guide strategies for the development of electrically controllable molecular spin qubits for quantum technologies.

Acceleration, simplification and potential parallelization of digital polymers sequencing by coupling tandem mass spectrometry with ion mobility

Sergent, I.; Obeid, G.; Schutz, T.; Lutz, J.-F.; Charles, L. *Nat. Comm.* **2025**, *17*, 11642

DOI: 10.1038/s41467-025-66762-0



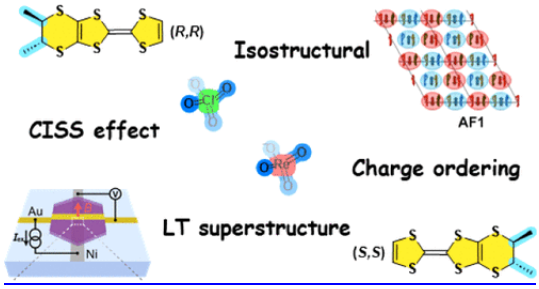
***Abstract*:** Tailoring the structure of digital polymers is an efficient strategy for reliable reading of large amounts of data by tandem mass spectrometry. Notably, full sequence coverage of chains containing up to 33 bytes of information is achieved for block-truncated poly(phosphodiester)s designed to undergo controlled fragmentations. However, the previously established reading methodology based on multiple MS stages performed sequentially remains slow and not prone to automation. Here, we report a full gas-phase bottom-up workflow enabling production, separation and sequencing of all sub-sequences of block-truncated poly(phosphodiester)s in a single run. To do so, a multidimensional coupling involving two activation stages in tandem with ion mobility spectrometry has been optimized. Since blocks to be sequenced have their mobility varying in a predictable manner, proper selection of tags used for their identification permits to achieve mobility resolution prior to sequencing. Performing this coupling with MALDI further paves the way to automated imaging-based reading approaches.

Chiral Metallic DM-EDT-TTF Radical Cation Salts: Anion Size-Dependent Structural and Electronic Transitions, Charge Ordering, and Chirality-Induced Spin Selectivity

Pop, F.; Mroweh, N.; Auban-Senzier, P.; Rikken, G. L. J. A.; Hirobe, D.; Yamamoto, H. M.; Frackowiak, A.; Olejniczak, I.; Pillet, S.; Bendeif, E.; Alemany, P.; Canadell, E.; Avarvari, N.

J. Am. Chem. Soc. **2025**, *147*, 27749–27767

DOI: 10.1021/jacs.5c06549



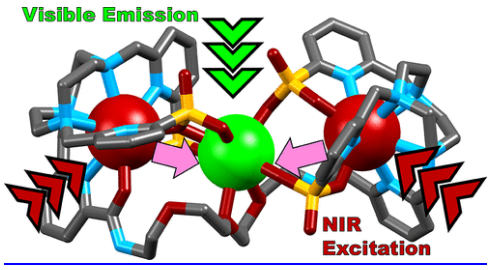
***Abstract*:** Both enantiomers (S,S) and (R,R) of the chiral mixed-valence radical cation salts (DM-EDT-TTF)2XO4 (X = Cl or Re) have been prepared by electrocrystallization. Single-crystal high-quality synchrotron radiation data allowed for the very accurate determination of their 298 and 18 K structures. At room temperature, they crystallize in the enantiomorphic space groups P6222 and P6422 for the (S,S) and (R,R) enantiomers, respectively, while at 18 K, the structures have been solved in the P62 and P64 space groups, respectively. This symmetry reduction results in a quadrupled unit cell containing four independent donors disordered over two inequivalent positions. In the perrhenate salts, there is strong structural evidence of the occurrence of charge ordering at 18 K as suggested by the alternation of charge-rich and charge-poor donors within the stacks. The easier establishment of charge disproportionation is very likely related to the higher metal-to-insulator transition temperature for perrhenate compared to perchlorate, as observed in the electrical resistance measurements. Spin-polarized DFT band structure calculations support the magnetic ground state of the materials and the activated low-temperature conductivity as a consequence of gap opening. Single-crystal Raman spectroscopy measurements indicate a stronger charge ordering degree at 10 K for the perrhenate than for the perchlorate salts. For the first time in chiral TTF-based conductors, the chirality-induced spin selectivity (CISS) effect is demonstrated through magnetoresistance measurements at room temperature on thin crystals of (DM-EDT-TTF)2ClO4, with a value of up to 30% for CISS-induced magnetoresistance.

Heteropolynuclear Lanthanide(III) Complexes for Cooperative Sensitization Upconversion in Water

Godec, L.; Knighton, R. C.; Hamon, N.; Thor, W.; Wong, K. L.; Tripier, R.; Charbonnière, L. J.

J. Am. Chem. Soc. **2025**, *147*, 31187–31197

DOI: 10.1021/jacs.5c09915



***Abstract*:** We report the synthesis of a tritopic ligand, L2, composed of two strongly binding lanthanide (Ln) sites using tris-functionalized triazacyclononane (tacn) scaffolds bridged by a weaker Ln binding triethylene glycol chain. Coordination chemistry of Ln3+ (Ln = Eu, Tb, Yb, Lu) was investigated by using NMR and photoluminescent spectroscopies. The first two Ln3+ ions are coordinated by the tacn scaffolds to form [LnL2] and [Ln2L2] species, followed by tri- and tetranuclear complexes, [Ln(Ln2L2)] and [Ln2(Ln2L2)]. The third and fourth exomacrocyclic binding events occur at the polyethylene glycol binding site, buttressed by a synergistic interaction of the phosphonate arms, confirmed by DFT modeling. [Ln2L2] (Ln = Tb, Eu, Yb, and Lu) homobimetallic complexes were prepared, and characterized and their spectroscopic properties determined in H2O and D2O. Titration of the [Yb2L2] dinuclear complex by Tb salts in D2O confirmed the formation of the tri- and tetranuclear species. Upon excitation into the 2F5/2 ← 2F7/2 absorption band of Yb at 980 nm, a cooperative sensitization upconversion process is evidenced, displaying visible Tb emission bands. Heating resulted in Ln scrambling in the tacn coordination sites, increasing the UC efficiency by ca. 103. The most efficient emitter for UC is the tetranuclear [TbYb(TbYbL2)], with one of each Ln3+ species in the tacn scaffolds and one of each Ln3+ species coordinated by the

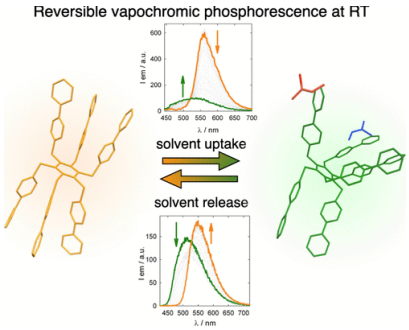
polyethylene glycol chain. Optimization on the pD led to an overall 9.0 × 10–7 UC quantum yield (λexc = 980 nm, P = 10.8 W·cm–2). The same experiment was repeated in water, affording UC at the molecular level.

Room-Temperature Phosphorescence Vapochromism through Conformational Control

Fermi, A.; Gahlot, S.; Jorand, E.; d'Agostino, S.; Dai, Y.; Negri, F.; Moustrou, C.; Gingras, M.; Ceroni, P.

J. Am. Chem. Soc. **2025**, *147*, 32309–32314

DOI: 10.1021/jacs.5c07339



***Abstract*:** Solid-state room-temperature phosphorescence is rarely observed in organic molecules, and the modification of its color upon application of physical or chemical stimuli is hardly achieved. In this work, we demonstrate that a decorated persulfurated benzene shows reversible phosphorescence switching in the solid state, as a consequence of conformational changes induced by inclusion of solvent molecules. Quantum-chemical calculations suggest that the luminescence changes are due to emission from triplet states of different character. These results display the close relationship between structural factors and phosphorescence in solid state emitters, representing a valuable benchmark for the design of all-organic luminescent sensors with the desired photophysical properties.

Bayesian Optimization for Multicomponent Supramolecular Systems

Jansen, S. A. H.; Markvoort, A. J.; de Graaf, F. V.; Rutten, M. G. T. A.; Dankers, P. Y. W.; Vantomme, G.; de Greef, T. F. A.; Meijer, E. W.

J. Am. Chem. Soc. **2025**, *147*, 33607–33614

DOI: 10.1021/jacs.5c08539

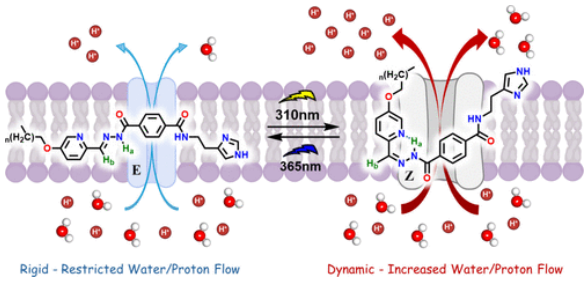
***Abstract*:** The diversity of noncovalent interactions makes the design space of multicomponent molecular systems highly complex. To efficiently explore supramolecular design space, data-driven strategies are needed. Here, we demonstrate a methodological framework for the targeted design of multicomponent molecular systems with noncovalent interactions using Bayesian optimization. Its effective applicability to supramolecular polymers is illustrated by three representative cases that reveal accelerated exploration of diverse multicomponent systems with a universal Bayesian optimization framework. The number of experiments required to arrive at optimal compositions is significantly reduced compared to random or uninformed sampling strategies, enabling the experimental study of high-dimensional design spaces. In this way, we can tune the formulation of intricate mixtures and achieve tailored macroscopic properties with minimal experimental effort. Our results show that Bayesian optimization is a general tool for developing multicomponent supramolecular systems with designed functionality.

Dynamic Regulation of Proton and Water Transport through an Acylhydrazone-Based Photoresponsive Channel

Wanjari, P.; Stroia, I.; van der Lee, A.; Baaden, M.; Barboiu, M.

J. Am. Chem. Soc. **2025**, *147*, 35264–35274

DOI: 10.1021/jacs.5c05942



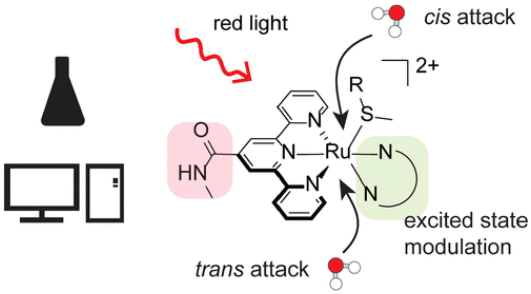
***Abstract*:** Proton transport is crucial for cellular energy, and synthetic systems having the ability to control this process offer promising applications in drug development and cancer treatment. Herein we report a unique light-responsive proton/water transport system using self-assembled acylhydrazone-imidazole channels with tunable activity via E–Z isomerization. Three channel-forming molecules with varying alkyl chains were synthesized, namely, 1a (C4), 1b (C8), and 1c (C12). The photoswitching behavior of the molecule was confirmed by UV–vis spectroscopy within the liposome. The crystallographic analysis revealed that the E-isomer forms an H-bonded proton transport pathway mediated by water molecules. Patch clamp assays confirmed proton channel formation for 1a with a transport rate of 2.18 × 107 H+/s/channel and high proton selectivity over other ions. Ion transport assays with EYPC-LUVs entrapped with HPTS and NaCl revealed the complete rejection of external cations and anions. The compounds demonstrated significant proton transport when combined with valinomycin, indicating transmembrane proton transport for 1a–c. Upon irradiation at 310 nm, all derivatives showed increased proton transport rates, which subsequently decreased after exposure to 365 nm, confirming the photoresponsive behavior of the system. A similar trend was observed in water transport, where the single-channel permeability of 1a increased from 6.5 × 106 to 3.5 × 107 water molecules/s/channel upon switching from the E to Z isomers, then decreased to 1.8 × 107 after reverting to the E conformer. Molecular simulation confirmed that stable supramolecular porous water crystal patches may form, featuring multivalent water H-bonding to acylhydrazone and imidazole units that serve as water-cluster relays within the channel.

Structure over States: Planarity, Not Energy, Dictates Photoactivation in Ru(II) PACT Agents

Hakkennes, M. L. A.; Regeni, I.; Husiev, Y.; Andreeva, V. D.; Siegler, M. A.; Buda, F.; Bonnet, S.

J. Am. Chem. Soc. **2025**, *147*, 35767–35787

DOI: 10.1021/jacs.5c12226



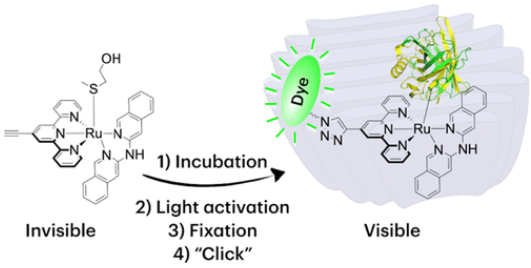
***Abstract*:** Photoactivated chemotherapy (PACT) employs light to precisely control the activity of prodrugs, enabling spatial and temporal regulation of therapeutic effects while minimizing systemic toxicity. Transition-metal complexes, particularly Ru(II) polypyridyl compounds, have emerged as promising PACT agents due to their ability to undergo photodissociation via triplet excited states. However, rationalizing and predicting photosubstitution quantum yields remain challenging due to complex excited-state dynamics, solvent effects, and limitations of traditional modeling approaches. In this study, we synthesized nine Ru(II) complexes incorporating a monodentate thioether ligand, a terpyridine ligand, and various bidentate polypyridyl ligands. Upon red-light irradiation in aqueous solution, these complexes showed selective photosubstitution of the thioether by an aqua ligand. Despite similar absorption properties, these compounds exhibited markedly different photosubstitution quantum yields that static DFT calculations failed to explain. These modeling difficulties prompted us to develop a novel triplet-state molecular dynamics protocol using the GFN-xTB method, explicit solvation, and enhanced sampling techniques. Our approach enabled full simulations of the ligand exchange process on the triplet hypersurface and comparison to experimental data. It revealed that both cis and trans substitution of the thioether by a water molecule is possible; it was also able to distinguish between photoactive and photoinactive compounds. Unexpectedly, we found that the deviation from planarity of the bidentate ligand, rather than the energy levels of the different triplet excited states (3MLCT, 3MC) involved in the photosubstitution reaction, was the primary determinant of photosubstitution efficiency, as it promoted access to the trans photosubstitution pathway. Furthermore, our simulations uniquely identified whether dissociative, interchange, or associative mechanisms governed the reactivity of each complex. These results provide for the first time mechanistic insights into Ru(II)-based photosubstitution reactions in a solvent and offer a practical, scalable computational tool for designing next-generation PACT agents with optimized light-responsive properties.

Visualizing the Invisible: Dual Click Imaging of Ruthenium-Based Photoactivated Chemotherapy Agents and Their DNA Synthesis Inhibition in Fixed Cancer Cells

Busemann, A.; Rieger, L.; Cunningham, R. M.; Davidse, S. C.; Regeni, I.; Flaspohler, I.; Schmidt, C.; Zhou, X. Q.; van Rixel, V.; Siegler, M. A.; Ott, I.; Le Devedec, S. E.; Wagenknecht, H. A.; DeRose, V. J.; Bonnet, S.

J. Am. Chem. Soc. **2025**, *147*, 42500–42510

DOI: 10.1021/jacs.5c13249



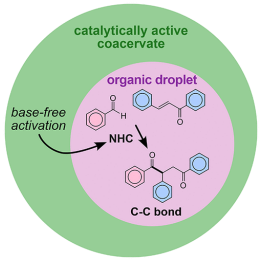
***Abstract*:** Like many drugs, ruthenium-based photoactivated chemotherapy (PACT) complexes are hard to follow in cells due to their absence of emissive properties. Here, two alkyne-functionalized Ru-based PACT compounds with the formula [Ru(HCC-tpy)(N̂N)(Hmte)](PF6)2 were synthesized, where HCC-tpy = 4′-ethynyl-2,2′:6′,2″-terpyridine, N̂N = 3,3′-biisoquinoline (i-biq, [2](PF6)2) or di(isoquinolin-3-yl)amine (i-Hdiqa, [4](PF6)2), and Hmte = 2-(methylthio)ethanol. Their challenging synthesis involved a protection–deprotection strategy to avoid the reaction of the free alkyne group with the coordinatively unsaturated ruthenium center. The thermal stability and photosubstitution quantum yield (Φ[2] = 0.022 and Φ[4] = 0.080) of the PACT complexes were essentially preserved upon alkyne functionalization. Interestingly, however, cellular uptake was doubled after alkyne functionalization, resulting in increased cytotoxicity against A549 cancer cells for both complexes in the dark and after green light activation (EC50,light = 5 and 7 μM, respectively). To follow the complexes and see the effect of light activation, post-treatment fluorophore labeling via copper-catalyzed azide–alkyne cycloaddition was realized in fixed cells at 2 different time points, which allowed for imaging the otherwise invisible molecules. The images showed that the Ru complexes accumulated in the cytoplasm only after light irradiation and that they colocalized with the lysosomes and the Golgi apparatus. Moreover, we combined this approach with metabolic labeling of DNA, and showed by dual click imaging that DNA replication was inhibited by complex 4. The strategy described herein, pioneered for nonemissive, photosubstitutionally active ruthenium complexes, opens a new avenue for investigating the selective attack of lung cancer cells by PACT.

Coacervate Droplets Drive Organocatalyzed Aqueous C–C Bond Formation via Interfacial Activation

Peyraud-Vicre, K.; Dechamps, C.; Martin, N.; Desvergnes, V.

J. Am. Chem. Soc. **2025**, *147*, 37337–37346

DOI: 10.1021/jacs.5c10731



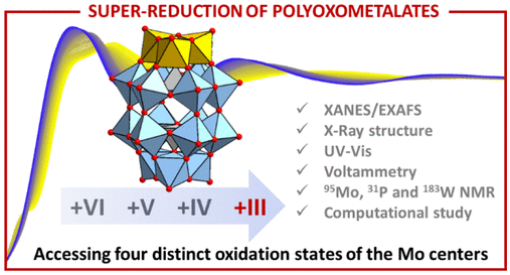
***Abstract*:** Compartmentalization is central to the regulation of biochemical reactions in living systems, with membraneless organelles formed by liquid–liquid phase separation (LLPS) offering dynamic environments that influence biochemical reactivity. Inspired by this principle, coacervate microdroplets have emerged as promising synthetic analogues for modulating both enzymatic and nonenzymatic reactions in water. Here, we report that coacervates can actively promote aqueous N-heterocyclic carbene (NHC) organocatalysis, enabling base-free carbon–carbon (C–C) bond formation via the Stetter reaction. Using a newly designed amphiphilic thiazolium precatalyst, we show that model polyelectrolyte coacervates not only sequester organic droplets containing the Stetter reactants, creating a unique coacervate/organic droplet interface, but also directly facilitate carbene generation. Remarkably, this activation arises from a strong electrostatic interaction between the thiazolium salt and the polyanion, which spontaneously coacervate together to form catalytically active droplets. These coacervates act as sacrificial reaction compartments, dissolving upon carbene formation while driving C–C bond formation in the absence of added base, highlighting the capacity of coacervates to restructure and respond dynamically during catalysis. Together, our results uncover a previously unrecognized mode of organocatalyst activation within LLPS-based materials, expanding the functional scope of phase-separated systems and suggesting broader potential for leveraging multiphase systems to modulate reactivity through emergent interfacial phenomena in water.

Super-reduction of Polyoxometalates: Unlocking the Oxidation State of Metalate Centers down to (III)

Kozma, K.; Priso, G. M.; Puiggali-Jou, J.; Haouas, M.; Leclerc, N.; Sole-Daura, A.; Cadot, E.; Carbo, J. J.; Briois, V.; Falaise, C.

J. Am. Chem. Soc. **2025**, *147*, 42926–42937

DOI: 10.1021/jacs.5c15650



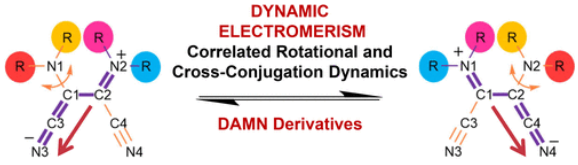
***Abstract*:** Predicting the number of electrons that polyoxometalates (POMs) can store, and whether these electrons are localized or delocalized, is a fundamental question with significant implications for energy storage and conversion. In this context, we report herein evidences that POM metalate centers can be reduced up to their trivalent state. This is exemplified by the super-reduction of the mixed metal Wells–Dawson POM [P2W15Mo3O62]6– in acidic media, achieving up to 12 electrons per POM. Structural and electronic changes induced by the reduction process have been unveiled using an integrative approach combining in situ measurements (quick XANES/EXAFS analyzed with chemometric tools), ex situ techniques (X-ray diffraction, UV–vis spectroscopy, voltammetry, and multinuclear NMR), and in silico studies (DFT, TD-DFT, and CASSCF calculations). Our findings show a significant molecular transformation after the insertion of six electrons, leading to the MoIV–MoIV bonds formation within the {Mo3O13} unit. This adaptive behavior of the metal-oxo frameworks, assisted by multiple proton transfers, unlocks access to the trivalent state of Mo centers without decomposition of the initial Dawson-type POM structure. We anticipate that these insights will contribute to advancing the application of POMs in electrochemical energy storage systems.

Dynamic Electromerism: Correlated Rotational and Cross-Conjugation Dynamics in DAMN (DiAminoMaleoNitrile) and DAFN (DiAminoFumaroNitrile) Derivatives

Aguilera-Roldan, M. J.; Roseiro, P.; Esteve, F.; Giuseppone, N.; Robert, V.; Lehn, J. M.

J. Am. Chem. Soc. **2025**, *147*, 44791–44803

DOI: 10.1021/jacs.5c09269



***Abstract*:** Conformational dynamics play key roles in molecular reactivity and the development of functional molecular machines. In this study, we investigate the competitive correlation between internal rotations about the C–NR2 bonds and cross-conjugation dynamics in DAMN, DAFN, and their derivatives. Using a combination of NMR spectroscopy, crystallographic analysis, and computational studies, we demonstrate that conjugation in one of the two push–pull π-systems restricts its own C–N bond rotation while suspending conjugation and facilitating rotation in the other system, leading to synchronized rotation-conjugation oscillation. Variable Temperature (VT)-NMR spectroscopy revealed that the presence of competing cross-conjugated pathways drastically lowers the C–N rotational barriers of the amino groups compared to those of reference compounds presenting a single π-system (11–14 kcal/mol at 298 K). Density functional theory (DFT) studies yielded rotational barriers as low as ∼2 kcal/mol for tetra-methylated DAMN, with a disrotatory mechanism. The introduction of steric effects increased the rotational barriers, yielding measurable NMR values of 7–9 kcal/mol at coalescence in the bulkiest DAMN derivative. Additionally, modulation of the structural desymmetrization of the coupled push–pull systems in monoimine derivatives of DAMN allowed determination of rotational barriers

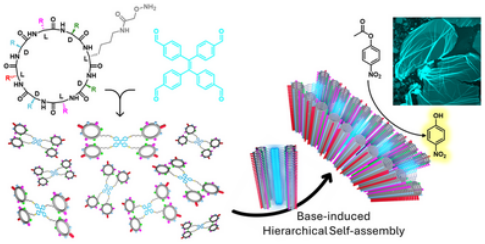
within the range of those of the reference compounds. These effects agreed with the presence of cross-conjugation, which was also supported by X-ray diffraction. The findings provide insight into the structural factors governing rotational barriers in cross-conjugated systems exhibiting correlated molecular motion. Thus, DAMN and DAFN present a dynamic electromerism process where oscillation between two different cross-conjugation pathways is regulated by the C–N rotation frequency.

2D Assemblies Based on a Tetraphenylethylene D,L-Cyclic Peptide Scaffold

A. Bayón-Fernández, A. Torrón-Celada, A. Méndez-Ardoy, M. Coste, D. Delgado-Gestoso, S. Ulrich, J. Montenegro, R. Granja

Angew. Chem. Int. Ed. **2025**, *64*, e14543

DOI: 10.1002/anie.202514543



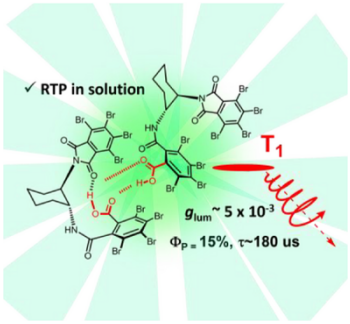
***Abstract*:** A new scaffold based on four nanotube-forming cyclic peptide units attached to a tetraphenylethene (TPE) core with pH-dependent self-assembly that provides light-emitting 2D nanosheets with controlled thickness is described.

Symmetry Breaking and Hydrogen Bonding in Phthalimide Compounds Enable Efficient Room-Temperature Circularly Polarized Phosphorescence in Solution

C. Demangeat, M. Rémond, J. M. Hudson, E. W. Evans, D. Jacquemin, L. Favereau

Angew. Chem. Int. Ed. **2025**, *64*, e202515218

DOI: 10.1002/anie.202515218



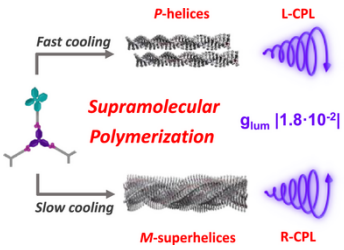
***Abstract*:** Purely organic chiral room-temperature phosphorescence (RTP) emitters are gaining increasing attention, but predicting the key factors governing polarized luminescence remains challenging, as RTP is rarely observed in solution. The crucial role of hydrogen bonding and symmetry breaking in modulating chiral triplet excited-state interactions via n-π* and π–π* state mixing is now highlighted, providing new molecular insights for enhancing circularly polarized RTP (g_{lum} up to 5×10^{-3}).

Inverting the Circularly Polarized Luminescence Handedness of Chiral Supramolecular Polymers Using Temperature

T.-A. Cucuiet, A. Vargas Jentzsch, F. Picini, M. Maaloum, G. Raffy, E. Moulin, D. M. Bassani, N. Giuseppone

Angew. Chem. Int. Ed. **2025**, *64*, e202516824

DOI: 10.1002/anie.202516824



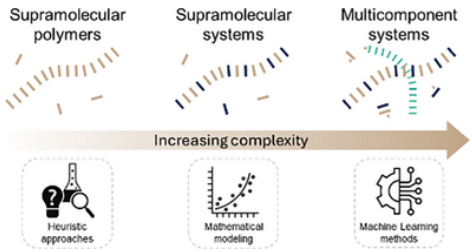
***Abstract*: *Abstract*:** The supramolecular polymerization of enantiopure triarylamine trisamide monomers bearing aggregation-induced emissive tetraphenylethene units, gave rise to a strong circularly polarized luminescence (with g_{lum} values as high as $|1.8 \cdot 10^{-2}|$). Strikingly, upon fast versus slow cooling rates, these monomers formed distinct hierarchical self-assemblies (i.e., (*P*)-helices versus (*M*)-superhelices) that emitted circularly polarized light of opposite handedness.

Evolving Data-Driven Strategies for the Characterization of Supramolecular Polymers and Systems

S. A. H. Jansen, G. Vantomme, E. W. Meijer

Angew. Chem. Int. Ed. **2025**, *64*, e202509122

DOI: 10.1002/anie.202509122



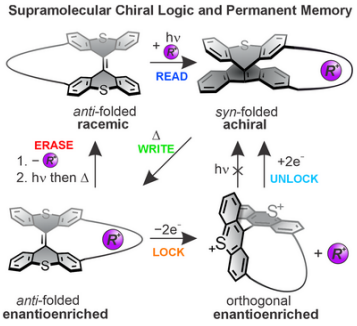
***Abstract*:** Research on supramolecular polymers has advanced rapidly toward the development of synthetic multicomponent systems. This review highlights recent progress in understanding their assembly mechanisms and how these influence structural and functional properties. Emerging data-driven approaches, particularly machine learning, offer new opportunities for rational design and characterization, shaping the future of supramolecular chemistry.

Chiral Induction and Memory via Supramolecular Deracemization

R. Hein, E. Sidler, Y. Gisbert, B. L. Feringa

Angew. Chem. Int. Ed. **2025**, *64*, e202510584

DOI: 10.1002/anie.202510584



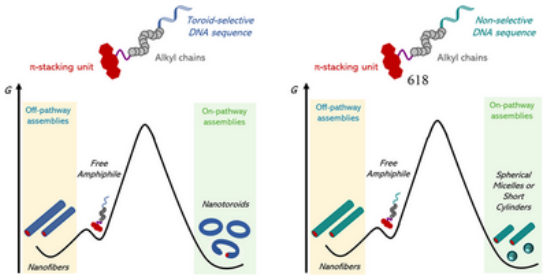
***Abstract*:** The helical chirality of a dynamic crown-ether switch can, by light- or redox-switching to a prochiral state, be erased and subsequently stereoselectively re-formed by relaxation in the presence of a point-chiral ammonium guest. This unique supramolecular deracemization enables facile transfer and stable memory of chiral information.

Complex Donuts: Small Variations in DNA Sequence Dictate Pathway Complexity in DNA Nanotoroids

M. Ghufran Rafique, Y. Wu, Y. Shi, Q. Laurent, A. Elmanzalawy, C. Saab, Y. Shi, D. F. Perepichka, J. Li, H. F. Sleiman

Angew. Chem. Int. Ed. **2025**, *64*, e202501441

DOI: 10.1002/anie.202501441



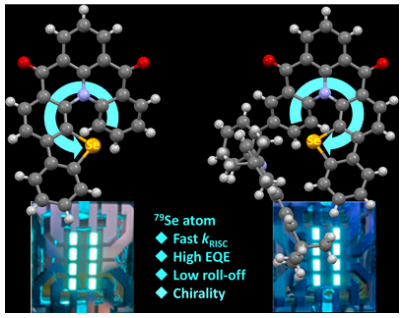
***Abstract*:** Chemical information encoded in the sequence of DNA amphiphiles enables the selective formation of kinetically trapped DNA nanotoroids through a complex self-assembly pathway. The toroids are formed as on-pathway structures via a competitive mechanism only when a toroid-selective DNA sequence is used.

Chiral Selenium-Integrated Multi-Resonant Thermally Activated Delayed Fluorescent Emitters Showing Improved Reverse Intersystem Crossing Rate

J. Wang, H. Hafeez, D. Chen, J. Sebastian Oviedo Ortiz, Y. Xu, A. P. McKay, D. B. Cordes, J. Crassous, I. D. W. Samuel, E. Zysman-Colman

Angew. Chem. Int. Ed. **2025**, *64*, e202506999

DOI: 10.1002/anie.202506999



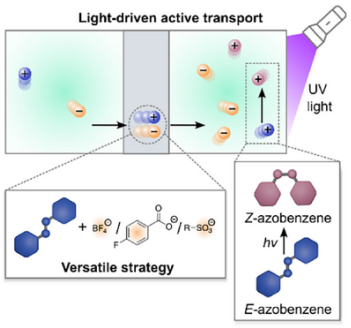
***Abstract*:** The selenium-based tBuCz-DiKTaSe emitter containing a twisted *ortho*-disposed *tert*-butylcarbazole shows high Φ_{PL}, suppressed ACQ, fast k_{RISC} and is chiral. The OLEDs show high EQE_{max} and alleviated efficiency roll-off compared to devices with carbonyl-based MR-TADF emitters.

A Versatile Strategy for Light-Driven Active Transport of Ions

S. Yahaya, S. Amano, F. Nicoli, G. Ragazzon

Angew. Chem. Int. Ed. **2025**, *64*, e20638

DOI: 10.1002/anie.202520638



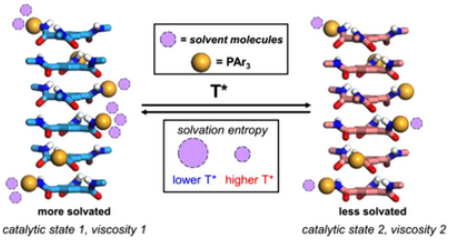
***Abstract*:** We report a light-driven primary active transport system based on an azobenzene carrier that drives uphill ion movement across phase-separated compartments. Tunable ion-pairing enables selective co-transport under buffered conditions, advancing synthetic systems that emulate biological ion pumps.

Solvation Entropy as a Lever for Steering the Macroscopic Properties of a Functional Supramolecular Helical Polymer

H. Kong, M. A. Martínez-Aguirre, Y. Li, T. Ikai, E. Yashima, G. Velpula, S. De Feyter, P.-A. Albouy, K. Akpo, P. Brocorens, R. Lazzaroni, L. Bouteiller, M. Raynal

Angew. Chem. Int. Ed. **2025**, *64*, e21365

DOI: 10.1002/anie.202521365



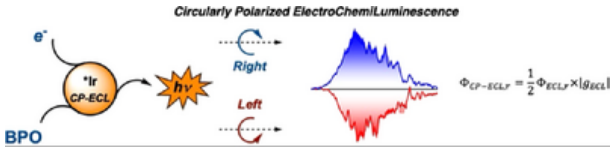
***Abstract*:** The structural transition between the two fully-characterized states of a supramolecular helical hydrogen-bonded polymer (represented as blue and light pink stacks) can be predictably varied over 85 K by changing the nature and amount of cosolvent; entropy of solvation (schematized as solvents of different sizes) is the main lever to tune the macroscopic properties of the resulting polymers.

Bright Circularly Polarized Electrochemiluminescence from Heterobinuclear Ir^{III}–Au^{I} Enantiomers

L. Ballerini, M. Liu, L. Arrico, S. Voci, C. Gourlaouen, C. Daniel, V. César, S. Bellemin-Laponnaz, F. Zinna, L. Bouffier, F. Polo, L. Di Bari, N. Sojic, M. Mauro

Angew. Chem. Int. Ed. **2025**, *64*, e10787

DOI: 10.1002/anie.202510787



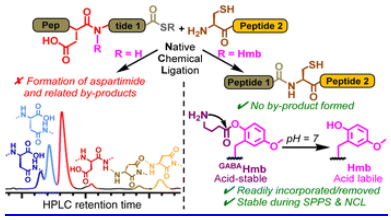
***Abstract*:** Efficient and bright circularly polarized electrochemiluminescence (CP-ECL) is achieved in a class of enantiopure hetobinuclear iridium(III)–gold(I) complexes owing to the combination of high ECL efficiency with stability, good emission dissymmetry factor and high brightness, thus paving the way to the next-generation of bright CP-ECL probes.v

Identification, occurrence and prevention of aspartimide-related byproducts in chemical protein synthesis

Cisse, E.; Aucagne, V.

Chem. Sci. **2025**, *16*, 14496–14508

DOI: 10.1039/D5SC03824C



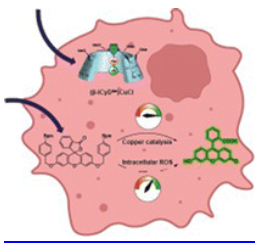
***Abstract*:** ormation of a five-membered ring aspartimide through the attack of a backbone amide to the side chain of aspartate and asparagine residues is a long-known side-reaction in solid phase peptide synthesis, and is also associated with in vivo protein ageing and instability of purified proteins. Conversely, its possible occurrence during chemical ligation-based protein synthesis, in particular when using the gold-standard reaction NCL (native chemical ligation), is dubious. We herein report a systematic study which demonstrates that the prevalence of this side-reaction may have been overlooked, due to the difficulty to identify it through standard HPLC analytical methods, but also the in situ conversion of aspartimide into other byproducts, having the same molecular mass as the parent aspartate residue. We show that the formation of aspartimide and derived byproducts can be limited by adopting “good NCL practices”, which involve restricting the ligation temperature and reaction times, as well as replacing the commonly used phosphate buffer with HEPES. However, the efficiency of such precautions is expected to vary considerably depending on the sequence of the target protein, and the amount of byproducts is expected to grow with the length of the target protein, as a result of the number of NCL reactions and potential aspartimide hotspots. To overcome such limitations, we developed a novel straightforward and potentially generally applicable methodology based on the temporary protection of the backbone nitrogen by a 2-(4-aminobutanoyloxy)-4-methoxybenzyl (GABA-Hmb) group. This strategy was validated by the byproduct-free synthesis of SUMO-2 and a SUMOylated peptide mimic.

Encapsulating NHC-capped copper(i) complexes inside cyclodextrin for catalysis in living cells

Figueiredo, F.; Madec, H.; Mesdom, P.; Salluce, G.; Tigherghar, Y.; Cariou, K.; Roland, S.; Sollogoub, M.; Gasser, G.

Chem. Sci. **2025**, *16*, 19727–19736

DOI: 10.1039/D5SC04711K



***Abstract*:** The development of “non-natural” chemical reactions inside living organisms is an expanding field of research. In this area, metal-based catalysis has been particularly scrutinised. However, most examples of catalysts developed so far are based on expensive and rare heavy metals such as ruthenium, iridium or palladium. For this reason, the development of catalysis in cells or in vivo with more accessible first-row metals is of great interest and could significantly increase the catalogue of reactions applicable in these complex environments. Herein, we demonstrate that encapsulating copper(I) N-heterocyclic carbene (NHC) catalysts inside the cavity of modified cyclodextrins, renders these notoriously toxic

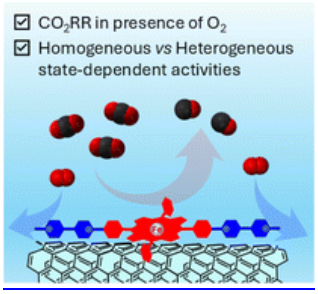
complexes harmless towards CT26 cells at high concentrations. Nevertheless, the catalytic activity of cyclodextrin (CD)–encapsulated NHC–copper complexes is preserved, allowing the deprotection of pinacol boronate ester groups outside and inside living cells to release phenol-based fluorophores. In cells, the production of fluorophore in the presence of CD–NHC–copper catalysts outperforms that induced by the cellular machinery alone and endogeneous ROS.

Iron porphyrin flanked by viologen redox units for persistent carbon dioxide reduction in the presence of oxygen

Rashid, H.; Dragoe, D.; Rana, A.; DeBeer, S.; Gotico, P.; Leibl, W.; Aukauloo, A.

Chem. Sci. **2025**, *16*, 20833–20842

DOI: 10.1039/D5SC02722E



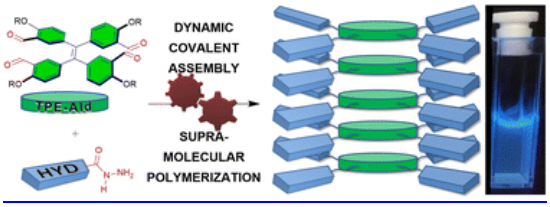
***Abstract*:** The electrocatalytic reduction of CO2 to energy-rich forms such as CO or hydrocarbons is typically realized with pure CO2. This is primarily to exclude O2, which is a far better oxidant and a major competitor upon reduction of the CO2/O2 feed gas. Furthermore, the presence of O2 can deactivate the catalytic material and reduce its effectiveness for CO2 reduction. To confront this major challenge, different strategies are being pursued. We utilize a molecular design approach by adjoining to a known catalyst a redox active module that can competitively divert the deleterious O2 activity. We tailored an iron porphyrin, a prominent catalyst for CO2 reduction, flanked by viologen units known for their efficient O2 reduction. Electrochemical studies on the homogeneous phase of the pre-catalyst, the iron(III)-μ-oxo form, show the independent activity of both modules. When heterogenized with carbon nanotubes on a carbon paper electrode, we found that the catalyst could sustain the aerobic (5% O2) reduction of CO2 to CO with a faradaic efficiency of 62%, while the activity of the unmodified iron porphyrin fell to 18% under the same experimental conditions.

Emergence of fluorescent aggregates through hierarchical self-assembly

Coste, M.; Ulrich, S.

Chem. Sci. **2025**, *16*, 22438–22446

DOI: 10.1039/D5SC04688B



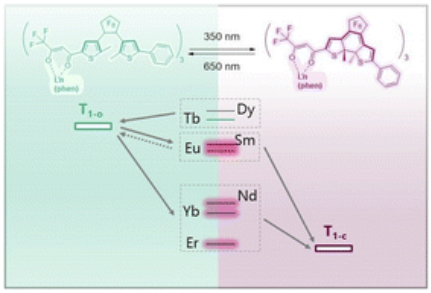
***Abstract*:** Controlling the growth of functional supramolecular nano-structures in aqueous media is a current challenge both for developing soft materials and for understanding the emergence of complex macromolecules by self-organization. We investigated here the growth of systems combining a non-fluorescent water-soluble tetraphenylethene tetraaldehyde with complementary hydrazide partners, and found that fluorescent aggregates, identified through a combinatorial screening assay, emerge through a hierarchical self-assembly involving dynamic covalent self-assembly followed by supramolecular aggregation. The process is controlled, on one hand, by external (concentration, pH) and internal (nature of side-chain) factors which dictates the outcome of the self-assembly, while, on the other hand, the supramolecular self-assembly exerts, through a feed-back loop, component selection and auto-catalytic growth which was observed using a β-sheet-forming pentapeptide.

From erbium(iii) to samarium(iii): generalized photomodulation of NIR to red lanthanide luminescence with a DTE ligand and its versatile role in the quenching processes

Phan, T. A.; Gendron, F.; Kiraev, S.; Galangau, O.; Fréroux, Y.; Al Sabea, H.; Mittelheisser, C.; Dallon, M.; Bouchet, A.; Riobé, F.; Métivier, R.; Sliwa, M.; Le Guennic, B.; Maury, O.; Banyasz, A.; Marekha, B.; Norel, L.; Rigaut, S.

Chem. Sci. **2025**, *16*, 20833–20842

DOI: 10.1039/D5SC07174G



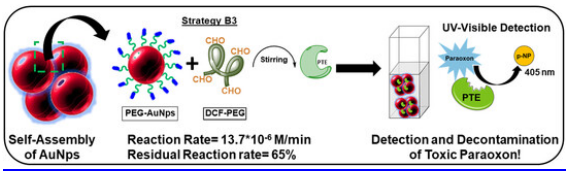
***Abstract*:** In this article, we report that a stable molecular system combining three DTE-β-diketonate units, a phenanthroline ligand and a lanthanide ion provides, for an unprecedented panel of lanthanide(III) ions, efficient luminescence together with an emission quenching process under UV light with very high efficiency. Indeed, this process is applicable to visible emitters (samarium(III) and europium(III)), and more importantly to different NIR emitters (ytterbium(III), neodymium(III) and erbium(III)), and it can be reversed under visible light irradiation in a highly repeatable way. The luminescence sensitizing and quenching mechanisms were further investigated with experimental and theoretical tools to decipher the peculiar and complex role of the DTE-β-diketonate units. In particular, these studies reveal the existence (i) of a very high cyclization quantum yield of the open isomer in the presence of oxygen with a triplet mediated mechanism depending on the lanthanide ion nature, and (ii) of a dark triplet state located on the closed isomer explaining the quenching of the NIR and visible emitters.

Gold Nanoparticles–Dynamic Constitutional Frameworks as Adaptive Hybrid Conjugates for Enzyme Immobilization

Daakour, S.; Mazzei, R.; Bazzarelli, F.; Vitola, G.; Giorno, L.; Barboiu, M.

ChemistryEurope **2025**, *e202500252*

DOI: 10.1002/ceur.202500252



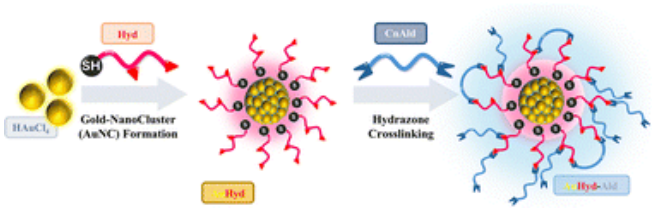
***Abstract*:** Dynamic constitutional frameworks (DCFs), connecting monomers via reversible covalent bonds, can initiate the assembly of gold nanoparticles (AuNps) with distinctive optoelectronic and surface chemical properties. A previous study indicated that these nanomaterials are particularly valuable for carbonic anhydrase immobilization and stabilization, with potential applications in biocatalysis and biosensing. However, further studies with different enzymes are needed to prove their universality. Therefore, this research focuses on immobilizing phosphotriesterase (PTE), an effective degrader of toxic organophosphates, on AuNp-DCF conjugates. PTE is integrated with citrate- and PEG-stabilized AuNps or imine-based DCFs resulting in stable, homogeneous PTE-AuNp-DCF assemblies. The conjugates exhibit high bonding affinity and changes in the PTE's secondary structure, which did not deactivate the enzyme. The catalytic performance of immobilized PTE is evaluated by measuring the p-nitrophenol (p-NP) production in a similar way is sense the paraoxon during its enzymatic hydrolysis, used as a model organophosphate. PTE immobilized to PEG2000-AuNps assembled with DCF-PEG1500 shows the highest reaction rate (13.7 × 10−6 ± 0.82 M min−1), outperforming that immobilized to citrate-stabilized AuNps (3.71 × 10−6 ± 0.21 M min−1). Furthermore, these PTE-PEG-AuNp-DCF conjugates at a 1/25 molar ratio display a residual reaction rate, 3.6 times higher than that of all other conjugates. Free amino groups exposed on the surface of AuNps facilitate optimal assembly with DCF-PEG through aldehyde/amino exchange reactions, preserving PTE activity. These results highlight the potential of PTE-DCF-AuNp conjugates to intercept and transform small molecules like paraoxon.

Tunable NIR-II photoluminescence in peptidic gold nanoclusters *via* dynamic covalent polymerization

F. Abdul Rezak, J. García Coll, G. V. Dubacheva, F. Loiseau, S. Ulrich, X. Le Guével

Chem. Commun. **2025**, *61*, 18697-18700

DOI: 10.1039/D5CC05491E



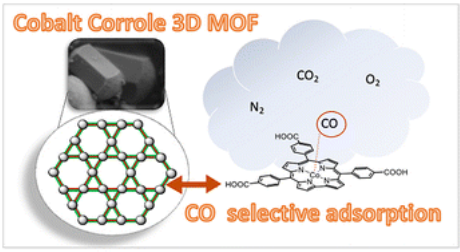
***Abstract*:** Tailoring the surface environment of gold nanoclusters is critical for enhancing their optical performance and expanding their applications in bioimaging, notably in the second near-infrared biological window. Here, we report hydrazide-rich peptide AuNCs featuring shell rigidification via dynamic covalent acylhydrazone formation with peptide bisaldehydes of varied hydrophobicity. This strategy restricts ligand motion, enhancing photoluminescence emission efficiency, and enables investigation of how the ligand shell hydrophobicity influences the optical properties of the nanoclusters.

A 3D cobalt corrole-based Zr-MOF for the selective adsorption of carbon monoxide

K. Rapady, J. Yang, S. Brandès, N. Desbois, L. André, C. P. Gros

Chem. Commun. **2025**, *61*, 17408-17411

DOI: 10.1039/D5CC04145G



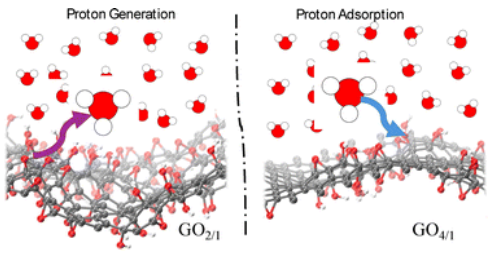
***Abstract*:** Two 3D MOFs based on triphenylcorrole and its cobalt-metalated analog (CoCorr-MOF) are presented. They show a hexagonal structure, a homogeneous particle size, and microporosity with a specific area of 390 and 304 $m^2 g^{-1}$, respectively. The CoCorr-MOF presents a better affinity for CO than for other interferents (N_2, CO_2 and O_2), demonstrating a CO chemisorption capacity of 7.2 $cm^3 g^{-1}$ with high selectivity.

Probing oxidation-controlled proton transfer at the graphene oxide-water interface with deep neural network force fields

G. Azom, T. O. Balogun, A. Milet, R. David, R. Kumar

Chem. Commun. **2025**, *61*, 15223-15226

DOI: 10.1039/D5CC03431K



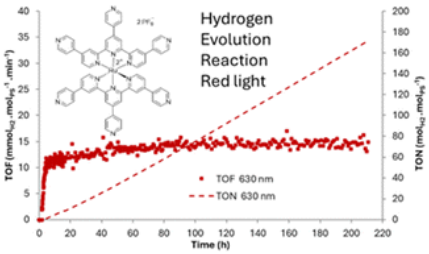
***Abstract*:** Understanding proton transfer at the aqueous graphene oxide (GO) interface is essential for developing and designing GO-based proton exchange membranes for fuel cells. By comparing GO sheets with two different oxidation levels using deep potential molecular dynamics (DPMD) simulations, we find that oxidized GO promotes interfacial proton release while reduced GO adsorbs protons.

A ruthenium terpyridine complex showing stable photocatalytic hydrogen evolution under red light

G. M. Mercier, E. Rousset, I. Oubaha, K. Bandyopadhyay, A. K. Pal, I. Ciofini, L.-M. Chamoreau, V. Marvaud, G. S. Hanan

Chem. Commun. **2025**, *61*, 14911-14914

DOI: 10.1039/D5CC04303D



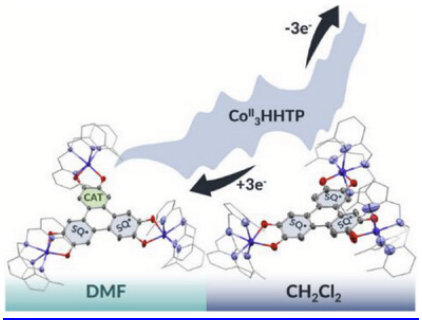
***Abstract*:** We report herein the synthesis of a tridentate ligand (tris-4,4′,4′′-(4′′′-pyridyl)-2,2′:6′,2′′-terpyridine) and its corresponding homoleptic ruthenium(II) complex, which shows stable hydrogen photoproduction under red light (TON of 174 mol_{H2} mol_{PS}^{-1} after 210 hours). A sustained activity under blue and green lights is also observed with TONs above 360 mol_{H2} mol_{PS}^{-1} after 168 hours.

Solvatochromism and Redox Multi-Switch in a Trinuclear Cobalt(II) Complex

Delaporte, S.; Bridonneau, N.; Lambert, F.; Guillot, R.; Suaud, N.; Guihéry, N.; Wang, G.; Rajeshkumar, T.; Maron, L.; Mallah, T.

Chem. Eur. J. **2025**, *31*, e202501455

DOI: 10.1002/chem.202501455



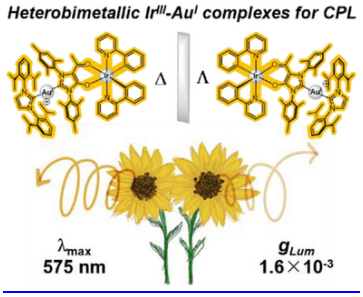
***Abstract*:** A trinuclear cobalt(II) complex incorporating the redox-active hexahydroxytriphenylene (H6HHTP) ligand was prepared and isolated in two different redox states: [CoII3(sq-sq-sq)]3+ (1) and [CoII3(cat-sq-sq)]2+ (2) (sq = semiquinone; cat = catecholate), enabled by its remarkable solvatochromic behavior. The ligand field tuning of the Co(II) centers through the ancillary ligand Me3TPA (tris(6-methyl-2-pyridylmethyl)amine) allowed accessing six reversible one-electron processes instead of only three with the parent TPA ligand, therefore increasing the range of redox-coupled magnetic and optical switching in this system. Upon reduction, the three redox processes are ligand-centered and involve the three sq center dot-/cat2- couples of hexahydroxytriphenylene (HHTP), while we hypothesize that some of the oxidation processes may involve the Co(II) metallic species.

Mono- IrIII versus Heterobimetallic IrIII-AuI Complexes for Circularly Polarized Luminescence

Ballerini, L.; Gourlaouen, C.; Delporte-Pébay, M.; Avila, C. C.; Voirin, E.; Cesar, V.; Bellemin-Laponnaz, S.; Crassous, J.; Daniel, C.; Mauro, M.

Chem. Eur. J. **2025**, *31*, e202501611

DOI: 10.1002/chem.202501611



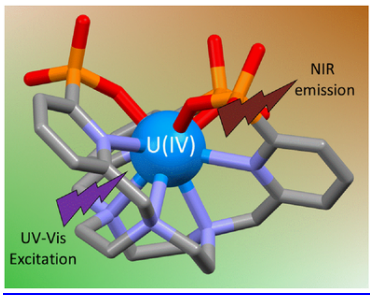
***Abstract*:** Fundamental rationalization of the structural—circularly polarized luminescence (CPL) activity relationship is a challenging task. Herein, a pair of enantiopure, heterobimetallic IrIII–AuI complexes IrAu-4 featuring chirality-at-metal is thoroughly investigated by means of spectroscopical and computational techniques, also including spin-orbital coupling (SOC) effects. Upon resolution of the racemic mixture of the starting chloro-bridged dimer via a chiral auxiliary ligand, the complexes IrIII–AuI are straightforwardly prepared in a stepwise procedure with retention of configuration in good yields. The IrAu-4 complexes display moderate orange phosphorescence arising from an admixed metal-to-ligand and ligand-to-ligand charge transfer (3MLCT/3LLCT) excited state and good chiroptical activity, as shown by both electronic circular dichroism (ECD) and CPL spectroscopy. A comparison between the parental mononuclear pairs Δ-Ir(ppy)2(acac) and Λ-Ir(ppy)2(acac) and the binuclear IrAu-4 counterparts also provides interesting insights. The latter possess higher dissymmetry factor (gLum) values despite the very similar ECD activity of the lower-lying 1MLCT band with enantiospecific polarization bias of the light dictated by the chiral-at-metal configuration. The different nature of the emissive excited state between the two families of complexes and its implication onto the radiative rate constant and the dipolar force is tentatively accounted for the increased CPL-activity observed in IrAu-4.

A Water Stable U(IV) Complex Based on a Macrocyclic Ligand Displaying NIR Emission

Jourdain, E.; Arab, M.; Platas-Iglesias, C.; Esteban-Gómez, D.; Natrajan, L. S.; Lecointre, A.; Elhabiri, M.; Charbonnière, L. J.

Chem. Eur. J. **2025**, *31*, e01723

DOI: 10.1002/chem.202501723



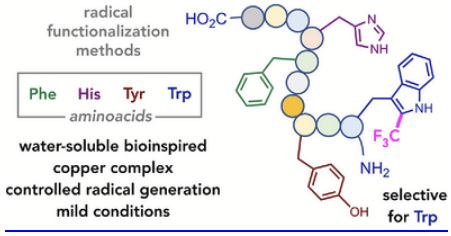
***Abstract*:** Complexation of U(IV) by encapsulation into the cavity of a 1,4,7-triazacyclonane (tacn) macrocycle functionalized by phosphonated pyridyl arms affords a water-stable and soluble [U(IV)L] complex. The coordination process was monitored by electronic UV-Vis-NIR absorption spectroscopy and the corresponding complex was characterized by 1H-, 13C- and 31P-NMR spectroscopy and by mass spectrometry. Density functional theory (DFT) modeling shows the cation to be embedded into the cavity of the nonadentate ligand, as confirmed by analysis of the paramagnetic contributions of U(IV) on the chemical shifts of the proton nuclei. This effective chelation enabled the observation of a broad NIR emission band centered at 1080 nm observed for the first time in addition to UV-visible emission arising from the U(IV) cation upon electronic excitation in the UV-blue region. The [U(IV)L] complex was shown to be hydrolytically stable for several weeks in aqueous solutions over a broad range of pH values (from 1.6 to 10) under aerobic conditions.

Mild and Selective Trifluoromethylation of Peptides at Tryptophane Residues by a Water-Soluble Copper Complex with Redox-Active Ligands

Tilly, M.-J.; Groslambert, L.; Le Breton, N.; Choua, S.; Melin, F.; Hellwig, P.; Weissenberger, T.; Faller, P.; Raibaut, L.; Desage-El Murr, M.

Chem. Eur. J. **2025**, *31*, e01765

DOI: 10.1002/chem.202501765



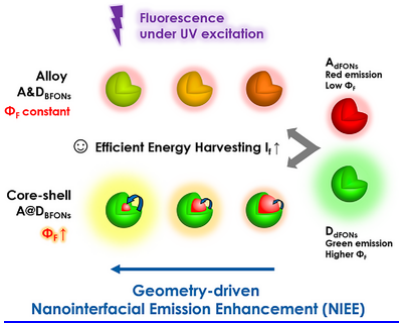
***Abstract*:** Selective chemical modifications of biomolecules are in high demand for the development and implementation of chemical biology strategies. Methods involving radicals have emerged as powerful options yet potentially generate side reactivities when involving harsh reaction conditions. We report the development of a mild catalytic method for the selective functionalization of tryptophane residues in peptides with a trifluoromethyl group using a water-soluble copper complex with redox-active ligands. This method displays both inter- and intramolecular selectivity for tryptophane residues and its synthetic relevance is demonstrated by the selective conversion of a 13-residue peptidic sequence and an endomorphine analogue in good yields.

Toward Organic Mimics of Metallic Nanoparticles: Tuning and Enhancing Fluorescence in Binary Dye-Based Nanoparticles

Kurek, E.; Rosendale, M.; Recher, G.; Verlhac, J.-B.; Marais, S.; Daniel, J.; Blanchard-Desce, M.

Chem. Eur. J. **2025**, *31*, e01698

DOI: 10.1002/chem.202501698



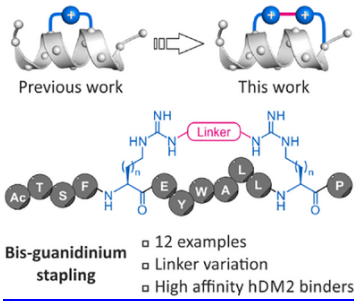
***Abstract*:** A key characteristic of binary metallic nanoparticles is the extreme tuneability of their optical properties through small changes in their composition and structure. Organic mimics of such binary metallic nanoparticles with similar properties would be of major interest. Here, we present Binary Fluorescent Organic Nanoparticles (hereafter termed BFONs) made from two structurally similar but optically complementary polar and polarizable dyes (PPDs) (i.e., energy donor D and energy acceptor A) as such potential mimics. We designed dye-based core-shell and alloy BFONs with varying composition (i.e., D versus A content) and investigated their fluorescence properties. In both core-shell and alloy BFONs, the donor dyes efficiently harvest energy–through Förster Resonance Energy Transfer (FRET)–resulting in substantial brightness values (up to 1.3 108 M−1cm−1 per nanoparticle). However, BFONs' luminescence properties were found to strongly depend on their nanostructuration. Core-shell BFONs exhibit a Nano Interfacial Emission Enhancement (NIEE) effect, consisting in a blue-shifted fluorescence and enhanced FRET-mediated fluorescence quantum yield, compared to alloy BFONs of identical composition–but devoid of a core-shell topology. Moreover, we demonstrate for the first time that the extent of this NIEE effect directly depends on BFONs composition, and increases with the D/A ratio. Furthermore, bioimaging in live cells reveals that BFONs retain their binary nature and unique fluorescence properties in cellular environments.

A General Synthesis Approach to Double-Guanidinium Stapled Peptides and Foldamers

Neuville, M.; Bornez, M. M.; Bourgeais, M.; Samueli, H.; Mauran, L.; Goudreau, S. R.; Khatib, A.-M.; Guichard, G.; Pasco, M.

Chem. Eur. J. **2025**, *31*, e02273

DOI: 10.1002/chem.202502273



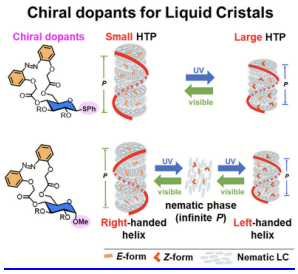
***Abstract*:** In the broader context of peptide macrocyclization, methods enabling the formation of specific crosslinks between orthogonally protected, amino-functionalized side chains (e.g., Lys–Lys crosslinks) are of potential interest for expanding molecular diversity and stabilizing peptide secondary structures. We recently introduced a solid-phase synthesis approach for the rapid generation of guanidinium stapled helical peptides and have shown their utility for inhibition of protein–protein interactions. Whereas our previous work concentrated on the formation of mono-guanidinium crosslinks, we show here that we can expand this approach to prepare bis-guanidinium stapled peptides and foldamers on-resin. The methodology similarly uses two orthogonally protected amino-functionalized side chains and features the use of a diamino connector. The two guanidinium groups are introduced sequentially, the first one intermolecularly and the second intramolecularly. The method is compatible with the i,i + 4 and i,i + 7 cyclization schemes and tolerates a diversity of diamino linkers. We applied the strategy to the synthesis of macrocyclic inhibitors of hDM2 and hDMX and identified several high affinity binders for the two proteins.

Azobenzene-Based Glycomacrocycles: Synthesis, Photoisomerization, and Photomodulation of Liquid Crystal Helical Pitch with Helix Inversion

Li, G.; Hatano, R.; Maisonneuve, S.; Iimura, K-i.; Kim, Y.; Xie, J.

Chem. Eur. J. **2025**, *31*, e02131

DOI: 10.1002/chem.202502131



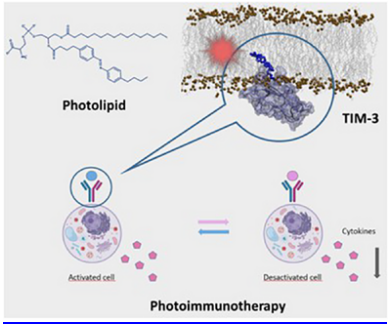
***Abstract*:** Novel azobenzene-embedded glycomacrolactones bearing different substituents on the glucopyranoside ring have been synthesized and characterized by NMR spectroscopy, UV/vis spectroscopy, and circular dichroism (CD), then applied for cholesteric liquid crystal photomodulation. All the macrocycles displayed good photochromic properties, fatigue resistance, thermal bistability, and chiroptical activity. As chiral dopants for nematic liquid crystal (NLC), an amplification of helix upon E to Z photoisomerization and enforcement of helical twisting power (HTP) at Z-rich state have been observed. We also demonstrated the critical influence of sugar-ring functionalization in governing chirality transfer and photoswitching behavior in cholesteric liquid crystals (CLCs). Two of the synthesized glycomacrocycles uniquely achieved photoinduced helix inversion—marking the first such example for this class of compounds.

Unraveling the Role of Azobenzene-Based Photoswitchable Lipids in Controlling Innate Immune Response

Delova, A.; Makhloutah, A.; Bernhard, Y.; Pasc, A.; Monari, A.

Chem. Eur. J. **2025**, *31*, e01824

DOI: 10.1002/chem.202501824



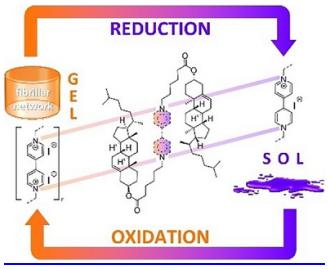
***Abstract*:** The control of the activation of the innate immune response, notably by using suitable visible light sources, may lead the way to the development of phototimmunotherapeutic strategies. In this contribution we analyze the effects of the E/Z interconversion on a phosphatidyl serine lipid containing an isomerizable azobenzene moiety, which has recently been shown to regulate the activation of natural killer cells and the production of cytokines [J. Am. Chem. Soc. 2022, 144, 3863 − 3874]. In particular, we analyze the differential interactions of the innate immune system TIM-3 sensors. We show, resorting to long-range molecular dynamic simulations including enhanced sampling, that the Z isomer leads to a slight decrease of the binding free energy coupled with a less pronounced rigidification of the protein compared to the E isomer and the native lipid, justifying its less pronounced activation of the immune response.

Reversible Self-assembly of a Viologen-based Supramolecular Gel Network under Electrochemical Control

Andrieux, V.; Savin, R.; Bauland, J.; Chevallier, F.; Gibaud, T.; Frath, D.; Bucher, C.

Chem. Eur. J. **2025**, *31*, e02489

DOI: 10.1002/chem.202502489



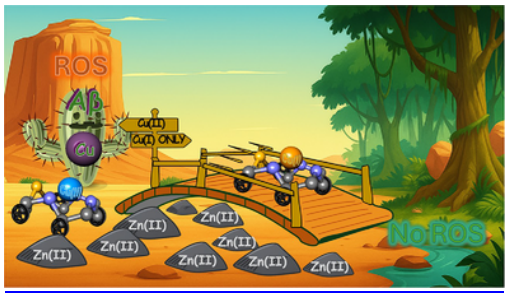
***Abstract*:** Redox-responsive supramolecular gels involving highly ordered assemblies of small molecules that can exist in different stable oxidation states are very promising soft materials for many applications ranging from catalysis to electronics. Stimulation of such materials has however so far relied mainly on the addition of chemical fuels (oxidizing or reducing agents) which makes the reversibility of the induced phenomena intrinsically limited. In this context, electrochemical stimulation is particularly interesting but unfortunately remains largely unexplored due to major scientific and technical obstacles. Here we present the electrochemical response of a supramolecular gel obtained by self-assembly of a low molecular weight gelator derived from 4,4'-bipyridinium salts into chiral hollow fibers. The reduction of this viologen-based supramolecular gel was carried out under both photochemical and electrochemical stimulation. The effects of reduction on sample composition and microstructure have been extensively studied using in operando optical microscopy and absorption spectroscopy measurements. We found that the reduction-triggered macroscopic changes result from the dissociation of charge-transfer complexes formed between the viologen acceptor and iodide counter-anions to form π-dimers. We have also developed different strategies to stimulate the viologen subunits that are embedded in the supramolecular network of the gel. The dissolution and reformation of the viologen-based supramolecular network could thus be achieved using different electrochemical stimuli. We therefore report here one of the very first low molecular weight gels capable of undergoing a reversible electrochemically-induced phase transition.

Cu(I) Is a Game Changer in the Arrest of Cu(Aβ)-Induced ROS Production in the Presence of Competing Zn(II) Ions

Drommi, M. ; Malikidogo, K. P. ; Atrián-Blasco, E. ; Esmieu, C. ; Hureau, C.

Chem. Eur. J. **2025**, e02352

DOI: 10.1002/chem.202502352



***Abstract*:** ROS production due to Cu(amyloid-β) redox cycling is proposed to contribute to the oxidative stress observed in Alzheimer's disease brains. We previously reported on a nitrogen and sulfur-containing ligand, L, able to arrest Cu(Aβ)-induced ROS production [Chem. Eur. J. 2023, 29,]. In the present study, the intricate mechanism by which L maintains its protective activity in the presence of Zn, an abundant endogenous metal ion found in the synaptic cleft, is disentangled with the use of complementary spectroscopic and analytical investigations. This mechanism, which we refer to as kinetic Cu(I) shunt, relies on a faster Cu(I) than Zn transfer from Cu,Zn(Aβ) to L, followed by a fast re-oxidation of Cu(I)(L) to Cu(II)(L), which is redox-inert (i.e. resistant against reduction from ascorbate). This study hence provides new insights into the kinetic involvement of Cu(I) ions in the inhibition of Cu(Aβ)-associated ROS production in presence of Zn.