Société Chimique de France
Le réseau des chimistes

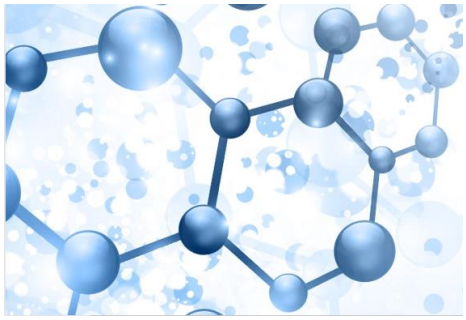
N° 12

ECHO DCO

Janvier 2022

La lettre du bureau de la Division de Chimie Organique

SOMMAIRE



LE MOT DE LA PRÉSIDENTE

Chers Sociétaires,

C'est au nom de l'ensemble du bureau, que je vous souhaite une excellente année 2022, qu'elle vous permette de vivre de nombreux bonheurs personnels et satisfactions professionnelles. Je me permets d'être raisonnablement optimiste pour penser pouvoir nous retrouver en présence plus facilement cette année !

Aussi, après une journée d'automne qui a rassemblé plus de 200 d'entre nous en mode hybride pour écouter des conférences passionnantes et inspirantes, prenez bien note de nos deux prochains rendez-vous : la Journée de Printemps le 5 avril prochain sur le site des Cordeliers à Paris et les Journées de Chimie Organique du 2 au 4 novembre 2022 à l'Ecole Polytechnique à Palaiseau. Vous allez pouvoir dans cette gazette découvrir les programmes que nous vous proposons ; les sites Web sont en cours de finalisation.

Nous lançons également l'appel d'offre pour les prix annuels de notre Division ; ils sont au nombre de 8, ils s'adressent à des candidatures directes ou par nomination, et sont à destination des chimistes organiciens adhérents à la SCF, à des stades différents de leur carrière. N'hésitez pas à concourir, ils sont là pour vous, pour promouvoir la chimie organique française en France et à l'International ; nous ne comptons chaque année que trop peu de candidatures féminines.

Au plaisir de vous retrouver très bientôt, nombreux, à nos manifestations pour des échanges fructueux.

Très cordialement,

Emmanuelle Schulz, Présidente de la DCO

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JOURNEE D'AUTOMNE 2021

La **Journée d'Automne de la DCO** s'est déroulée le mercredi **1 décembre 2021** sur le campus des Cordeliers de Sorbonne Université. Pour la première fois depuis presque 2 années, nous avons eu le plaisir de nous retrouver en présentiel et avons innové avec un mode hybride. Ainsi, en plus des participants, nombre d'entre vous ont pu suivre la journée grâce au streaming organisé avec le concours de Chemistry-Europe et d' *Eur. J. Org. Chem.* Nous remercions chaleureusement leurs équipes, et en particulier Anne Nijs et Leana Travaglini pour ce partenariat renouvelé.

Au cours de cette journée, nous avons eu le plaisir d'écouter Christoph Sparr, de nombreux récipiendaires des prix de la DCO (Jeanne Crassous, Julien Leclaire, Julie Oble, Yannick Geiger, Sophie Feuillastre, Charlotte Lorton, Davide Audisio) et de renouer avec la tradition des communications orales (Lucile Anthore-Dalion, Vincent Bizet, Rafael Gramage-Doria et Jennifer Molloy).

Cette journée a été un franc succès, que cela soit en présentiel et en distanciel et l'expérience de l'hybride sera renouvelée !

DISTINCTIONS AU SEIN DE LA SCF

Le Pr Cyrille Kouklovsky a été nommé membre distingué de la SCF. Cyrille a, entre autres, occupé la présidence de la DCO pendant le mandat 2015-2018 ; nous le félicitons chaleureusement !

https://new.societechimiquedefrance.fr/distinctions_cat/membres-distingues/

AVOS AGENDAS : Journée de Printemps 2022 de la DCO

La Division de Chimie Organique a le plaisir de vous annoncer que la **Journée de Printemps de la DCO** se déroulera le mardi **5 avril 2022** à l'amphi Farabeuf du campus des Cordeliers de Sorbonne Université (métro Cluny-La Sorbonne ou Odéon).

Le programme comprendra:
- 2 conférenciers invités:

Prof Nathalie KATSONIS del'Université de Groningen (Pays-Bas) http://www.katsonis.eu/

Prof Ryan GILMOUR de l'Université de Münster (Allemagne). https://www.uni-muenster.de/Chemie.oc/gilmour/

- 4 lauréats des prix de la DCO 2021:

Gilles GUICHARD	Prix de la DCO 2021, IECB, Bordeaux
William ERB	Prix Jean NORMANT 2021, ISCR, Rennes
Samir MESSAOUDI	Prix Jean-Marie LEHN 2021, BioCIS, Chatenay-Malabry
Johanna FREY	Prix de thèse Henri KAGAN 2021, LIMA, Strasbourg

- 5 communications orales jeunes chercheurs. Retrouvez l'appel à candidature ci-dessous et sur notre site web https://new.societechimiquedefrance.fr/divisions/chimie-organique/

Pour rappel, ces journées de la DCO sont gratuites, même si l'inscription est obligatoire, et réservées aux adhérents de la SCF. Pour les non-adhérents, elles constituent une occasion pour rejoindre la SCF. https://new.societechimiquedefrance.fr/adherer-a-la-scf/

Cette journée sera effectuée en mode hybride et donc accessible en visioconférence. Les informations seront disponibles sur le site web. L'accès en présentiel sera conditionné à la présentation du pass vaccinal. Toutes les informations sont disponibles sur le site https://dco-spring-22.sciencesconf.org

APPEL A COMMUNICATION ORALES POUR LA JOURNEE DE PRINTEMPS 2022

Dans le cadre de sa prochaine **Journée de Printemps 2022** (mardi 5 avril 2022), la Division de Chimie Organique lance un appel à candidature pour des communications orales auprès de ses membres sociétaires occupant une position permanente depuis moins de 7 ans.
Le bureau de la DCO sélectionnera **5 personnes** qui seront invitées à présenter une communication orale à la Journée de Printemps. Les frais de voyage et d'hébergement seront à la charge des lauréats.

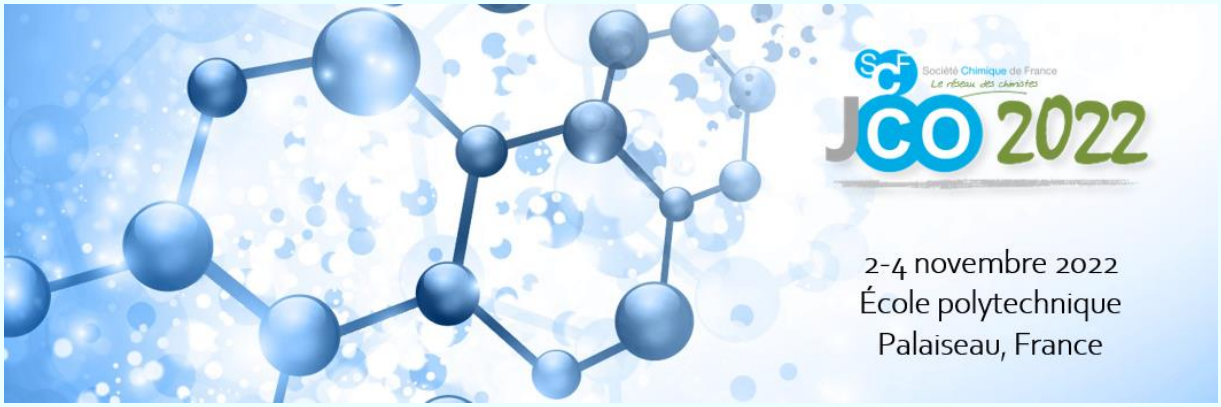
Critères d'éligibilité :
- Être sociétaire de la SCF depuis au moins 1 an.
- Occuper une position permanente (académique ou industrielle) depuis moins de 7 ans (nomination à partir de 2015).

Procédure :
- Communication en anglais de 15 minutes (questions comprises).
- Les résumés des communications (1 page max. en pdf suivant le template) doivent être envoyés sous forme électronique uniquement **avant le 4 mars 2022 à 17 h** à : Morgan Donnard donnard@unistra.fr

L'appel à candidature et le template peuvent être trouvés sur le site internet de la DCO : https://new.societechimiquedefrance.fr/divisions/chimie-organique/

A VOS AGENDAS : Journées de Chimie Organique 2022

La Division de Chimie Organique a le plaisir de vous annoncer que les **Journées de Chimie Organique 2022** se dérouleront du **2 au 4 novembre 2022** à l'Ecole polytechnique.



Conférenciers invités

Clémence ALLAIN	ENS Paris-Saclay, *France*
Valentine ANANIKOV	Zelinsky Institute of Organic Chemistry, *Russia*
Margaret BRIMBLE	University of Auckland, *New Zealand*
Louis-Charles CAMPEAU	Merck, *USA*
Sukbok CHANG	Korea Advanced Institute of Science and Technology (KAIST), *Korea*
Mélanie ETHEVE-QUELQUEJEU	Université de Paris, *France*
Nicolas GIUSEPPONE	Université de Strasbourg, *France*
Shū KOBAYASHI	University of Tokyo, *Japan*
Eric MEGGERS	University of Marburg, *Germany*
Laurence MULARD	Institut Pasteur, *France*
Timothy NOEL	University of Amsterdam, *Netherlands*
Monica PEREZ-TEMPRANO	Institut Català d'Investigació Química (ICIQ), *Spain*
Sarah REISMAN	California Institute of Technology, *USA*

Le programme sera complété par des conférences données par des industriels et les lauréats des prix de la DCO 2022.

De nombreuses communications orales ouvertes aux jeunes chercheurs seront sélectionnées dans des domaines variés tels que la catalyse, les nouvelles méthodes en synthèse organique, la synthèse totale de produits naturels, la chimie médicinale, la chimie durable, la chimie bio-organique, la chémo-biologie, la chimie supramoléculaire, ainsi que les applications dans le domaine des matériaux et de l'énergie. Deux sessions de présentations de posters seront également programmées.

Des Packs « inscription 5+1 » sont ouverts à tous les membres de la SCF.

Date limite d'inscription pour bénéficier de tarifs réduits : **15 juillet 2022**

Société Chimique de France
Le réseau des chimistes

APPEL A CANDIDATURE POUR LES PRIX DE LA DCO 2022

Date limite de candidature : le **mardi 16 mars 2022** à midi.

La Division de Chimie Organique attribuera en 2022 :

- Deux prix de thèse Dina Surdin et Henri Kagan (candidature par nomination)
- Prix Emergence Marc Julia (candidature directe)
- Deux prix jeunes chercheur et enseignant-chercheur Jean-Pierre Sauvage et Jean Normant (candidature directe)
- Un prix chercheur enseignant-chercheur avancé Jean-Marie Lehn (candidature directe)
- Un prix industriel Yves Chauvin (candidature par nomination)
- Le prix de la DCO (candidature par nomination)

Quelques généralités avant le détail prix par prix.

- Les candidats et candidates pour tous ces prix doivent être membres de la SCF affiliés à la DCO.
- Pour les dossiers présentés par nomination *(cf ci-dessous au cas par cas)*, la personne qui propose et présente une candidature doit également être membre de la SCF.
- Pour les candidatures par nomination *(cf ci-dessous en fonction des prix)*, les candidats et candidates nominés devront, après avoir été informés, envoyer eux-mêmes leur dossier.
- L'ensemble des pièces demandées doit être envoyé en version électronique aux personnes indiquées *(cf ci-dessous)*.
- Les lauréats et lauréates seront invités à présenter leurs travaux lors des manifestations de la DCO.

Prix de thèse Dina SURDIN et Henri KAGAN

La division de Chimie organique de la SCF attribuera 2 prix de thèse : le prix de thèse Henri Kagan et le prix Dina Surdin. Sont éligibles, les thèses soutenues pendant l'année civile précédant l'année du prix (2021).

Les doctorants encadrés ou co-encadrés par les membres du bureau de la DCO ne sont pas éligibles.

Les dossiers de candidature devront être adressés à Stéphanie Norsikian uniquement par mail (stephanie.norsikian@cnrs.fr) avant le 16 mars 2022 à midi et comporter :

- CV du candidat
- Avis du responsable de l'encadrement et/ou du directeur d'équipe et/ou du directeur du laboratoire.
- Résumé du manuscrit de thèse (3 pages max.) sous format pdf
- La copie des publications (format pdf).

Les **candidatures se feront par nomination**, c'est-à-dire que le dossier devra être présenté par exemple par les sections régionales de la SCF, les directeurs de Laboratoire, d'équipes ou de groupes ou encore les directeurs de thèse.

Prix Emergence Marc JULIA (*moins de 6 ans de métier de la recherche après la thèse*)

La Division de Chimie Organique attribue un prix à un docteur, membre de la SCF-DCO, ayant soutenu sa thèse après le **1er mars 2016**.(1)

Les candidatures doivent être accompagnées d'un CV détaillé, d'un document de titres et travaux, 1 à 3 diapositives résumant les faits marquants des travaux, des tirés à part des 5 publications jugées les plus significatives (format pdf), et être envoyées avant le 16 mars 2022 à midi à Anis Tlili (anis.tlili@univ-lyon1.fr).

Le principe retenu pour le dépôt de dossier est celui de la **candidature spontanée**.

(1) Pour les femmes, la limite est reculée d'un an par enfant à charge né pendant cette période.

Prix Jeune Enseignant-Chercheur Jean NORMANT (*moins de 8 ans de carrière*)
La Division de Chimie Organique attribue un prix à un jeune enseignant-chercheur en poste au plus tôt depuis la rentrée universitaire 2014-2015,[(1)] effectuant ses travaux en France, et membre de la SCF-DCO depuis au moins trois ans. Les candidatures doivent être accompagnées d'un CV détaillé, d'un document de titres et travaux, 1 à 3 diapositives résumant les faits marquants des travaux, des tirés à part des 5 publications jugées les plus significatives (format pdf), et être envoyées avant le 16 mars 2022 à midi à Cyril Ollivier (cyril.ollivier@sorbonne-universite.fr).
Le principe retenu pour le dépôt de dossier est celui de la **candidature spontanée**.

Prix Jeune Chercheur Jean-Pierre SAUVAGE (*moins de 8 ans de carrière*)
La Division de Chimie Organique attribue un prix à un jeune chercheur en poste au plus tôt depuis la rentrée universitaire 2014-2015,[(1)] effectuant ses travaux en France, et membre de la SCF-DCO depuis au moins trois ans. Les candidatures doivent être accompagnées d'un CV détaillé, d'un document de titres et travaux, 1 à 3 diapositives résumant les faits marquants des travaux, des tirés à part des 5 publications jugées les plus significatives (format pdf), et être envoyées avant le 16 mars 2022 à midi à Samir Messaoudi (samir.messaoudi@universite-paris-saclay.fr).
Le principe retenu pour le dépôt de dossier est celui de la **candidature spontanée.**

Prix Chercheur Enseignant-Chercheur Avancé Jean-Marie LEHN (*8-15 ans de carrière*)
La Division de Chimie Organique attribue un prix à un chercheur ou enseignant-chercheur avancé ayant pris ses fonctions entre les rentrées universitaires 2007-2008 et 2013-2014,[(1)] effectuant ses travaux en France, et membre de la SCF-DCO depuis au moins trois ans. Les candidatures doivent être accompagnées d'un CV détaillé, d'un document de titres et travaux, 1 à 3 diapositives résumant les faits marquants des travaux, des tirés à part des 5 publications jugées les plus significatives (format pdf), et être envoyées avant le 16 mars 2022 à midi à Sébastien Vidal (sebastien.vidal@cnrs.fr). Le principe retenu pour le dépôt de dossier est celui de la **candidature spontanée**.

Prix Industriel Yves CHAUVIN
La Division de Chimie Organique attribue un prix à un chimiste ou une chimiste développant ses travaux en milieu industriel. Les candidatures doivent être accompagnées d'un CV détaillé, d'un document de titres et travaux, et être envoyées avant le 16 mars 2022 à midi à Morgan Donnard (donnard@unistra.fr).
Le principe retenu pour le dépôt de dossier est celui de la **candidature spontanée ou par nomination** (par une entité de la SCF, ou un responsable scientifique académique ou industriel).

Prix de la DCO
Le Prix de la Division Chimie Organique est attribué à un chimiste ou une chimiste confirmé ayant effectué des travaux de recherche reconnus au niveau national et international, et membre de la SCF-DCO depuis au moins trois ans. Les candidatures doivent être accompagnées d'un CV détaillé, d'un document de titres et travaux, et être envoyées avant le 16 mars 2022 à midi à Emmanuelle Schulz (emmanuelle.schulz@universite-paris-saclay.fr).
Le principe retenu pour le dépôt de dossier est celui de la **candidature par nomination** (par une entité de la SCF, ou un responsable scientifique académique ou industriel).

[(1)] Pour les femmes, la limite est reculée d'un an par enfant à charge né pendant cette période

CONGRES A VENIR SOUTENUS PAR LA DCO

- Le 4ème **International Green Catalysis Symposium** se déroulera du 19 au 22 avril 2022 à Rennes, avec le soutien de la DCO. La deadline pour les demandes de communications orales est fixée au 15/02/2022
  https://igcs2020.sciencesconf.org
- Le 3ème **Colloque Français de Chimie du Fluor** (CFCF), qui se déroulera à Forges-les-Eaux en Seine-Maritime du 16 au 19 mai 2022 a reçu le soutien financier de la DCO. La date limite pour les demandes de communications orales est fixée au 31/01/2022 et pour les posters au 15/03/2022.
  https://cfcf2022.sciencesconf.org/

COMMUNICATION DU GROUPE SUPRA ET APPEL A CANDIDATURE AUX PRIX

Chères collègues, Chers collègues,

Vous êtes plus de 400 à avoir rejoint le groupe **supraSCF** depuis sa création, démontrant l'intérêt fort de la communauté pour la chimie supramoléculaire, une aventure interdisciplinaire qui rassemble des chimistes français.es de nombreux domaines, tels que la chimie (métallo-)organique, la chémobiologie, ou encore la science des matériaux. Nous vous remercions pour votre soutien et poursuivrons nos efforts vers la promotion de notre discipline en 2022:

- Dans la continuité du succès du congrès **Supr@Strasbourg 2021** et dans l'attente de **Supr@Paris 2023**, nous vous proposons de nous réunir le **19 et 20 mai 2022 à Lyon** pour les **Journées de Chimie Supramoléculaire**. En plus de l'intervention de trois scientifiques de renom (Jean-Pierre Majoral, Emilie Moulin et Julien Leclaire), ce symposium souhaite donner une large part à l'intervention des jeunes chercheuses et de jeunes chercheurs (doctorant·e·s et post-doctorant·e·s) qui sont l'avenir de notre discipline.
- Deux chercheurs exceptionnels (Mir Wais Hosseini et Sébastien Goeb) avaient été récompensés en 2020 par les **Prix Senior et Junior du Groupe de Chimie Supramoléculaire** de la Société Chimique de France. Cette année, ces récompenses seront à nouveau décernées mais deviennent les **prix André Collet** et **Christiane Dietrich-Buchecker**, permettant ainsi d'honorer la mémoire de deux géants de la chimie supramoléculaire française. Les lauréat·e·s seront invité·e·s à présenter leurs travaux lors de **Supr@Paris 2023**. Le principe retenu pour le dépôt des dossiers est celui de la candidature spontanée, et la date limite de candidature est le 22 avril 2022 à midi.

Le prix **Christiane Dietrich-Buchecker** est attribué à un·e chimiste de moins de 45 ans effectuant ses travaux en France et membre de la SCF depuis au moins trois ans. 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@univ-lyon1.fr).
Le prix **André Collet** est attribué à un·e chimiste confirmé·e ayant effectué des travaux de recherche reconnus au niveau national et international, et membre de la SCF depuis au moins trois ans. 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 Jean-François Nierengarten (nierengarten@unistra.fr).

Vous pouvez également retrouver les actualités du groupe sur notre site internet https://new.societechimiquedefrance.fr/groupes/chimie-supramoleculaire et sur notre compte Twitter @supraSCF
Dans l'attente d'échanges féconds avec vous en 2022, les membres du bureau du groupe supraSCF vous adressent leurs meilleurs vœux pour cette nouvelle année que nous vous souhaitons de vivre avec beaucoup de succès et de bien-être.
Bien à vous,
Le Bureau du Groupe de Chimie Supramoléculaire

LES HIGHLIGHTS DE LA CHIMIE DE LA DCO

Le bureau de la Division de Chimie Organique se propose de mettre en valeur chaque semestre les articles les plus significatifs dont les auteurs correspondants sont membres de notre division.

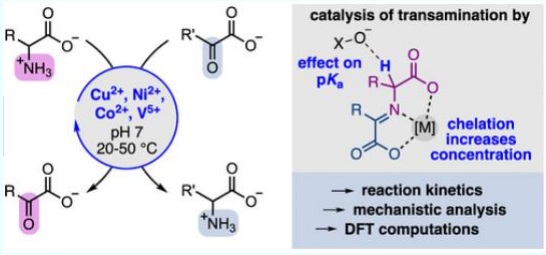
Vous trouverez dans les pages suivantes un choix d'articles publiés sur la période juillet 2021-décembre 2022 dans les journaux suivants :
- *J. Am. Chem. Soc.*
- *Chem. Sci.*
- *Chem*
- *Angew. Chem. Int. Ed.*

Nous avons conscience que ce choix d'articles est arbitraire. N'hésitez pas à nous faire part de vos remarques, et, éventuellement, à nous soumettre des propositions de travaux à « mettre en lumière ».

Mechanistic Insight into Metal Ion-Catalyzed Transamination

Robert J. Mayer, Harpreet Kaur, Sophia A. Rauscher, and Joseph Moran* *J. Am. Chem. Soc.* **2021**, *143*, 19099–19111

https://dx.doi.org/10.1021/jacs.1c08535

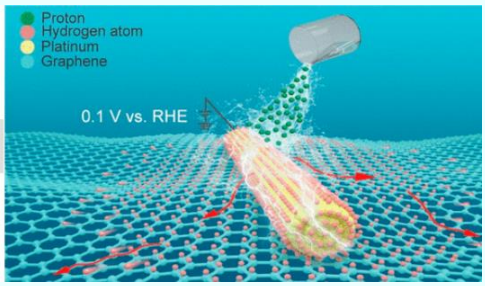


Several classes of biological reactions that are mediated by an enzyme and a co-factor can occur, to a slower extent, not only without the enzyme but even without the co-factor, under catalysis by metal ions. This observation has led to the proposal that metabolic pathways progressively evolved from using inorganic catalysts to using organocatalysts of increasing complexity. Transamination, the biological process by which ammonia is transferred between amino acids and α-keto acids, has a mechanism that has been well studied under enzyme/co-factor catalysis and under co-factor catalysis, but the metal ion-catalyzed variant was generally studied mostly at high temperatures (70–100 °C), and the details of its mechanism remained unclear. Here, we investigate which metal ions catalyze transamination under conditions relevant to biology (pH 7, 20–50 °C) and study the mechanism in detail. Cu^{2+}, Ni^{2+}, Co^{2+}, and V^{5+} were identified as the most active metal ions under these constraints. Kinetic, stereochemical, and computational studies illuminate the mechanism of the reaction. Cu^{2+} and Co^{2+} are found to predominantly speed up the reaction by stabilizing a key imine intermediate. V^{5+} is found to accelerate the reaction by increasing the acidity of the bound imine. Ni^{2+} is found to do both to a limited extent. These results show that direct metal ion-catalyzed amino group transfer is highly favored even in the absence of co-factors or protein catalysts under biologically compatible reaction conditions.

Electrochemical Storage of Atomic Hydrogen on Single Layer Graphene

Quanfeng He, Lanping Zeng, Lianhuan Han*, Matthew M. Sartin, Juan Peng, Jian-Feng Li, Alexander Oleinick, Irina Svir, Christian Amatore*, Zhong-Qun Tian, and Dongping Zhan* *J. Am. Chem. Soc.* **2021**, *143*, 18419–18425

https://dx.doi.org/10.1021/jacs.1c05253

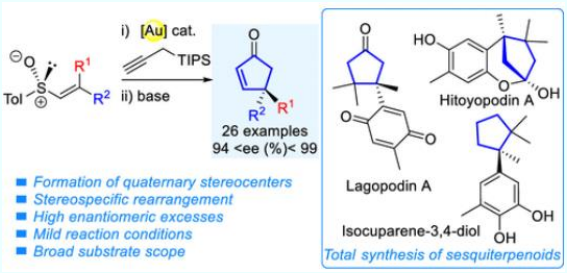


If hydrogen can be stored and carried safely at a high density, hydrogen-fuel cells offer effective solutions for vehicles. The stable chemisorption of atomic hydrogen on single layer graphene (SLG) seems a perfect solution in this regard, with a theoretical maximum storage capacity of 7.7 wt %. However, generating hydrogenated graphene from H_2 requires extreme temperatures and pressures. Alternatively, hydrogen adatoms can easily be produced under mild conditions by the electroreduction of protons in solid/liquid systems. Graphene is electrochemically inert for this reaction, but H-chemisorption on SLG can be carried out under mild conditions via a novel Pt-electrocatalyzed "spillover-surface diffusion-chemisorption" mechanism, as we demonstrate using dynamic electrochemistry and isotopic Raman spectroscopy. The apparent surface diffusion coefficient (~10–5 cm2 s–1), capacity (~6.6 wt %, ~85.7% surface coverage), and stability of hydrogen adatoms on SLG at room temperature and atmospheric pressure are significant, and they are perfectly suited for applications involving stored hydrogen atoms on graphene.

Synthesis of Cyclopentenones with C4-Quaternary Stereocenters via Stereospecific [3,3]-Sigmatropic Rearrangement and Applications in Total Synthesis of Sesquiterpenoids

Weiping Zhou and Arnaud Voituriez**J. Am. Chem. Soc.* **2021**, *143*, 17348–17353

https://dx.doi.org/10.1021/jacs.1c07966

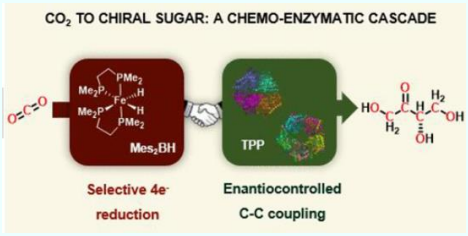


A cationic gold(I)-catalyzed asymmetric [3,3]-sigmatropic rearrangement of sulfonium leads after cyclization to cyclopentenones with a C4-quaternary stereocenter. Starting with simple vinyl sulfoxides and propargyl silane, numerous compounds were isolated with moderate to good yields and excellent enantiomeric excesses (26 examples). The application of this simple methodology allowed the efficient total synthesis of five natural sesquiterpenoids, including enokipodin A and B, hitoyopodin A, lagopodin A, and isocuparene-3,4-diol.

Enantioselective Reductive Oligomerization of Carbon Dioxide into l-Erythrulose via a Chemoenzymatic Catalysis

Sarah Desmons*, Katie Grayson-Steel, Nelson Nuñez-Dallos, Laure Vendier, John Hurtado, Pere Clapés, Régis Fauré, Claire Dumon, and Sébastien Bontemps**J. Am. Chem. Soc.* **2021**, *143*, 16274-16283

https://dx.doi.org/10.1021/jacs.1c07872

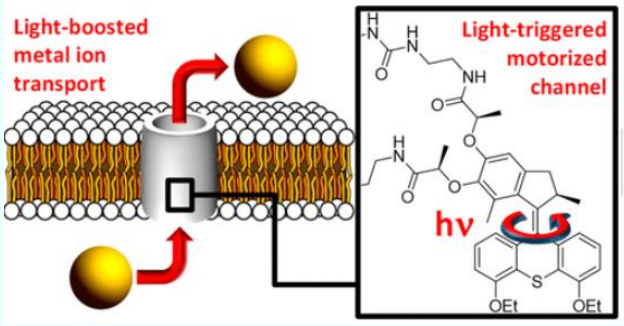


A cell-free enantioselective transformation of the carbon atom of CO_2 has never been reported. In the urgent context of transforming CO_2 into products of high value, the enantiocontrolled synthesis of chiral compounds from CO_2 would be highly desirable. Using an original hybrid chemoenzymatic catalytic process, we report herein the reductive oligomerization of CO_2 into C3 (dihydroxyacetone, DHA) and C4 (l-erythrulose) carbohydrates, with perfect enantioselectivity of the latter chiral product. This was achieved with the key intermediacy of formaldehyde. CO_2 is first reduced selectively by 4e– by an iron-catalyzed hydroboration reaction, leading to the isolation and complete characterization of a new bis(boryl)acetal compound derived from dimesitylborane. In an aqueous buffer solution at 30 °C, this compound readily releases formaldehyde, which is then involved in selective enzymatic transformations, giving rise either (i) to DHA using a formolase (FLS) catalysis or (ii) to l-erythrulose with a cascade reaction combining FLS and d-fructose-6-phosphate aldolase (FSA) A129S variant. Finally, the nature of the synthesized products is noteworthy, since carbohydrates are of high interest for the chemical and pharmaceutical industries. The present results prove that the cell-free de novo synthesis of carbohydrates from CO_2 as a sustainable carbon source is a possible alternative pathway in addition to the intensely studied biomass extraction and de novo syntheses from fossil resources.

Light-Driven Molecular Motors Boost the Selective Transport of Alkali Metal Ions through Phospholipid Bilayers

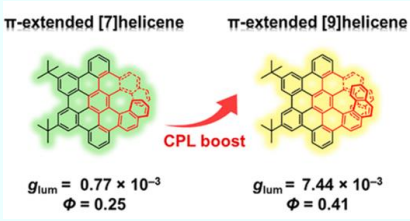
Wen-Zhi Wang, Li-Bo Huang, Shao-Ping Zheng, Emilie Moulin, Odile Gavat, Mihail Barboiu*, and Nicolas Giuseppone* *J. Am. Chem. Soc*. **2021**, *143*, 15653-15660

https://dx.doi.org/10.1021/jacs.1c05750



A hydrophobic light-driven rotary motor is functionalized with two 18-crown-6 macrocycles and incorporated into phospholipid bilayers. In the presence of this molecular construct, fluorescence assays and patch clamp experiments show the formation of selective alkali ion channels through the membrane. Further, they reveal a strongly accelerated ion transport mechanism under light irradiation. This increase of the fractional ion transport activity (up to 400%) is attributed to the out-of-equilibrium actuation dynamics of the light-driven rotary motors, which help to overcome the activation energy necessary to achieve translocation of alkali ions between macrocycles along the artificial channels.

Amplification of Dissymmetry Factors in π-Extended [7]- and [9]Helicenes

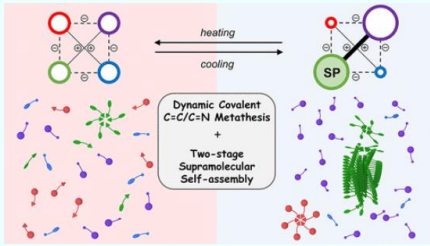


Zijie Qiu, Cheng-Wei Ju, Lucas Frédéric, Yunbin Hu, Dieter Schollmeyer, Grégory Pieters*, Klaus Müllen*, and Akimitsu Narita* *J. Am. Chem. Soc.* **2021**, *143*, 4661–4667

https://dx.doi.org/10.1021/jacs.0c13197

π-Extended helicenes constitute an important class of polycyclic aromatic hydrocarbons with intrinsic chirality. Herein, we report the syntheses of π-extended [7]helicene **4** and π-extended [9]helicene **6** through regioselective cyclodehydrogenation in high yields, where a "prefusion" strategy plays a key role in preventing undesirable aryl rearrangements. The unique helical structures are unambiguously confirmed by X-ray crystal structure analysis. Compared to the parent pristine [7]helicene and [9]helicene, these novel π-extended helicenes display significantly improved photophysical properties, with a quantum yield of 0.41 for **6**. After optical resolution by chiral high-performance liquid chromatography, the chiroptical properties of enantiomers **4**-*P*/*M* and **6**-*P*/*M* are investigated, revealing that the small variation in helical length from [7] to [9] can cause an approximately 10-fold increase in the dissymmetry factors. The circularly polarized luminescence brightness of **6** reaches 12.6 M^{-1} cm^{-1} as one of the highest among carbohelicenes.

Constitutional Dynamic Selection at Low Reynolds Number in a Triple Dynamic System: Covalent Dynamic Adaptation Driven by Double Supramolecular Self-Assembly

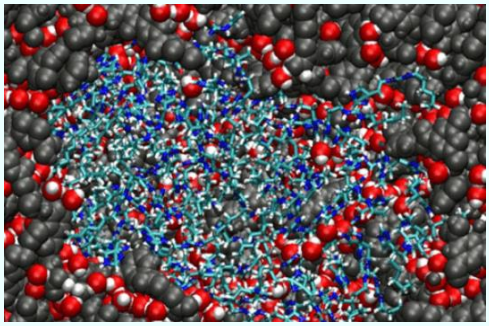


Ruirui Gu and Jean-Marie Lehn* *J. Am. Chem. Soc.* **2021**, *143*, 14136-14146

https://dx.doi.org/10.1021/jacs.1c04446

A triple dynamic complex system has been designed, implementing a dynamic covalent process coupled to two supramolecular self-assembly steps. To this end, two dynamic covalent libraries (DCLs), DCL-1 and DCL-2, have been established on the basis of dynamic covalent C═C/C═N organo-metathesis between two Knoevenagel derivatives and two imines. Each DCL contains a barbituric acid-based Knoevenagel constituent that may undergo a sequential double self-organization process involving first the formation of hydrogen-bonded hexameric supramolecular macrocycles that subsequently undergo stacking to generate a supramolecular polymer SP yielding a viscous gel state. Both DCLs display selective self-organization-driven amplification of the constituent that leads to the SP. Dissociation of the SP on heating causes reversible randomization of the constituent distributions of the DCLs as a function of temperature. Furthermore, diverse distribution patterns of DCL-2 were induced by modulation of temperature and solvent composition. The present dynamic systems display remarkable self-organization-driven constitutional adaption and tunable composition by coupling between dynamic covalent component selection and two-stage supramolecular organization. In more general terms, they reveal dynamic adaptation by component selection in low Reynolds number conditions of living systems where frictional effects dominate inertial behavior.

Bilayer versus Polymeric Artificial Water Channel Membranes: Structural Determinants for Enhanced Filtration Performances



Li-Bo Huang, Maria Di Vincenzo, M. Göktuğ Ahunbay, Arie van der Lee, Didier Cot, Sophie Cerneaux, Guillaume Maurin*, and Mihail Barboiu* *J. Am. Chem. Soc.* **2021**, *143*, 14386-14393

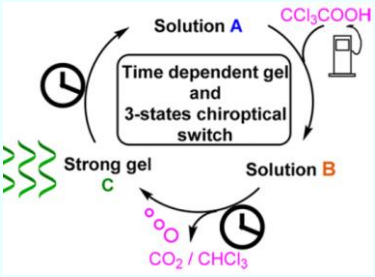
https://dx.doi.org/10.1021/jacs.1c07425

Artificial water channels (AWCs) and their natural aquaporin counterparts selectively transport water. They represent a tremendous source of inspiration to devise biomimetic membranes for several applications, including desalination. They contain variable water-channel constructs with adaptative architectures and morphologies. Herein, we critically discuss the structural details that can impact the performances of biomimetic I quartets, obtained via adaptive self-assembly of alkylureido-ethylimidazoles HC_4–HC18 in bilayer or polyamide (PA) membranes. We first explore the performances in bilayer membranes, identifying that hydrophobicity is an essential key parameter to increase water permeability. We compare various I quartets with different hydrophobic tails (from HC_4 to HC18), and we reveal that a huge increase in single-channel water permeability, from 104 to 107 water molecules/s/channel, is obtained by increasing the size of the alkyl tail. Quantitative assessment of AWC–PA membranes shows that water permeability increases roughly from 2.09 to 3.85 L m–2 h–1 bar–1, for HC_4 and HC6 reverse osmosis membranes, respectively, while maintaining excellent NaCl rejection (99.25–99.51%). Meanwhile, comparable HC8 loading induces a drop of performance reminiscent of a defective membrane formation. We show that the production of nanoscale sponge-like water channels can be obtained with insoluble, low soluble, and low dispersed AWCs, explaining the observed subpar performance. We conclude that optimal solubility enabling breakthrough performance must be considered to not only maximize the inclusion and the stability in the bilayer membranes but also achieve an effective homogeneous distribution of percolated particles that minimizes the defects in hybrid polyamide membranes.

Chemically Fueled Three-State Chiroptical Switching Supramolecular Gel with Temporal Control

Enzo Olivieri, Guilhem Quintard, Jean-Valère Naubron, and Adrien Quintard* *J. Am. Chem. Soc.* **2021**, *143*, 12650-12657

https://dx.doi.org/10.1021/jacs.1c05183

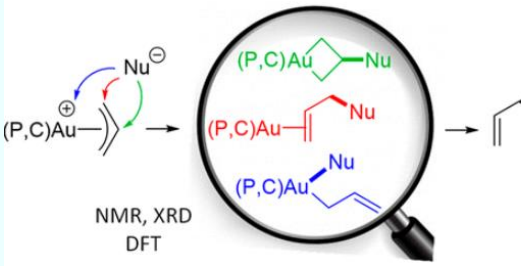


The recent discovery of temporally controlled gels opens broad perspectives to the field of smart functional materials. However, to obtain fully operative systems, the design of simple and robust gels displaying complex functions is desirable. Herein, we fuel dissipative gelating materials through iterative additions of trichloroacetic acid (TCA). This simple fuel enables to switch over time an acid/base-dependent commercially available amino acid gelator/DBU combination between three distinct states (anionic, cationic, and neutral), while liberating volatile CO_2 and $CHCl_3$ upon fuel consumption. Of interest, the anionic resting state of the system is obtained through trapping of 1 equiv of CO_2 through the formation of a carbamate. The system is tunable, robust, and resilient over time with over 25 consecutive sol–gel–sol cycles possible without significant loss of properties. Most importantly, because of the chiral nature of the amino acid gelator, the system features chiroptical switching properties moving reversibly between three distinct states as observed by ECD. The described system considerably enhances the potential of smart molecular devices for logic gates or data storage by adding a time dimension based on three states to the gelating materials. It is particularly simple in terms of chemical components involved, but it enables sophisticated functions.

Nucleophilic Addition to π-Allyl Gold(III) Complexes: Evidence for Direct and Undirect Paths

Jessica Rodriguez, Marte Sofie Martinsen Holmsen, Yago García-Rodeja, E. Daiann Sosa Carrizo, Pierre Lavedan, Sonia Mallet-Ladeira, Karinne Miqueu*, and Didier Bourissou* *J. Am. Chem. Soc.* **2021**, *143*, 11568-11581

https://dx.doi.org/10.1021/jacs.1c04282

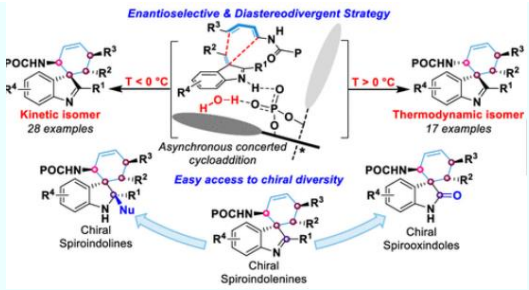


π-Allyl complexes play a prominent role in organometallic chemistry and have attracted considerable attention, in particular the π-allyl Pd(II) complexes which are key intermediates in the Tsuji–Trost allylic substitution reaction. Despite the huge interest in π-complexes of gold, π-allyl Au(III) complexes were only authenticated very recently. Herein, we report the reactivity of (P,C)-cyclometalated Au(III) π-allyl complexes toward β-diketo enolates. Behind an apparently trivial outcome, i.e. the formation of the corresponding allylation products, meticulous NMR studies combined with DFT calculations revealed a complex and rich mechanistic picture. Nucleophilic attack can occur at the central and terminal positions of the π-allyl as well as the metal itself. All paths are observed and are actually competitive, whereas addition to the terminal positions largely prevails for Pd(II). Auracyclobutanes and π-alkene Au(I) complexes were authenticated spectroscopically and crystallographically, and Au(III) σ-allyl complexes were unambiguously characterized by multinuclear NMR spectroscopy. Nucleophilic additions to the central position of the π-allyl and to gold are reversible. Over time, the auracyclobutanes and the Au(III) σ-allyl complexes evolve into the π-alkene Au(I) complexes and release the C-allylation products. The relevance of auracyclobutanes in gold-mediated cyclopropanation was demonstrated by inducing C–C coupling with iodine. The molecular orbitals of the π-allyl Au(III) complexes were analyzed in-depth, and the reaction profiles for the addition of β-diketo enolates were thoroughly studied by DFT. Special attention was devoted to the regioselectivity of the nucleophilic attack, but C–C coupling to give the allylation products was also considered to give a complete picture of the reaction progress.

Enantioselective and Diastereodivergent Synthesis of Spiroindolenines via Chiral Phosphoric Acid-Catalyzed Cycloaddition

Thomas Varlet, Mateja Matišić, Elsa Van Elslande, Luc Neuville, Vincent Gandon*, and Géraldine Masson* *J. Am. Chem. Soc.* **2021**, *143*, 11611-11619

https://dx.doi.org/10.1021/jacs.1c04648

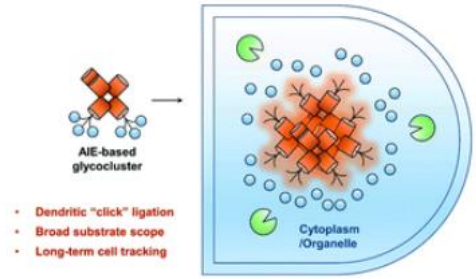


A diastereodivergent and enantioselective synthesis of chiral spirocyclohexyl-indolenines with four contiguous stereogenic centers is achieved by a chiral phosphoric acid-catalyzed cycloaddition of 2-susbtituted 3-indolylmethanols with 1,3-dienecarbamates. Modular access to two different diastereoisomers with high enantioselectivities was obtained by careful choice of reaction conditions. Their functional group manipulation provides an efficient access to enantioenriched spirocyclohexyl-indolines and -oxindoles. The origins of this stereocontrol have been identified using DFT calculations, which reveal an unexpected mechanism compared to our previous work dealing with enecarbamates.

A general strategy to the intracellular sensing of glycosidases using AIE-based glycoclusters

Lei Dong, Min-Yu Zhang,Hai-Hao Han, Yi Zang, Guo-Rong Chen, Jia Li, Xiao-Peng He* and Sébastien Vidal* *Chem. Sci.* **2022**, 13, 247-256

https://dx.doi.org/10.1039/D1SC05057E

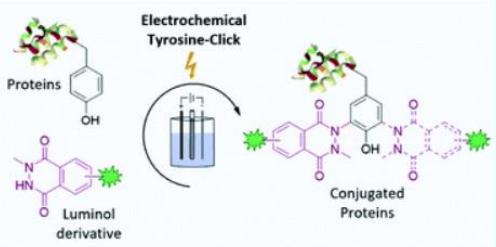


Glycosidases, which are the enzymes responsible for the removal of residual monosaccharides from glycoconjugates, are involved in many different biological and pathological events. The ability to detect sensitively the activity and spatiotemporal distribution of glycosidases in cells will provide useful tools for disease diagnosis. However, the currently developed fluorogenic probes for glycosidases are generally based on the glycosylation of the phenol group of a donor–acceptor type fluorogen. This molecular scaffold has potential drawbacks in terms of substrate scope, sensitivity because of aggregation-caused quenching (ACQ), and the inability for long-term cell tracking. Here, we developed glycoclusters characterized by aggregation-induced emission (AIE) properties as a general platform for the sensing of a variety of glycosidases. To overcome the low chemical reactivity associated with phenol glycosylation, here we developed an AIE-based scaffold, which is composed of tetraphenylethylene conjugated with dicyanomethylene-4H-pyran (TPE–DCM) with a red fluorescence emission. Subsequently, a pair of dendritic linkages was introduced to both sides of the fluorophore, to which six copies of monosaccharides (D-glucose, D-galactose or L-fucose) were introduced through azide–alkyne click chemistry. The resulting AIE-active glycoclusters were shown to be capable of (1) fluorogenic sensing of a diverse range of glycosidases including β-D-galactosidase, β-D-glucosidase and α-L-fucosidase through the AIE mechanism, (2) fluorescence imaging of the endogenous glycosidase activities in healthy and cancer cells, and during cell senescence, and (3) glycosidase-activated, long-term imaging of cells. The present study provides a general strategy to the functional, in situ imaging of glycosidase activities through the multivalent display of sugar epitopes of interest onto properly designed AIE-active fluorogens.

Luminol anchors improve the electrochemical-tyrosine-click labelling of proteins

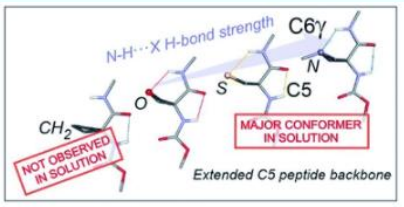
Sébastien Depienne,* Dimitri Alvarez-Dorta, Mikael Croyal, Ranil C. T. Temgoua, Cathy Charlier, David Deniaud, Mathieu Mével, Mohammed Boujtita and Sébastien G. Gouin *Chem. Sci.* **2021**, *12*, 15374-15381

https://dx.doi.org/10.1039/D1SC04809K



New methods for chemo-selective modifications of peptides and native proteins are important in chemical biology and for the development of therapeutic conjugates. Less abundant and uncharged amino-acid residues are interesting targets to form less heterogeneous conjugates and preserve biological functions. Phenylurazole (PhUr), N-methylphenylurazole (NMePhUr) and N-methylluminol (NMeLum) derivatives were described as tyrosine (Y) anchors after chemical or enzymatic oxidations. Recently, we developed the first electrochemical Y-bioconjugation method coined eY-click to activate PhUr in biocompatible media. In this work, we assessed the limitations, benefits and relative efficiencies of eY-click conjugations performed with a set of PhUr, NMePhUr and NMeLum derivatives. Results evidenced a high efficiency of NMeLum that showed a complete Y-chemoselectivity on polypeptides and biologically relevant proteins after soft electrochemical activation. Side reactions on nucleophilic or heteroaromatic amino-acids such as lysine or tryptophan were never observed during mass spectrometry analysis. Myoglobine, bovine serum albumin, a plant mannosidase, glucose oxidase and the therapeutically relevant antibody trastuzumab were efficiently labelled with a fluorescent probe in a two-step approach combining eY-click and strain-promoted azide–alkyne cyclization (SPAAC). The proteins conserved their structural integrity as observed by circular dichroism and the trastuzumab conjugate showed a similar binding affinity for the natural HER2 ligand as shown by bio-layer interferometry. Compared to our previously described protocol with PhUr, eY-click with NMeLum species showed faster reaction kinetics, higher (complete) Y-chemoselectivity and reactivity, and offers the interesting possibility of the double tagging of solvent-exposed Y.

N–H···X interactions stabilize intra-residue C5 hydrogen bonded conformations in heterocyclic α-amino acid derivatives

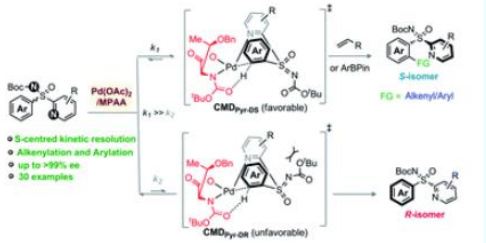


Venkateswara Rao Mundlapati, Zeynab Imani, Viola C. D'mello, Valérie Brenner, Eric Gloaguen, Jean-Pierre Baltaze, Sylvie Robin, Michel Mons * and David J. Aitken* *Chem. Sci.* **2021**, *12*, 14826-14832

https://dx.doi.org/10.1039/D1SC05014A

Nature makes extensive and elaborate use of hydrogen bonding to assemble and stabilize biomolecular structures. The shapes of peptides and proteins rely significantly on N–H···O[double bond, length as m-dash]C interactions, which are the linchpins of turns, sheets and helices. The C5 H-bond, in which a single residue provides both donor and acceptor, is generally considered too weak to force the backbone to adopt extended structures. Exploiting the synergy between gas phase (experimental and quantum chemistry) and solution spectroscopies to decipher IR spectroscopic data, this work demonstrates that the extended C5-based conformation in 4-membered ring heterocyclic α-amino acid derivatives is significantly stabilized by the formation of an N–H···X H-bond. In this synergic system the strength of the C5 interaction remains constant while the N–H···X H-bond strength, and thereby the support provided by it, varies with the heteroatom.

Kinetic resolution of sulfur-stereogenic sulfoximines by Pd(ii)–MPAA catalyzed C–H arylation and olefination

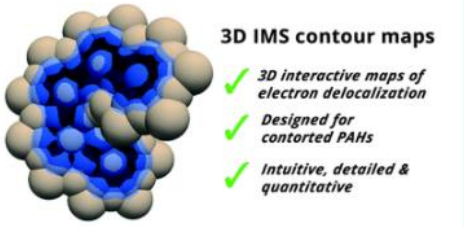


Kallol Mukherjee, Nicolas Grimblat, Somratan Sau, Koushik Ghosh, Majji Shankar, Vincent Gandon * and Akhila K. Sahoo* *Chem. Sci.*, **2021**, *12*, 14863-14870

https://dx.doi.org/10.1039/D1SC04299H

A direct Pd(II)-catalyzed kinetic resolution of heteroaryl-enabled sulfoximines through an ortho-C–H alkenylation/arylation of arenes has been developed. The coordination of the sulfoximine pyridyl-motif and the chiral amino acid MPAA ligand to the Pd(II)-catalyst controls the enantio-discriminating C(aryl)–H activation. This method provides access to a wide range of enantiomerically enriched unreacted aryl-pyridyl-sulfoximine precursors and C(aryl)–H alkenylation/arylation products in good yields with high enantioselectivity (up to >99% ee), and selectivity factor up to >200. The coordination preference of the directing group, ligand effect, geometry constraints, and the transient six-membered concerted-metalation–deprotonation species dictate the stereoselectivity; DFT studies validate this hypothesis.

Visualizing electron delocalization in contorted polycyclic aromatic hydrocarbons

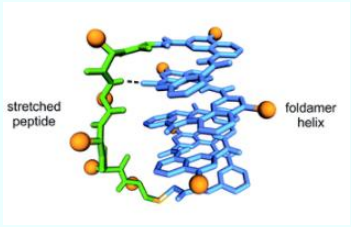


Albert Artigas, Denis Hagebaum-Reignier, Yannick Carissan* and Yoann Coquerel* *Chem. Sci.* **2021**, *12*, 13092-13100

https://dx.doi.org/10.1039/D1SC03368A

Electron delocalization in contorted polycyclic aromatic hydrocarbon (PAH) molecules was examined through 3D isotropic magnetic shielding (IMS) contour maps built around the molecules using pseudo-van der Waals surfaces. The resulting maps of electron delocalization provided an intuitive, yet detailed and quantitative evaluation of the aromatic, non aromatic, and antiaromatic character of the local and global conjugated cyclic circuits distributed over the molecules. An attractive pictural feature of the 3D IMS contour maps is that they are reminiscent of the Clar π-sextet model of aromaticity. The difference in delocalization patterns between the two faces of the electron circuits in contorted PAHs was clearly visualized. For π-extended contorted PAHs, some splits of the π system resulted in recognizable patterns typical of smaller PAHs. The differences between the delocalization patterns of diastereomeric chiral PAHs could also be visualized. Mapping IMS on pseudo-van der Waals surfaces around contorted PAHs allowed visualization of their superimposed preferred circuits for electron delocalization and hence their local and global aromaticity patterns.

Conformational interplay in hybrid peptide–helical aromatic foldamer macrocycles

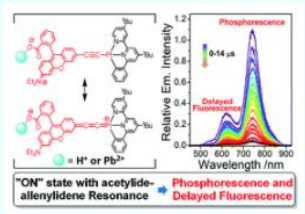


Sebastian Dengler, Pradeep K. Mandal, Lars Allmendinger, Céline Douat and Ivan Huc* *Chem. Sci.* **2021**, *12*, 11004-11012.

https://dx.doi.org/10.1039/D1SC03640H

Macrocyclic peptides are an important class of bioactive substances. When inserting an aromatic foldamer segment in a macrocyclic peptide, the strong folding propensity of the former may influence the conformation and alter the properties of the latter. Such an insertion is relevant because some foldamer–peptide hybrids have recently been shown to be tolerated by the ribosome, prior to forming macrocycles, and can thus be produced using an in vitro translation system. We have investigated the interplay of peptide and foldamer conformations in such hybrid macrocycles. We show that foldamer helical folding always prevails and stands as a viable means to stretch, i.e. unfold, peptides in a solvent dependent manner. Conversely, the peptide systematically has a reciprocal influence and gives rise to strong foldamer helix handedness bias as well as foldamer helix stabilisation. The hybrid macrocycles also show resistance towards proteolytic degradation.

The switchable phosphorescence and delayed fluorescence of a new rhodamine-like dye through allenylidene formation in a cyclometallated platinum(ii) system

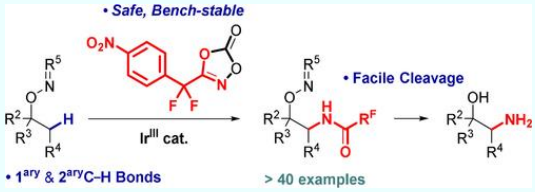


Shunan Zhao, Yifan Zhu, Ling Li, Véronique Guerchais, * Julien Boixel * and Keith Man-Chung Wong* *Chem. Sci.* **2021**, *12*, 11056-11064

https://dx.doi.org/10.1039/D1SC02787E

A new rhodamine-like alkyne-substituted ligand (Rhodyne) was designed to coordinate a cyclometallated platinum(II) system. The chemo-induced "ON–OFF" switching capabilities on the spirolactone ring of the Rhodyne ligand with an end-capping platinum(II) metal centre can modulate the interesting acetylide–allenylidene resonance. The long-lived 3IL excited state of Rhodyne in its ON state as an optically active opened form was revealed via steady-state and time-resolved spectroscopy studies. Exceptional near-infrared (NIR) phosphorescence and delayed fluorescence based on a rhodamine-like structure were observed at room temperature for the first time. The position of the alkyne communication bridge attached to the platinum(II) unit was found to vary the lead(II)-ion binding mode and also the possible resonance structure for metal-mediated allenylidene formation. The formation of a proposed allenylidene resonance structure was suggested to rationalize these phenomena.

A New Dioxazolone for the Synthesis of 1,2-Aminoalcohols via Iridium(III)-Catalyzed C(sp(3))-H Amidation

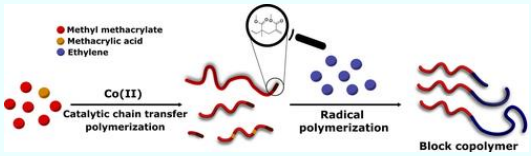


Kevin Antien, Andrea Geraci, Michael Parmentier, Olivier Baudoin* *Angew. Chem. Int. Ed.* **2021**, *60*, 22948

https://doi.org/10.1002/anie.202110019

A safe and bench-stable dioxazolone reagent was developed for the oxime-directed iridium(III)-catalyzed amidation of unactivated C(sp^3)–H bonds in tertiary and secondary alcohol-based substrates. The amidation reaction is mild, general and compatible with both primary and secondary C–H bonds.

Block Copolymers Based on Ethylene and Methacrylates Using a Combination of Catalytic Chain Transfer Polymerisation (CCTP) and Radical Polymerisation

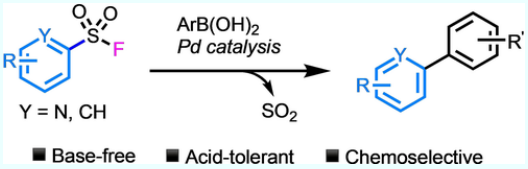


Florian Baffie, Georgios Patias, Ataulla Shegiwal, Fabrice Brunel, Vincent Monteil, Ludmilla Verrieux, Lionel Perrin, David M. Haddleton,* Franck D'Agosto* *Angew. Chem. Int. Ed.* **2021**, *60*, 25356

https://doi.org/10.1002/anie.202108996

Catalytic chain transfer polymerisation was used to produce methacrylic macromonomers. Those were involved in a simple radical polymerisation of ethylene to form block copolymers featuring a polyethylene segment and various polymethacrylic segments.

Desulfonative Suzuki-Miyaura Coupling of Sulfonyl Fluorides

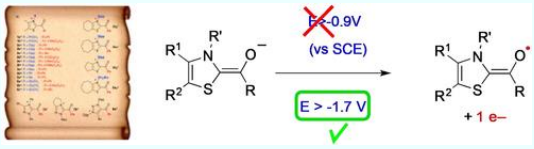


Paul Chatelain, Cyprien Muller, Dr. Abhijit Sau, Daria Brykczyńska, Maryam Bahadori, Christopher N. Rowley, Joseph Moran* *Angew. Chem. Int. Ed.* **2021**, *60*, 25307

https://doi.org/10.1002/anie.202111977

Aryl sulfonyl fluorides, typically inert to transition metal catalysis, undergo a Pd-catalyzed desulfonative Suzuki–Miyaura coupling. The reaction can occur without added base and turns the −SO2F group into a divergent handle for C−C or S−Nu coupling.

Critical Assessment of the Reducing Ability of Breslow-type Derivatives and Implications for Carbene-Catalyzed Radical Reactions



Ludivine Delfau, Samantha Nichilo, Florian Molton, Julie Broggi, Eder Tomás-Mendivil,* David Martin* *Angew. Chem. Int. Ed.* **2021**, *60*, 26783

https://doi.org/10.1002/anie.202111988

A major cleanup for starting anew: Bio-inspired Breslow-type enolates, which mimic thiamine derivatives, are far better reducing agents than previously considered. The reevaluation of the redox ability of these key intermediates refutes established misconceptions and sheds a new light on radical processes involving N-heterocyclic carbene catalysis.

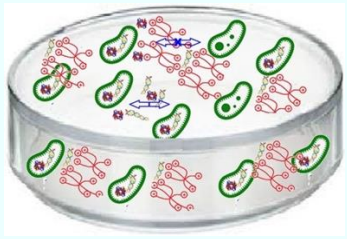
Impact of the Difluoromethylene Group in the Organocatalyzed Acylative Kinetic Resolution of alpha,alpha-Difluorohydrins

Titouan Desrues, Jérémy Merad, Daniela Andrei, Jean-Marc Pons, Jean-Luc Parrain, Maurice Médebielle,* Adrien Quintard,* Cyril Bressy* *Angew. Chem. Int. Ed.* **2021**, *60*, 24924

https://doi.org/10.1002/anie.202107041

A new interaction was discovered between $C(sp^3)F_2$ and an acylated chiral isothiourea, allowing an enantioselective recognition. This interaction was explored theoretically and experimentally in the kinetic resolution of racemic difluorohydrins, affording optically active organofluorines with a high level of enantioselectivity.

Dynamic Constitutional Frameworks as Antibacterial and Antibiofilm Agents

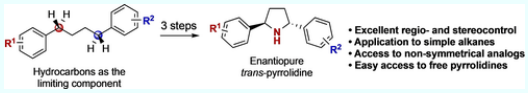


Andrei Diaconu, Tom Coenye, Mihail Barboiu,* Stéphane P. Vincent* *Angew. Chem. Int. Ed.* **2021**, *60*, 22505

https://doi.org/10.1002/anie.202109518

Dynamic constitutional frameworks are expressed in the presence of bacteria templating from dynamic covalent libraries made of aromatic cores, PEGylated connectors, and ionic heads. These templated DCFs further translate into the multivalent presentation of cationic heads, subsequently promoting antibacterial and antibiofilm activities.

Asymmetric Synthesis of Enantiopure Pyrrolidines by C(sp(3))-H Amination of Hydrocarbons

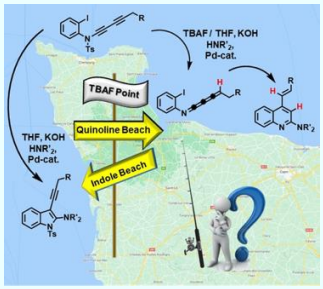


Yanis Lazib, Pascal Retailleau, Tanguy Saget,* Benjamin Darses,* Philippe Dauban* *Angew. Chem. Int. Ed.* **2021**, *60*, 21708

https://doi.org/10.1002/anie.202107898

Simple hydrocarbons such as alkanes are shown to be useful building blocks for the asymmetric synthesis of heterocycles. They are converted in only two steps to pyrrolidines by application of stereoselective $C(sp^3)$–H amination reactions. Symmetrical and non-symmetrical enantiopure 2,5-disubstituted pyrrolidines are isolated in good yields.

Media-Driven Pd-Catalyzed Reaction Cascades with 1,3-Diynamides Leading Selectively to Either Indoles or Quinolines

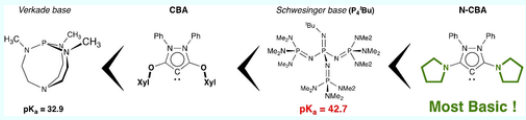


Illia Lenko, Alexander Mamontov, Carole Alayrac,* Rémi Legay, Bernhard Witulski* *Angew. Chem. Int. Ed.* **2021**, *60*, 22729

https://doi.org/10.1002/anie.202110221

Which coast to take? Divergent Pd-catalyzed reaction cascades with 1,3-diynamides and primary or secondary amines result by adding or omitting TBAF. In the absence of TBAF 2-amino-3-alkynylindoles are formed, whereas the addition of TBAF leads selectively to 2-amino-4-alkenylquinolines. The latter pathway involves the unprecedented formation of [4]cumulenimines from 1,3-diynamides.

Stable Singlet Carbenes as Organic Superbases

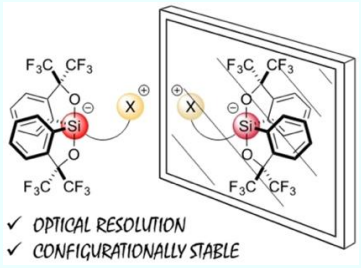


François Vermersch, Sima Yazdani, Glen P. Junor, Douglas B. Grotjahn, Rodolphe Jazzar,* Guy Bertrand* *Angew. Chem. Int. Ed.* **2021**, *60*, 27253

https://doi.org/10.1002/anie.202111588

Pyrazol-4-ylidenes, a type of mesoionic carbenes, also named cyclic-bentallenes (CBA), can be more basic than Verkade proazaphosphatrane and even Schwesinger phosphazene P_4(tBu). With these results it is demonstrated that carbenes should not be overlooked as neutral purely organic superbases.

Synthesis and Optical Resolution of Configurationally Stable Zwitterionic Pentacoordinate Silicon Derivatives

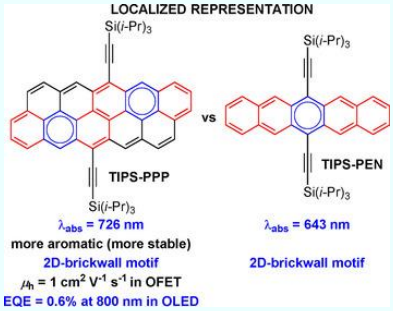


Thomas Deis, Julien Maury, Fabrizio Medici, Marion Jean, Jérémy Forte, Nicolas Vanthuyne, Louis Fensterbank,* Gilles Lemière* *Angew. Chem. Int. Ed.* **2022**, *61*, e202113836

https://doi.org/10.1002/anie.202113836

The synthesis of air- and water-tolerant zwitterions featuring a chiral pentacoordinate silicon moiety is described. Their stability toward moisture and aerobic conditions allowed their optical resolution by means of chiral HPLC, which constitutes a premiere in the chemistry of organosilicon compounds. Studies on the kinetics of racemisation of enantiomerically pure substrates attest for their high configurational stabilities in solution.

Synthesis, Aromaticity, and Application of peri-Pentacenopentacene: Localized Representation of Benzenoid Aromatic Compounds

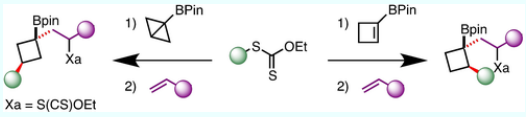


Tanguy Jousselin-Oba, Masashi Mamada,* Karen Wright, Jérome Marrot, Chihaya Adachi, Abderrahim Yassar, Michel Frigoli* *Angew. Chem. Int. Ed.* **2022**, *61*, e202113333

https://doi.org/10.1002/anie.202112794

Acenes and peri-acenoacenes should be seen as π-conjugated systems containing one and two localized aromatic sextets, respectively, flanked with ortho-fused diene fragments. The vertical extension of TIPS-PEN, TIPS-PPP, has been prepared from a dione precursor and absorbs at longer wavelengths, is 16 times more stable, exhibits a 2D brickwall motif in crystals with stronger π–π interactions and a smaller reorganization energy.

A Modular Access to 1,2- and 1,3-Disubstituted Cyclobutylboronic Esters by Consecutive Radical Additions



Jean Michalland,* Nicolas Casaretto, Samir Z. Zard* *Angew. Chem. Int. Ed.* **2022**, *61*, e202113333

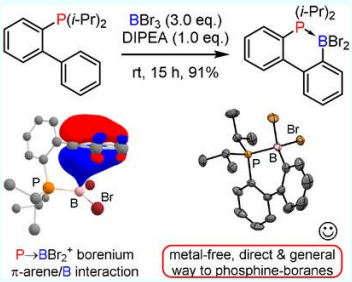
https://doi.org/10.1002/anie.202113333

Using the strain inherent in a cyclobutyl ring to counteract the stabilization of a radical adjacent to a boronic ester allows the synthesis of a broad variety of 1,2- and 1,3-disubstituted cyclobutylboronic esters.

Metal-Free Phosphorus-Directed Borylation of C(sp2)–H Bonds

Omar Sadek, Arnaud Le Gac, Nereida Hidalgo, Sonia Mallet-Ladeira, Karinne Miqueu, Ghenwa Bouhadir, Didier Bourissou*
Angew. Chem. Int. Ed. **2022**, *61*, e202110102

https://doi.org/10.1002/anie.202110102

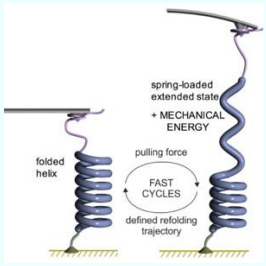


Phosphines turned to be powerful directing groups for the electrophilic C–H borylation of arenes. The reaction involves P-stabilized boreniums as key intermediates. It provides a direct, efficient, and general way of preparing phosphine–boranes.

Single-molecule mechanics of synthetic aromatic amide helices: Ultrafast and robust non-dissipative winding

Floriane Devaux , Xuesong Li, Damien Sluysmans, Victor Maurizot, Evangelos Bakalis, Francesco Zerbetto, Ivan Huc,* Anne-Sophie Duwez* *Chem* **2021**, *7*, 1333

https://doi.org/10.1016/j.chempr.2021.02.030

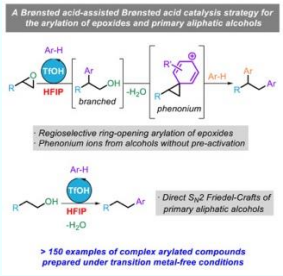


Because of proteins' many degrees of conformational freedom, programming protein folding dynamics, overall elasticity, and motor functions remains an elusive objective. Instead, smaller and simpler objects, such as synthetic foldamers, may be amenable to design. However, little is known about their mechanical performance. Here, we show that reducing molecular size may not compromise mechanical properties. We report that helical aromatic oligoamides as small as 1 nm possess outstanding elasticity and outperform most natural helices. Using single-molecule force spectroscopy, we characterize their folding trajectories and intermediate states. We show that they cooperatively and reversibly unwind at high forces. They extend up to 3.8 times their original length and rewind against considerable forces on a timescale of 10 µs. Pulling and relaxing cycles follow the same trace up to a very high loading rate, indicating that the mechanical energy accumulated during the stretching does not dissipate and is immediately reusable.

Unlocking the Friedel-Crafts arylation of primary aliphatic alcohols and epoxides driven by hexafluoroisopropanol

Shaofei Zhang, Marie Vayer, Florent Noël, Christopher N. Rowley, David Lebœuf,* Joseph Moran* *Chem* **2021**, *7*, 3425

https://doi.org/10.1016/j.chempr.2021.10.023



Alcohols and epoxides are arguably ideal electrophiles for the Friedel-Crafts alkylation, since they are widely available, require no pre-activation, and produce no stoichiometric waste beyond water. However, neither primary aliphatic alcohols nor most classes of terminal epoxides are compatible with existing intermolecular Friedel-Crafts methodologies, and sequential Friedel-Crafts reactions starting from epoxides consequently remain underexplored. Here, we report that these limitations are easily overcome using Brønsted acid catalysis in hexafluoroisopropanol (HFIP) as a solvent. Electron-poor aromatic epoxides and aliphatic epoxides undergo stereospecific arylation to give an alcohol which, depending on the reaction conditions, can partake in a second nucleophilic substitution with a different arene in one pot. Phenyl ethanols react through a phenonium intermediate, whereas simple aliphatic alcohols participate in a rare intermolecular SN2 Friedel-Crafts process, delivering linear products exclusively. This work provides an alternative to metal-catalyzed cross-couplings for accessing important scaffolds, widening the range of applications of the Friedel-Crafts reaction.