Société Chimique de France
Le réseau des chimistes

N° 9

ECHO DCO

Octobre
2020

La lettre du bureau de la Division de Chimie Organique

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LE MOT DU PRÉSIDENT

Chers Sociétaires,

En cette triste période de reconfinement, j'espère que chacun de vous se porte bien et supporte cette épreuve sereinement. La situation sanitaire a bouleversé l'agenda de la DCO, et nos rendez-vous de printemps et d'automne n'ont pas pu avoir lieu à notre grand regret. Cependant, ce n'est pas une année blanche pour la DCO, nous avons distribué nos prix et nous sommes très fiers de nos récipiendaires ! Et puis, nous avons organisé en collaboration avec la rédaction d'EurJOC, un séminaire virtuel qui a eu un très grand succès, puisque nous avons été plus de 600 à suivre les conférences ! Je tire deux leçons de cet événement exceptionnel : tout d'abord notre communauté est dynamique et ces évènements sont des moments fédérateurs, et puis nous avons besoin d'un lien fort avec nos journaux scientifiques.

Je voudrais insister ici sur ce deuxième point. Les journaux scientifiques sont notre moyen de faire connaître et de partager notre recherche. Les journaux édités par Chemistry Europe appartiennent aux Sociétés Chimiques Européennes, dont évidemment la SCF. Pour que notre communauté de chimistes vive et soit visible, nous avons besoin de journaux forts. Nous avons donc intérêt à publier dans nos journaux - pour la DCO, EurJOC et ChemEurJ - même si je sais bien que leurs IF ne sont pas aussi hauts qu'on pourrait l'espérer. Mais sans ces journaux, la chimie en France et en Europe continentale sera marginalisée encore davantage. Donc soutenons-les et essayons de contribuer à leur attractivité !

Matthieu SOLLOGOUB, Président de la DCO

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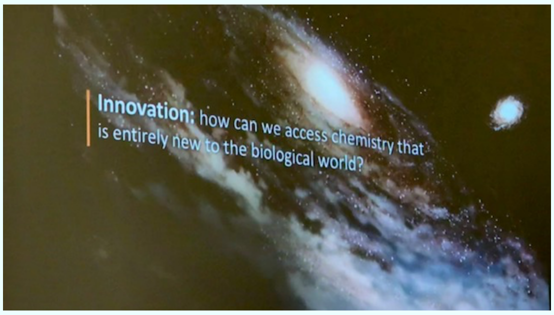
LA E-JOURNÉE DCO-EurJOC : UNE BELLE ASSEMBLEE VIRTUELLE

La journée de printemps de la DCO n'ayant pu se dérouler ce printemps à la Sorbonne, celle-ci a été remplacée par une série de conférences selon un nouveau format de plus en plus à la mode depuis l'émergence du coronavirus. En collaboration avec Anne Nijs et Charlotte Gers-Panther, éditrices de « European Journal of Organic Chemistry », une série de présentations en visioconférence a pu être diffusée grâce à la plateforme mise à notre disposition par Chemistry Europe.

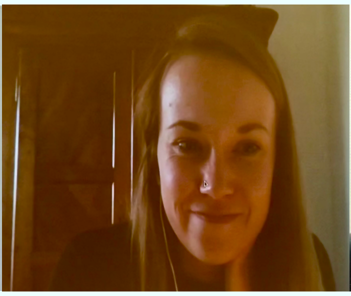
Ce sont 600 personnes, originaires de toute l'Europe (Allemagne, Espagne, Italie, Royaume-Uni, Suisse, Autriche, Belgique, Pays-Bas, Pologne, Suède, Finlande, Russie, etc.) voire même du monde entier (Etats-Unis, Canada, Japon, Inde, Hong-Kong, Chine, Viet-Nam, Philippines, Perou, Nigeria, etc.), qui ont « assisté » aux conférences données par :

- Prof. Frances ARNOLD (Caltech Pasadena, EU), **Prix NOBEL de CHIMIE 2018**
- Prof. Thomas CARRELL (LMU Munich, Allemagne),
- Dr. Jean-François NIERENGARTEN (LCMM, Strasbourg), **Prix DCO 2019**
- Dr. Ludovic FAVEREAU (ISCR, Rennes), **Prix Marc JULIA 2019**
- Dr. Xavier BUGAUT (ISM2, Marseille), **Prix Jean NORMANT 2019**


Frances ARNOLD


Innovation: how can we access chemistry that is entirely new to the biological world?


Anne NIJS


Charlotte GERS-PANTHER


Matthieu SOLLOGOUB

Cette journée a permis de renforcer les liens entre la DCO et les éditeurs des journaux européens de chimie dont la SCF est partenaire. Une expérience à renouveler.

A VOS AGENDAS : LA JOURNÉE DE PRINTEMPS 2021

La prochaine journée de la DCO est programmée le **mardi 23 mars 2021** sous un format qui sera précisé ultérieurement. Le programme comprendra entre autres les conférences données par 4 des lauréats des prix de la DCO 2020 (les autres lauréats seront invités à présenter leurs travaux au congrès SCF21) :

- **Prix Thèse Dina SURDIN :** Dr. Clément GHIAZZA (ICBMS, Lyon),
- **Prix Marc JULIA :** Dr. Angélique FERRY (Université CY Cergy-Paris),
- **Prix Jean-Pierre SAUVAGE :** Dr. Jean-François SOULÉ (ISCR, Rennes),
- **Prix Jean-Marie LEHN :** Dr. Arnaud VOITURIEZ (ICSN, Gif-sur-Yvette).

A VOS AGENDAS : PROCHAINES ÉLECTIONS DU BUREAU DE LA DCO

Le Bureau de la Division Chimie Organique sera bientôt renouvelé par le biais d'une élection programmée au cours du premier trimestre 2021. Cette élection fera l'objet d'un appel à candidatures.

Tous les membres de la Société Chimique de France rattachés à la Section Division Chimie Organique et à jour de leur cotisation peuvent se présenter.

Tout membre souhaitant se porter candidat devra alors adresser à la Société Chimique de France un Curriculum vitæ et une lettre d'intention limités à une page pour chacun des documents.

A VOS AGENDAS : CONGRÈS SCF21 À NANTES

Le prochain congrès trisannuel de la Société Chimique de France, **SCF21**, se tiendra du 28 au 30 juin 2021 à Nantes.

La remise des autres Prix 2020 de la SCF se fera à l'occasion de cette manifestation, qui s'ouvrira par un week-end grand public au Muséum de Nantes, les samedi 26 et dimanche 27 juin, avec environ quinze ateliers et une exposition temporaire de peintures autour du thème « Chimie, Lumière, Couleur », organisés par la commission Chimie et Société sur le mois de juin 2021. Articulées autour de conférences plénières, la programmation scientifique s'organisera en sept sessions parallèles placées sous l'égide des divisions de la SCF. Trois jours d'échanges scientifiques à la Cité des congrès de Nantes permettront à la communauté de la chimie, étudiants et permanents, de présenter leurs derniers résultats dans tous les domaines de la chimie. Une session particulière sera également dédiée au thème transversal « Chimie, Lumière, Couleur ».

Réservez les dates dans vos agendas, pour faire de cette manifestation LE rendez-vous des chimistes français en 2021 !

NOUVEAU GROUPE THÉMATIQUE DE CHIMIE SUPRAMOLÉCULAIRE

La chimie supramoléculaire, comme elle a été définie par Jean-Marie Lehn lors de l'obtention du Prix Nobel de Chimie en 1987, est la chimie au-delà de la molécule.[1] Elle se concentre sur les systèmes chimiques constitués de molécules assemblées au travers d'interactions faibles ou de liaisons covalentes réversibles. Ces interactions qui peuvent être de nature très différentes (liaisons hydrogène, de coordination, électrostatiques par exemple) permettent la construction d'architectures plus ou moins complexes dont les propriétés sont en général supérieures à celles de leurs constituants isolés. Les assemblages supramoléculaires constituent donc des matériaux dynamiques et stimulables aux propriétés innovantes dans des domaines très variés tels que la catalyse, la détection et le piégeage de polluants, la biomédecine et l'optoélectronique. La communauté française des chercheuses et chercheurs est très active dans le domaine de la chimie supramoléculaire comme cela a pu récemment être démontré lors la tenue du congrès Supr@Lyon en décembre 2018.[2] Cet évènement — premier congrès d'envergure internationale en chimie supramoléculaire organisé par des équipes françaises — fut non seulement l'occasion de la rencontre d'un certain nombre des actrices et acteurs de la communauté, mais a aussi confirmé la grande diversité et qualité des recherches françaises, dans un pays qui compte aujourd'hui deux prix Nobel de chimie dans le domaine après la consécration récente de Jean-Pierre Sauvage en 2016. Le succès de Supr@Lyon fut l'impulsion nécessaire vers la création d'un groupe thématique de la société chimique de France, ainsi que vers la pérennisation d'un évènement français majeur dédié à la chimie supramoléculaire avec la tenue du congrès Supr@Strasbourg au printemps 2021 sous la forme d'une e-conférence.[3]

Le bureau de ce nouveau groupe thématique a été constitué au début de cette année (Figure 1), et le nombre d'adhérents est supérieur à 300. La diversité géographique et thématique des membres de ce bureau est très certainement un gage de représentativité de la majorité des chercheuses et chercheurs en chimie supramoléculaire en France. C'est tout naturellement que le groupe s'est associé à la division de chimie organique de la société chimique de France, puisque les techniques associées à la synthèse des molécules et à leur caractérisation sont communes aux deux disciplines. Les spécificités de la chimie supramoléculaire, tant en matière de techniques de caractérisation que des applications très variées, offrent aussi la possibilité de créer des passerelles multidisciplinaires entre les différents acteurs du domaine. Le périmètre du GT couvre différents domaines tels que l'élaboration et la synthèse de molécules associatives de nature totalement synthétique ou hybride, la caractérisation multi-échelle et multidimensionnelle des assemblages supramoléculaires résultant de leur association, la rationalisation expérimentale et théorique de nouveaux types d'interactions et des propriétés d'association des molécules, et l'exploitation des propriétés des assemblages supramoléculaires.

Au-delà de l'organisation d'un congrès biennal en chimie supramoléculaire qui se propose de visiter le plus grand nombre d'universités françaises avec le temps, le groupe de chimie supramoléculaire souhaite également permettre l'échange d'informations dans la communauté française (actualité scientifique des équipes françaises, offres de thèses, de financements, de postes, etc…) au travers de sa Newsletter, son site web,[4] son compte Twitter,[5] ou encore une liste de diffusion par courrier électronique aux adhérents.

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[1] Lehn, J.-M. *Angew. Chem. Int. Ed.* **1988**, *27*, 89.

[2] http://supralyon.univ-lyon1.fr/fr

[3] https://suprastras.chimie.unistra.fr/

[4] http://www.societechimiquedefrance.fr/Groupe-de-chimie-supramoleculaire.html

[5] https://twitter.com/supraSCF

Finalement, la reconnaissance de la qualité de certains travaux français se fera au travers de la remise de « Prix Biannuels du Groupe de Chimie Supramoléculaire de la Société Chimique de France ». Les deux premiers lauréats « junior » et « senior », Sébastien Goeb et Wais Hosseini, présenteront leurs travaux de recherche lors du congrès Supr@Strasbourg. Toutes ces actions permettront dans un futur très proche de fédérer les équipes nationales impliquées dans la chimie supramoléculaire afin d'accroître leur visibilité et leur reconnaissance par les institutions publiques et les groupes industriels. La création du groupe de chimie supramoléculaire de la société chimique de France est donc une bonne nouvelle pour une communauté très dynamique qui porte un héritage prestigieux dans le domaine, et dont l'avenir ne le sera pas moins. Nous espérons vous accueillir nombreux au sein de ce nouveau groupe thématique.

Figure 1. Membres du bureau du groupe de chimie supramoléculaire, dans le sens de la lecture: Damien Bourgeois (CEA Marcoule), Jean-Pierre Dutasta (ENS Lyon), Claire Fave (Université Paris Diderot), David Leboeuf (Université de Strasbourg), Nathan McClenaghan (Université de Bordeaux), Jean-François Nierengarten (Université de Strasbourg), Matthieu Raynal (Sorbonne Université), Olivia Reinaud (Université Paris Descartes), Sébastien Ulrich (Université de Montpellier), Laurent Vial (Université de Lyon).

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 signés par les membres de notre division travaillant dans les laboratoires français. Vous trouverez dans les pages suivantes un choix d'articles publiés en 2020 dans les journaux suivants :

- *Nature Chemistry et Nature Communications,*
- *Angewandte Chemie International Edition,*
- *Journal of the American Chemical Society,*
- *Chemical Science.*

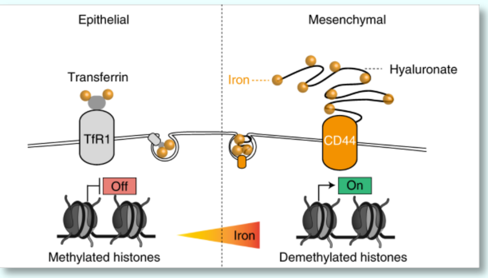
Nous avons conscience que ce choix d'articles est arbitraire. N'hésitez pas à nous faire part de vos remarques, et, éventuellement, à nous soumettre vos travaux à « highlighter ».

CD44 regulates epigenetic plasticity by mediating iron endocytosis

Nat. Chem. **2020**, *12*, 929

S. Muller, F. Sindikubwabo, T. Caneque, A. Lafon, A. Versini, B. Lombard, D. Loew, T.-D. Wu, C. Ginestier, E. Charafe-Jauffret, A. Durand, C. Vallot, S. Baulande, N. Servant, R. Rodriguez

https://doi.org/10.1038/s41557-020-0513-5



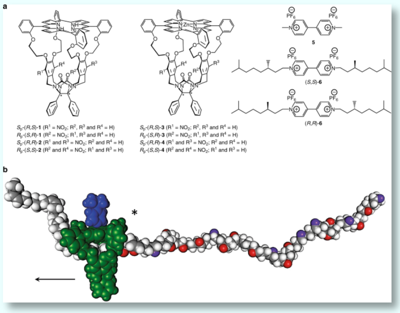
CD44 is a transmembrane glycoprotein linked to various biological processes reliant on epigenetic plasticity, which include development, inflammation, immune responses, wound healing and cancer progression. Although it is often referred to as a cell surface marker, the functional regulatory roles of CD44 remain elusive. Here we report the discovery that CD44 mediates the endocytosis of iron-bound hyaluronates in tumorigenic cell lines, primary cancer cells and tumours. This glycan-mediated iron endocytosis mechanism is enhanced during epithelial–mesenchymal transitions, in which iron operates as a metal catalyst to demethylate repressive histone marks that govern the expression of mesenchymal genes. CD44 itself is transcriptionally regulated by nuclear iron through a positive feedback loop, which is in contrast to the negative regulation of the transferrin receptor by excess iron. Finally, we show that epigenetic plasticity can be altered by interfering with iron homeostasis using small molecules. This study reveals an alternative iron-uptake mechanism that prevails in the mesenchymal state of cells, which illuminates a central role of iron as a rate-limiting regulator of epigenetic plasticity.

Absolute configuration and host-guest binding of chiral porphyrin-cages by a combined chiroptical and theoretical approach

Nat. Communications **2020**, *11*, 4776

J. Ouyang, A. Swartjes, M. Geerts, P. J. Gilissen, D. Wang, P. C. P. Teeuwen, P. Tinnemans, N. Vanthuyne, S. Chentouf, F. P. J. T. Rutjes, J.-V. Naubron, J. Crassous, J. A. A. W. Elemans, R. J. M. Nolte

https://doi.org/10.1038/s41467-020-18596-1



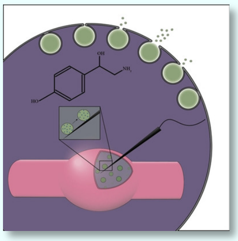
Porphyrin cage-compounds are used as biomimetic models and substrate-selective catalysts in supramolecular chemistry. In this work we present the resolution of planar-chiral porphyrin cages and the determination of their absolute configuration by vibrational circular dichroism in combination with density functional theory calculations. The chiral porphyrin-cages form complexes with achiral and chiral viologen-guests and upon binding one of the axial enantiomorphs of the guest is bound selectively, as is indicated by induced-electronic-dichroism-spectra in combination with calculations. This host-guest binding also leads to unusual enhanced vibrational circular dichroism, which is the result of a combination of phenomena, such as rigidification of the host and guest structures, charge transfer, and coupling of specific vibration modes of the host and guest. The results offer insights in how the porphyrin cage-compounds may be used to construct a future molecular Turing machine that can write chiral information onto polymer chains.

Intracellular Electrochemical Nanomeasurements Reveal that Exocytosis of Molecules at Living Neurons is Subquantal and Complex

Angew. Chem. Int. Ed. **2020**, *59*, 6711

A.Larsson, S. Majdi, A. Oleinick, I. Svir, J. Dunevall, C. Amatore, A. G. Ewing

https://doi.org/10.1002/anie.201914564



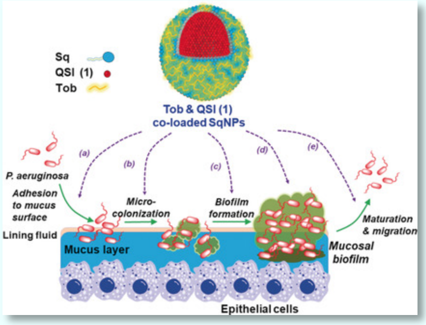
Partial chemical release: Partial chemical release allows nerve cells to control the signal at the site of release during individual events, in which the smaller the fraction released, the greater the range of regulation. Intracellular electrochemistry at a nanotip electrode combined with theoretical modeling shows that the vesicular octopamine content is very large and the exocytotic fraction released from a living Drosophila larval neuro-muscular neuron is very small.

Squalenyl Hydrogen Sulfate Nanoparticles for Simultaneous Delivery of Tobramycin and an Alkylquinolone Quorum Sensing Inhibitor Enable the Eradication of P. aeruginosa Biofilm Infections

Angew. Chem. Int. Ed. **2020**, *59*, 10292

D.-K. Ho, X. Murgia, C. De Rossi, R. Christmann, A. G. Hüfner de Mello Martins, M. Koch, A. Andreas, J. Herrmann, R. Müller, M. Empting, R. W. Hartmann, D. Desmaele, B. Loretz, P. Couvreur, C.-M. Lehr

https://doi.org/10.1002/anie.202001407



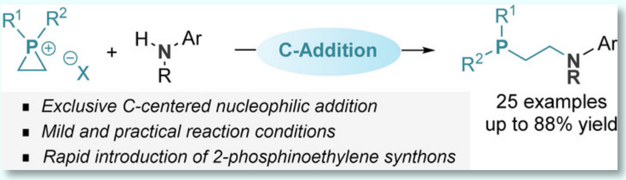
Breaking through: Tob and QSI (1) co-loaded squalenyl hydrogen sulfate nanoparticles (SqNPs) are shown to act on all stages of P. aeruginosa infections to eradicate bacterial infection [(a–c) and (e)] and penetrate biofilm, preventing its formation and recurrence (d).

Taming the Reactivity of Phosphiranium Salts: Site-Selective C-Centered Ring Opening for Direct Synthesis of Phosphinoethylamines

Angew. Chem. Int. Ed. **2020**, *59*, 11769

J. Gasnot, C. Botella, S. Comesse, S. Lakhdar, C. Alayrac, A.-C. Gaumont, V. Dalla, C. Taillier

https://doi.org/10.1002/anie.201916449



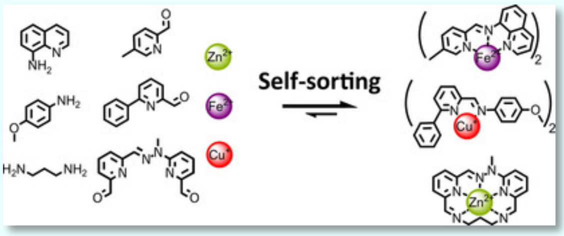
C versus P selectivity: Quaternary phosphiranium salts (QPrS) are a fascinating yet underutilized class of phosphorus building blocks with instability and site-electrophilicity issues. The challenging C-centered nucleophilic ring opening of these salts, by reaction with aniline derivatives, is now reported and demonstrates the potential synthetic utility of QPrS.

Triple Self-Sorting in Constitutional Dynamic Networks: Parallel Generation of Imine-Based Cu^{I}, Fe^{II}, and Zn^{II} Complexes

Angew. Chem. Int. Ed. **2020**, *59*, 12584

J.–F. Ayme, S. Dhers, J.-M. Lehn

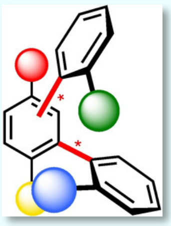
https://doi.org/10.1002/anie.201912812



Simplifying matters: Three imine-based metal complexes, having no overlap in terms of their compositions, have been simultaneously generated from the self-sorting of a constitutional dynamic library containing three amines, three aldehydes, and three metal salts. The mechanism and the driving forces underlying the self-sorting process have been examined.

Enantioselective Synthesis of Atropisomers with Multiple Stereogenic Axes

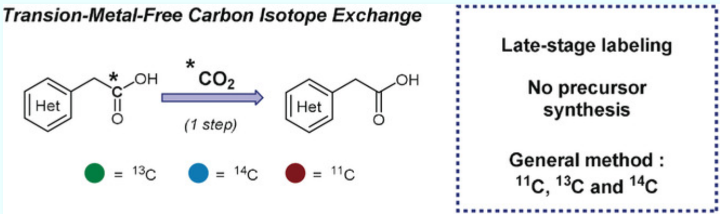
Angew. Chem. Int. Ed. **2020**, *59*, 12623
X. Bao, J. Rodriguez, D. Bonne
https://doi.org/10.1002/anie.202002518



Forging axes: Atropisomers with multiple stereogenic axes offer intriguing topologies in comparison to simple monoaxially chiral molecules. This Minireview covers some very recent breakthroughs in the enantioselective synthesis of atropisomers featuring multiple stereogenic axes.

Transition-Metal-Free Carbon Isotope Exchange of Phenyl Acetic Acids

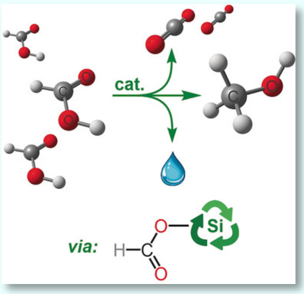
Angew. Chem. Int. Ed. **2020**, *59*, 13490
G. Destro, K. Horkka, O. Loreau, D.-A. Buisson, L. Kingston, A. Del Vecchio, M. Schou, C. S. Elmore, F. Taran, T. Cantat, D. Audisio
https://doi.org/10.1002/anie.202002341



Just labeled: Transition-metal-free carbon isotope exchange on phenyl acetic acids is described. Utilizing the universal precursor CO_2, the carbon isotope can be inserted into the carboxylic acid position, with no need of precursor synthesis. This procedure enabled the labeling of 15 pharmaceuticals and was compatible with [^{14}C] and [^{13}C]. A proof of concept with [^{11}C] was also obtained with low molar activity valuable for distribution studies.

Catalytic Disproportionation of Formic Acid to Methanol by using Recyclable Silylformates

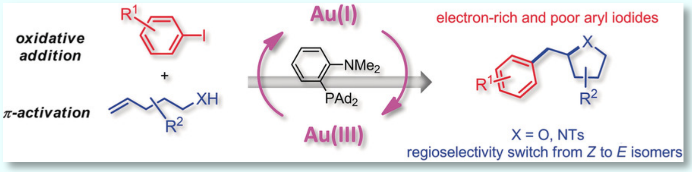
Angew. Chem. Int. Ed. **2020**, *59*, 14019
C. Chauvier, A. Imberdis, P. Thuéry, T. Cantat
https://doi.org/10.1002/anie.202002062



The efficient catalytic disproportionation of formic acid to methanol is enabled by shutting down the dehydrogenation of formic acid by using a cycle that involves recyclable silylformates and ruthenium-based catalysts. The procedure enables the formation of methanol in yields of up to 77 % isolated product.

Gold(I)/Gold(III) Catalysis that Merges Oxidative Addition and π-Alkene Activation

Angew. Chem. Int. Ed. **2020**, *59*, 16625
M. Rigoulet, O. Thillaye du Boullay, A. Amgoune, D. Bourissou
https://doi.org/10.1002/anie.202006074



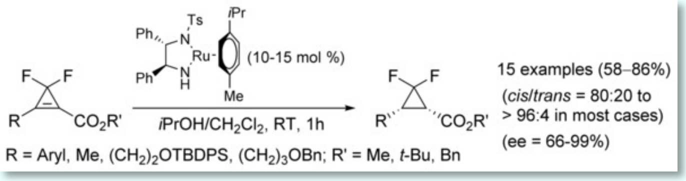
Two-in-one: A (MeDalphos)AuCl complex promotes both oxidative addition of aryl iodides and π-activation of alkenols/alkenamines. The reaction is robust and general (>30 examples including internal alkenes, 5-, 6-, and 7-membered rings). It is regioselective and leads exclusively to trans addition products.

Asymmetric Transfer Hydrogenation of gem-Difluorocyclopropenyl Esters: Access to Enantioenriched gem-Difluorocyclopropanes

Angew. Chem. Int. Ed. **2020**, *59*, 18505

K. Yamani, H. Pierre, A. Archambeau, C. Meyer, J. Cossy

https://doi.org/10.1002/anie.202008572



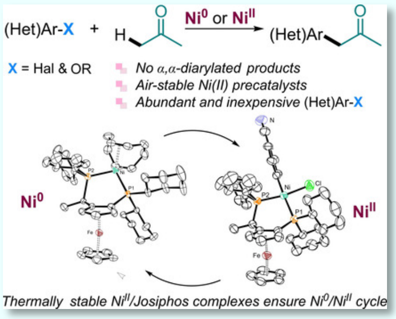
Asymmetric transfer hydrogenation of gem-difluorocyclopropenyl esters using the Noyori–Ikariya catalyst and isopropanol as the hydrogen donor provides access to enantioenriched gem-difluorocyclopropanes (ee=66–99 %), which are emerging fluorinated motifs of interest in medicinal chemistry.

Nickel-Catalyzed Mono-Selective α-Arylation of Acetone with Aryl Chlorides and Phenol Derivatives

Angew. Chem. Int. Ed. **2020**, *59*, 18948

S. A. Derhamine, T. Krachko, N. Monteiro, G. Pilet, J. Schranck, A. Tlili, A. Amgoune

https://doi.org/10.1002/anie.202006826



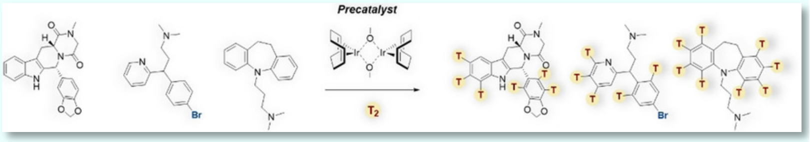
A nickel/Josiphos-based catalytic system is shown to be very efficient for the mono-**α**-arylation of acetone with (hetero)aryl chlorides and phenol derivatives. Broad functional-group tolerance was observed, and the desired products were obtained in good to excellent yields. Mechanistic studies allowed the isolation of catalytic intermediates and provided a rationale for the key role of the ligand.

Multiple Site Hydrogen Isotope Labelling of Pharmaceuticals

Angew. Chem. Int. Ed. **2020**, *59*, early view

M. Daniel-Bertrand, S. Garcia-Argote, A. Palazzolo, I. Mustieles Marin, P.-F. Fazzini, S. Tricard, B. Chaudret, V. Derdau, S. Feuillastre, G. Pieters

https://doi.org/10.1002/anie.202008519



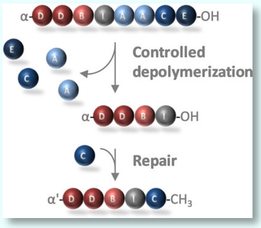
A general method for the multiple site hydrogen isotope labelling of complex molecules using the commercially available and air-stable iridium precatalyst $[Ir(COD)(OMe)]_2$ is reported. This new synthetic method possesses multiple key features far beyond the state-of-the-art methods for tritium labelling, including a very broad substrate scope and an exceptional functional group tolerance facilitating the access to complex pharmaceuticals with high molar activities.

Damage and Repair in Informational Poly(N-substituted urethane)s

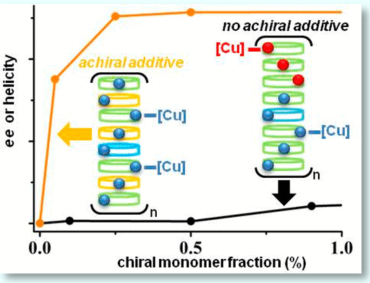
Angew. Chem. Int. Ed. **2020**, *59*, early view

T. Mondal, L. Charles, J.-F. Lutz

https://doi.org/10.1002/anie.202008864



In nature, the monomer sequences of informational biopolymers undergo damage, mutation, and repair. We show that comparable modifications can be obtained in non-natural sequence-defined poly(N-substituted urethane)s. Polymers containing ethyl carbamate main-chain repeat units and an **ω**-OH end-group depolymerize under basic conditions. However, through careful monomer design, this behavior can be controlled and repair can be performed.



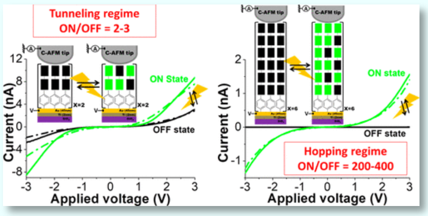
Emergence of Homochiral Benzene-1,3,5-tricarboxamide Helical Assemblies and Catalysts upon Addition of an Achiral Monomer

J. Am. Chem. Soc. **2020**, *142*, 5676

Y. Li, A. Hammoud, L. Bouteiller, M. Raynal

https://doi.org/10.1021/jacs.9b13157

We report on the counterintuitive ability of an achiral molecule to suppress conformational defects in supramolecular helices, thus leading to the emergence of homochirality in a system containing a very small chiral bias. We focus our investigation on supramolecular helices composed of an achiral benzene-1,3,5-tricarboxamide (BTA) ligand, coordinated to copper, and an enantiopure BTA comonomer. Amplification of chirality as probed by varying the amount (sergeants and soldiers effect) or the optical purity (diluted majority-rules effect) of the enantiopure comonomer are modest in this initial system. However, both effects are hugely enhanced upon addition of a second achiral BTA monomer, leading to a perfect control of the helicity either by means of a remarkably low amount of sergeants (0.5%) or a small bias from a racemic mixture of enantiopure comonomers (10% ee). Such an enhancement in the amplification of chirality is only achieved by mixing the three components, i.e. the two achiral and the enantiopure comonomers, highlighting a synergistic effect upon coassembly of the three monomers. Investigation of the role of the achiral additive by multifarious analytical techniques supports its ability to stabilize the helical coassemblies and suppress helix reversals: i.e., conformational defects. Implementation of these helical copper precatalysts in the hydrosilylation of 1-(4-nitrophenyl)ethanone confirms that the effect of the achiral BTA additive is also operative under the conditions of the catalytic experiment. A highly enantioenriched product (90% ee) is produced by a supramolecular catalyst operating with ppm levels of chiral species.



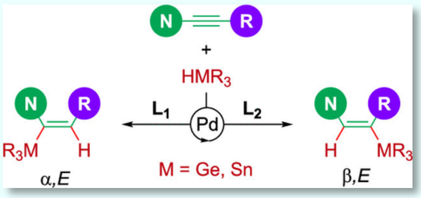
Highly Efficient Photoswitch in Diarylethene-Based Molecular Junctions

J. Am. Chem. Soc. **2020**, *142*, 7732

I. Hnid, D. Frath, F. Lafolet, X. Sun, J.-C. Lacroix

https://doi.org/10.1021/jacs.0c01213

Thin layers of diarylethene oligomers (oligo(DAE)) were deposited by electrochemical reduction of a diazonium salt on glassy carbon and gold electrodes. The layers were fully characterized using electrochemistry, XPS, and AFM, and switching between open and closed forms using light was evidenced. Solid-state molecular junctions (MJs), in which a C-AFM tip is used as the top contact, were fabricated with total layer thicknesses fixed at 2–3 nm and 8–9 nm, i.e. below and above the direct tunneling limit. DAE was then photoswitched between its open and closed forms. Oligo(DAE) MJs using the open form of DAE are highly resistive while those with DAE in the closed form are more conductive. ON/OFF ratios of 2–3 and 200–400 were obtained for 3-nm- and 9-nm-thick DAE MJs, respectively.



Ligand-Controlled Regiodivergent Palladium-Catalyzed Hydrogermylation of Ynamides

J. Am. Chem. Soc. **2020**, *142*, 11153

V. Debrauwer, A. Turlik, L. Rummler, A. Prescimone, N. Blanchard, K. N. Houk, V. Bizet

https://doi.org/10.1021/jacs.0c03556

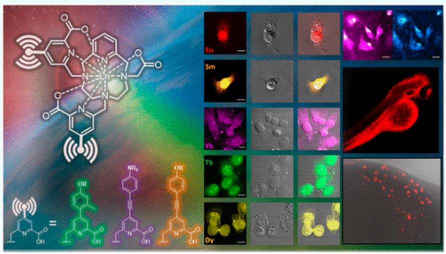
We report synthetic and DFT investigations of palladium-catalyzed ligand-controlled regiodivergent hydrometalation reactions of ynamides. Germylated and stannylated enamides are obtained with excellent **α**,E- or **β**,E-selectivities and a broad functional group tolerance. Such a regiodivergent palladium-catalyzed process is unique in ynamide chemistry and allows for the elaboration of metalated enamides that are useful building blocks for cross-coupling reactions or heterocyclic chemistry. DFT calculations fully support the experimental data and demonstrate the crucial roles of the trans-geometry of the [H-Pd(L)-Ge] complex, as well as of the steric requirements of the phosphine ligand. In addition, these calculations support the prevalence of a hydro-palladation pathway over a metal palladation of the π system of the ynamide.

Pyclen-Based Ln(III) Complexes as Highly Luminescent Bioprobes for In Vitro and In Vivo One- and Two-Photon Bioimaging Applications

J. Am. Chem. Soc. **2020**, *142*, 10184

N. Hamon, A. Roux, M. Beyler, J.-C. Mulatier, C. Andraud, C. Nguyen, M. Maynadier, N. Bettache, A. Duperray, A. Grichine, S. Brasselet, M. Gary-Bobo, O. Maury, R. Tripier

https://doi.org/10.1021/jacs.0c03496



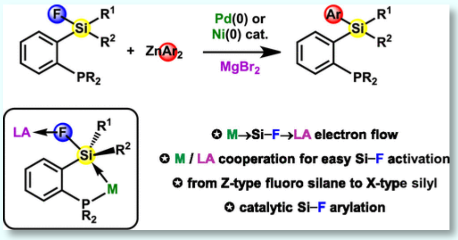
In addition to the already described ligand L^{4a}, two pyclen-based lanthanide chelators, L^{4b} and L^{4c}, bearing two specific picolinate two-photon antennas (tailor-made for each targeted metal) and one acetate arm arranged in a dissymmetrical manner, have been synthesized, to form a complete family of lanthanide luminescent bioprobes: $[EuL^{4a}]$, $[SmL^{4a}]$, $[YbL^{4b}]$, $[TbL^{4c}]$, and $[DyL^{4c}]$. Additionally, the symmetrically arranged regioisomer $L^{4a'}$ was also synthesized as well as its $[EuL^{4a'}]$ complex to highlight the astonishing positive impact of the dissymmetrical N-distribution of the functional chelating arms. The investigation clearly shows the high performance of each bioprobe, which, depending on the complexed lanthanide, could be used in various applications. Each presents high brightness, quantum yields, and lifetimes. Staining of the complexes into living human breast cancer cells was observed. In addition, in vivo two-photon microscopy was performed for the first time on a living zebrafish model with $[EuL^{4a}]$. No apparent toxicity was detected on the growth of the zebrafish, and images of high quality were obtained.

Fluorosilane Activation by Pd/Ni→Si–F→Lewis Acid Interaction: An Entry to Catalytic Sila-Negishi Coupling

J. Am. Chem. Soc. **2020**, *142*, 14039

JH. Kameo, H. Yamamoto, K. Ikeda, T. Isasa, S. Sakaki, H. Matsuzaka, Y. Garcia-Rodeja, K. Miqueu, D. Bourissou

https://doi.org/10.1021/jacs.0c04690



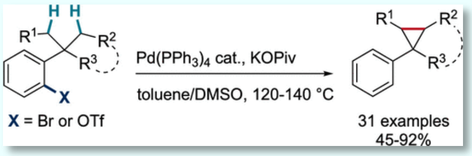
A new mode of bond activation involving M→Z interactions is disclosed. Coordination to transition metals as **σ**-acceptor ligands was found to enable the activation of fluorosilanes, opening the way to the first transition-metal-catalyzed Si–F bond activation. Using phosphines as directing groups, sila-Negishi couplings were developed by combining Pd and Ni complexes with external Lewis acids such as $MgBr_2$. Several key catalytic intermediates have been authenticated spectroscopically and crystallographically. Combined with DFT calculations, all data support cooperative activation of the fluorosilane via Pd/Ni→Si–F→Lewis acid interaction with conversion of the Z-type fluorosilane ligand into an X-type silyl moiety.

Direct Synthesis of Cyclopropanes from gem-Dialkyl Groups through Double C–H Activation

J. Am. Chem. Soc. **2020**, *142*, 15355

A. Clemenceau, P. Thesmar, M. Gicquel, A. Le Flohic, O. Baudoin

https://doi.org/10.1021/jacs.0c04690



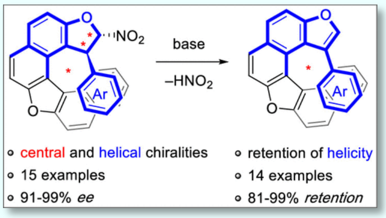
Cyclopropanes are important structural motifs found in numerous bioactive molecules, and a number of methods are available for their synthesis. However, one of the simplest cyclopropanation reactions involving the intramolecular coupling of two C–H bonds on gem-dialkyl groups has remained an elusive transformation. We demonstrate herein that this reaction is accessible using aryl bromide or triflate precursors and the 1,4-Pd shift mechanism. The use of pivalate as the base was found to be crucial to divert the mechanistic pathway toward the cyclopropane instead of the previously obtained benzocyclobutene product. Stoichiometric mechanistic studies allowed the identification of aryl- and alkylpalladium pivalates, which are in equilibrium via a five-membered palladacycle. With pivalate, a second $C(sp^3)$–H activation leading to the four-membered palladacycle intermediate and the cyclopropane product is favored. A catalytic reaction was developed and showed a broad scope for the generation of diverse arylcyclopropanes, including valuable bicyclo[3.1.0] systems. This method was applied to a concise synthesis of lemborexant, a recently approved anti-insomnia drug.

Simultaneous Control of Central and Helical Chiralities: Expedient Helicoselective Synthesis of Dioxa[6]helicenes

J. Am. Chem. Soc. **2020**, *142*, 16199

P. Liu, X. Bao, J.-V. Naubron, S. Chentouf, S. Humbel, N. Vanthuyne, M. Jean, L. Giordano, J. Rodriguez, D. Bonne

https://doi.org/10.1021/jacs.0c07995



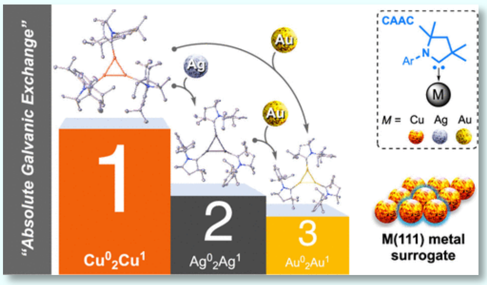
An expedient synthesis of a new family of configurationally stable dioxa[6]helicenes was established using a sequential helicoselective organocatalyzed heteroannulation/eliminative aromatization via enantioenriched fused 2-nitro dihydrofurans featuring both central and helical chiralities. Starting from simple achiral precursors, a broad range of these previously unknown chiral heterocyclic scaffolds were obtained with good efficiency, and their aromatization proceeded with very high enantiopurity retention in most cases.

Absolute Templating of M(111) Cluster Surrogates by Galvanic Exchange

J. Am. Chem. Soc. **2020**, *142*, 16479

J. L. Peltier, M. Soleilhavoup, D. Martin, R. Jazzar, G. Bertrand

https://doi.org/10.1021/jacs.0c07990



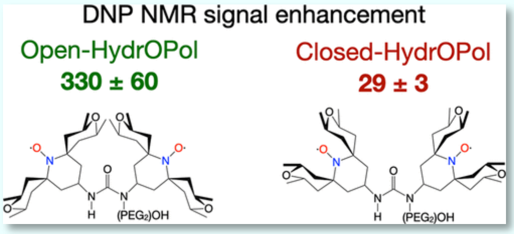
The precise preparation of monodisperse nanomaterials is among the most fundamental tasks in inorganic synthesis and materials science. Achieving this goal by galvanic exchange is hardly predictable and often results in major structural changes and polydisperse mixtures. Taking advantage of the enhanced stability imparted by ambiphilic carbenes, we report and rationalize the absolute templating, the complete exchange of metals in a template, of group 11 clusters across the entire coinage metal family by means of galvanic exchange. We further delineate that these species provide a molecular model for better understanding the reduction of CO_2 at M(111) coinage metal surfaces.

Open and Closed Radicals: Local Geometry around Unpaired Electrons Governs Magic-Angle Spinning Dynamic Nuclear Polarization Performance

J. Am. Chem. Soc. **2020**, *142*, 16587

G. Stevanato, G. Casano, D. J. Kubicki, Y. Rao, L. E. Hofer, G. Menzildjian, H. Karoui, D. Siri, M. Cordova, M. Yulikov, G. Jeschke, M. Lelli, A. Lesage, O. Ouari, L. Emsley

https://doi.org/10.1021/jacs.0c04911



The development of magic-angle spinning dynamic nuclear polarization (MAS DNP) has allowed atomic-level characterization of materials for which conventional solid-state NMR is impractical due to the lack of sensitivity. The rapid progress of MAS DNP has been largely enabled through the understanding of rational design concepts for more efficient polarizing agents (PAs). Here, we identify a new design principle which has so far been overlooked. We find that the local geometry around the unpaired electron can change the DNP enhancement by an order of magnitude for two otherwise identical conformers. We present a set of 13 new stable mono- and dinitroxide PAs for MAS DNP NMR where this principle is demonstrated. The radicals are divided into two groups of isomers, named open (O-) and closed (C-), based on the ring conformations in the vicinity of the N–O bond. In all cases, the open conformers exhibit dramatically improved DNP performance as compared to the closed counterparts. In particular, a new urea-based biradical named HydrOPol and a mononitroxide O-MbPyTol yield enhancements of 330 ± 60 and 119 ± 25, respectively, at 9.4 T and 100 K, which are the highest enhancements reported so far in the aqueous solvents used here. We find that while the conformational changes do not significantly affect electron spin–spin distances, they do affect the distribution of the exchange couplings in these biradicals. Electron spin echo envelope modulation (ESEEM) experiments suggest that the improved performance of the open conformers is correlated with higher solvent accessibility.

Expedient synthesis of conjugated triynes via alkyne metathesis

Chem. Sci. **2020**, *11*, 4934

I. Curbet, S. Colombel-Rouen, R. Manguin, A. Clermont, A. Quelhas, D. S. Müller, T. Roisnel, O. Baslé, Y. Trolez, M. Mauduit

https://doi.org/10.1039/D0SC01124J

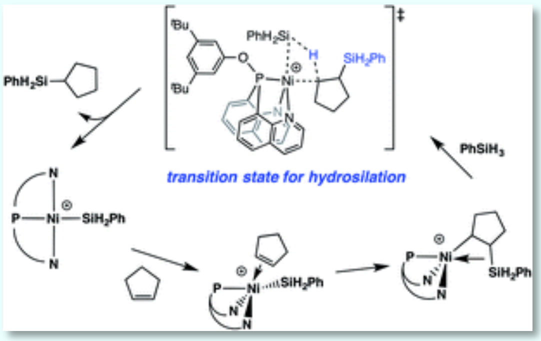
The first synthesis of symmetrical and dissymmetrical conjugated triynes by self- and cross-metathesis was successfully achieved thanks to the use of hindered diynes.

Efficient alkene hydrosilation with bis(8-quinolyl)phosphine (NPN) nickel catalysts. The dominant role of silyl-over hydrido-nickel catalytic intermediates

Chem. Sci. **2020**, *11*, 5043

J. Yang, V. Postils, M. I. Lipschutz, M. Fasulo, C. Raynaud, E. Clot, O. Eisenstein, T. Don Tilley

https://doi.org/10.1039/D0SC00997K



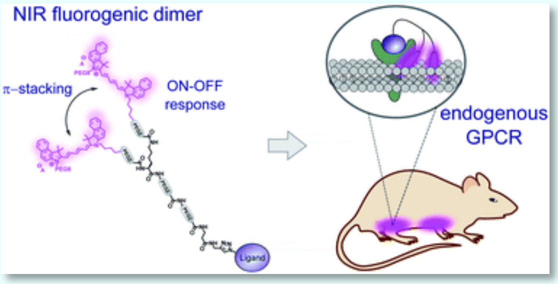
A cationic nickel complex of the bis(8-quinolyl)(3,5-di-tert-butylphenoxy)phosphine (NPN) ligand, [(NPN)NiCl]+, is a precursor to efficient catalysts for the hydrosilation of alkenes with hydrosilanes under mild conditions and low catalyst loadings.

A near-infrared fluorogenic dimer enables background-free imaging of endogenous GPCRs in living mice

Chem. Sci. **2020**, *11*, 6824

L. Esteoulle, F. Daubeuf, M. Collot, S. Riché, T. Durroux, D. Brasse, P. Marchand, I. A. Karpenko, A. S. Klymchenko, D. Bonnet

https://doi.org/10.1039/D0SC01018A



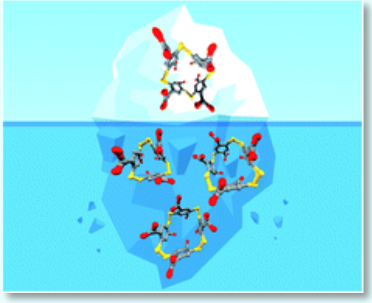
A near-infrared emitting fluorogenic dimer with environment-sensitive folding and exceptional brightness enables background-free and target-specific imaging of the naturally expressed oxytocin GPCR in living mice.

The dark side of disulfide-based dynamic combinatorial chemistry

Chem. Sci. **2020**, *11*, 8151

M. Dumartin, J. Septavaux, M. Donnier-Maréchal, E. Jeamet, E. Dumont, F. Perret, L. Vial, J. Leclaire

https://doi.org/10.1039/D0SC02399J



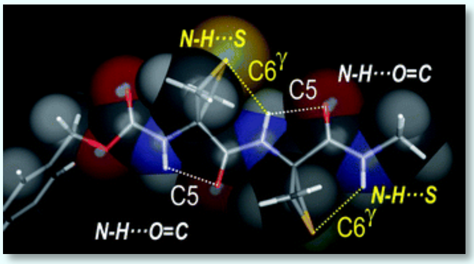
We show that multiple analytical tools are necessary in order to describe the different phenomena within disulfide-based dynamic combinatorial libraries in terms of size, stereochemistry, affinity and selectivity.

Conformation control through concurrent N–H···S and N–H···O=C hydrogen bonding and hyperconjugation effects

Chem. Sci. **2020**, *11*, 9191

Z. Imani, V. R. Mundlapati, G. Goldsztejn, V. Brenner, E. Gloaguen, R. Guillot, J.-P. Baltaze, K. Le Barbu-Debus, S. Robin, A. Zehnacker, M. Mons, D. J. Aitken

https://doi.org/10.1039/D0SC03339A



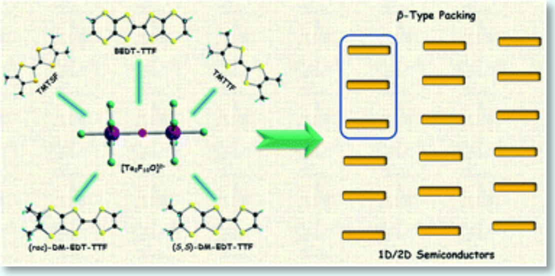
In addition to N–H···O[double bond, length as m-dash]C bonds, less conventional N–H···S hydrogen bonds are found to stabilize extended backbone geometries in derivatives of a thietane **α**-amino acid, providing a promising tool for the design of new peptidomimetic architectures.

Conservation of structural arrangements and 3:1 stoichiometry in a series of crystalline conductors of TMTTF, TMTSF, BEDT-TTF, and chiral DM-EDT-TTF with the oxo-bis[pentafluorotantalate(V)] dianion

Chem. Sci. **2020**, *11*, 10078

N. Mroweh, C. Mézière, M. Allain, P. Auban-Senzier, E. Canadell, N. Avarvari

https://doi.org/10.1039/D0SC03665J



Conducting radical cation salts of TMTTF, TMTSF, BEDT-TTF and DM-EDT-TTF with the oxo-bis(pentafluorotantalate) dianion [Ta2F10O]2− show similar packing and stoichiometry.