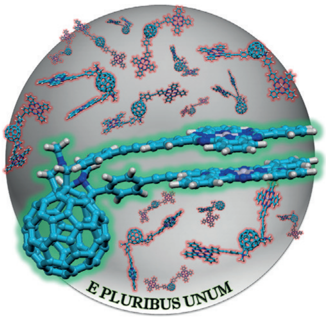
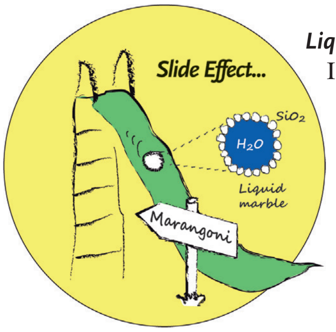
Hitherto considered inert C–H bonds …

… can react in formal annulation reactions using metal-catalyzed activation, which allows the conversion of readily available substrates into highly valuable cyclic products in a rapid and sustainable manner. In their Review on page 11000 ff., M. Gulías and J. L. Mascareñas make a classification of these powerful synthetic transformations on the basis of the mechanism and consideration of the number of atoms involved in the annulation.

Supramolecular Chemistry

The use of noncovalent interactions between untethered residues to amplify the regio-, stereo-, and atropselective formation of a C_{60} fullerene bisadduct racemate is described by G. Bottari, D. M. Guldi, T. Torres et al. in their Communication on page 11020 ff.



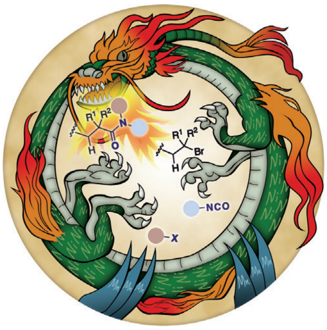


Liquid Marbles

In their Communication on page 11183 ff., D. Baigl et al. describe how floating liquid marbles can be transported on a photosensitive surfactant-laden solution by light-induced Marangoni flows, moving upstream (anti-Marangoni motion) at a low substrate thickness.

Nickel Catalysis

In their Communication on page 11207 ff., R. Martin and E. Serrano report a versatile method for the Ni-catalyzed reductive amidation of unactivated primary, secondary, and tertiary alkyl bromides with isocyanates to form a wide range of aliphatic amides.



How to contact us:

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Fax: (+49) 6201–606-331
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Editorial

“ ... The 6th EuCheMS Chemistry Congress will take place in Seville in September 2016. EuCheMS represents more than 160 000 chemists from more than 40 member societies. ChemPubSoc Europe is an organization of 16 European chemical societies from 15 countries. These initiatives have contributed significantly to the creation of a European identity for chemistry ...”
Read more in the Editorial by Luis A. Oro.

Service

Author Profile

“When I was eighteen I wanted to be a chemist. The principal aspect of my personality is curiosity. …”
This and more about Antonio M. Echavarren can be found on page 10952 – 10953.

News


G. Férey


C. Moberg


B. L. Feringa


J.-M. Tarascon


N. Martín


F. Würthner

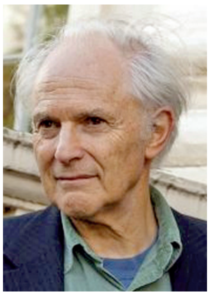

F. Diederich


P. J. Hergenrother


J. A. Lercher


D. Milstein

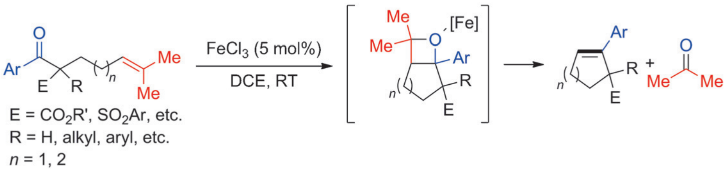
Obituaries



The Nobel Laureate Harry Kroto passed away aged 76 on April 30, 2016. His name will always be associated with the discovery of C_{60}, for which he was awarded the Nobel Prize in Chemistry 1996 together with Rick Smalley and Robert Curl. Experiments designed to aid the discovery of molecules in space ultimately led to an entirely new branch of condensed-phase physics and chemistry.

Highlights

Metathesis



Recent developments in catalytic carbonyl–olefin metathesis are summarized in this Highlight. Schindler and co-workers have reported that the environmentally benign $FeCl_3$ catalyst promotes ring-closing carbonyl–olefin metathesis (RCCOM) in high yield under very mild conditions.

For the USA and Canada:
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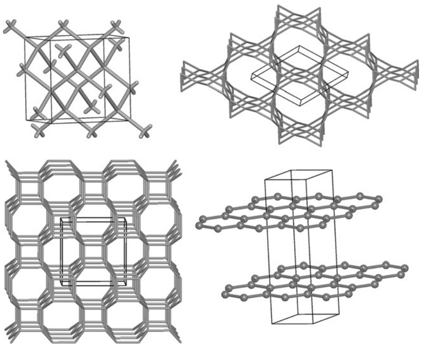
Essays

Citation Ethics

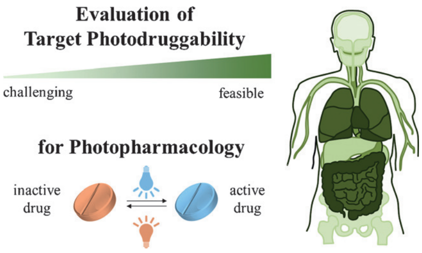
Cite we must, cite we do. We cite because we are links in a chain, using properties and methods validated by others. We also cite to negotiate the anxiety of influence. And to be fair. After outlining the reasons for citation, we use two case studies of citation amnesia in the field of hypothetical carbon allotropes to present a computer-age search tool (SACADA) in that subsubfield. Finally, we advise on good search practice, including what to do if you miss a citation.



Reviews

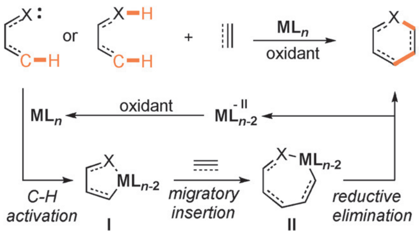
Medicinal Chemistry

Spotlight on the patient: The impressive advances made in the field of photopharmacology in recent years are critically reviewed with respect to the "photodruggability" of medicinal targets and prospects for the selective delivery of light to different organs. This Review is meant to provide a stimulus for chemists to enter this exciting field, with fascinating opportunities to bring "smart" molecular design to the realm of clinical use.



Annulation

Formal notice: Recent years have witnessed an upsurge in annulations based on C–H activation that can be formally considered as cycloaddition processes. These transformations are particularly appealing from a synthetic perspective because they allow the conversion of readily available substrates into highly valuable cyclic products in a rapid and sustainable manner.

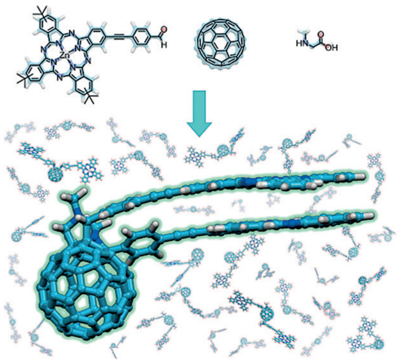


Front Cover

Communications

Supramolecular Chemistry

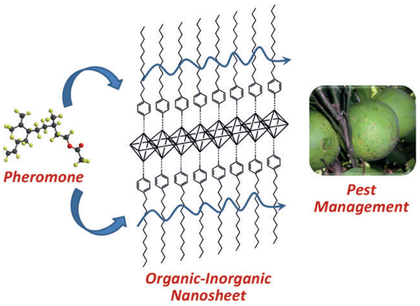
E pluribus unum: A conceptually novel, supramolecular-directed functionalization approach is presented in which noncovalent interactions between untethered residues have been used to amplify (> 2800-fold) the regio-, stereo-, and atropselective formation of a C_{60} fullerene bisadduct racemate. Remarkably, both enantiomers represent the first examples of fullerene derivatives with combined central, axial, and helical chirality.



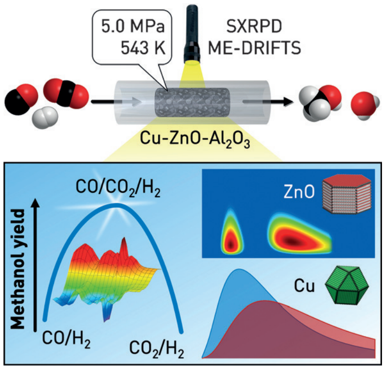
Frontispiece

Layered Hybrid Materials

Come into my layer: Layered organic–inorganic materials, based on ordered nickel nanoribbons separated by alkyl arylic monocarboxylate spacers located perpendicular to the 1D inorganic chains, act as a matrix for the controlled release of active principles (pheromones) in environmentally friendly pest management.

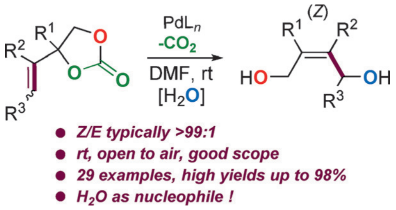


Heterogeneous Catalysis

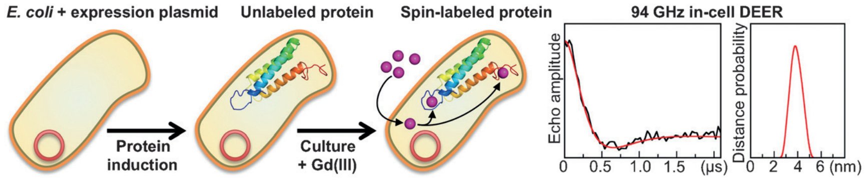


A methanol synthesis catalyst at work: Operando synchrotron X-ray powder diffraction and modulated-excitation infrared spectroscopy studies on Cu-ZnO-Al_2O_3 reveal that, under the optimal $CO/CO_2/H_2$ gas mixture, sintering of Cu and ZnO particles is prevented and ZnO adopts a preferred morphology which favors the water-gas shift reaction. The results offer an explanation for the long-debated promotional effect by CO_2.

Homogeneous Catalysis



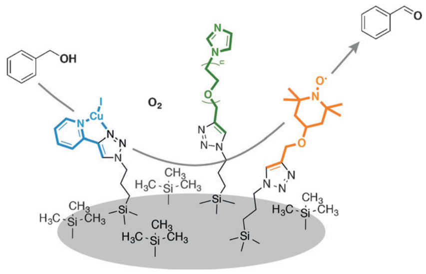
A highly efficient and stereoselective Pd-mediated synthesis of substituted (*Z*)-1,4-diols is described using allyl surrogates derived from vinyl cyclic carbonates. The method features operational simplicity, high yields, and stereocontrol using water as a nucleophilic reagent. Control experiments support the view that hyperconjugation plays an imperative role in these stereospecific conversions.



In a spin: A 3-helix bundle flanked by two lanthanide-binding tags was expressed in *E. coli*. Gd^{III} added to the medium is able to enter the cell and bind to the protein tags to give a fully biosynthetic spin-labeled protein. DEER measurements on intact cells showed that this is a feasible approach for in-cell structural studies of proteins under native cell conditions.

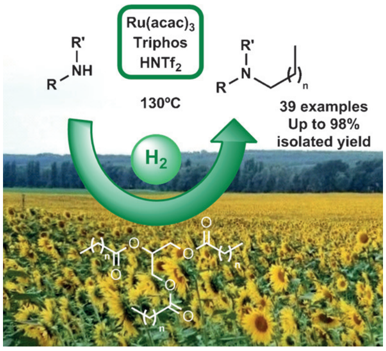
Protein Structures

A simple and modular strategy is reported for the preparation and engineering of trifunctional supported catalysts bearing Cu, TEMPO, and NMI sites for application in the aerobic oxidation of alcohols. Variation of the linker length on the NMI component and optimization of surface composition allowed synergistic interactions to be tailored for optimal activity and recycling.



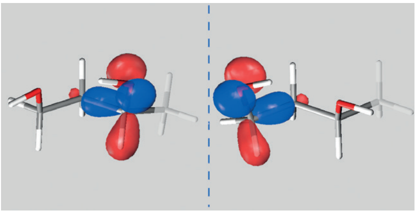
Supported Catalysis

Give me an alkyl group: Triglycerides are used as bio-based N-alkylating agents. In a single-step process with hydrogen, a broad range of amines are synthesized using a specific Ru catalyst.



Homogeneous Catalysis

Methyl substitution at a terminal carbon of 1,3-propanediol creates a new stereogenic center, and hence permanent *R* and *S* configurational enantiomers of 1,3-butanediol. However, the HOMO electron dynamics are predicted to continue displaying marked conformational pseudo-enantiomerism analogous to the transient conformational chirality in 1,3-propanediol.



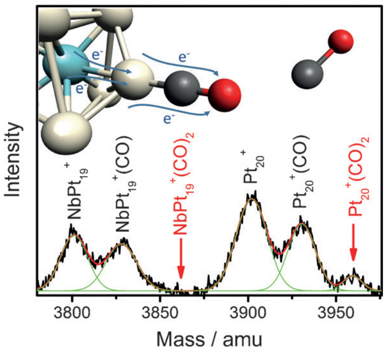
Chirality

Cluster Chemistry

P. Ferrari, L. M. Molina,* V. E. Kaydashev,
J. A. Alonso, P. Lievens,
E. Janssens* ———— **11059 – 11063**

Controlling the Adsorption of Carbon Monoxide on Platinum Clusters by Dopant-Induced Electronic Structure Modification

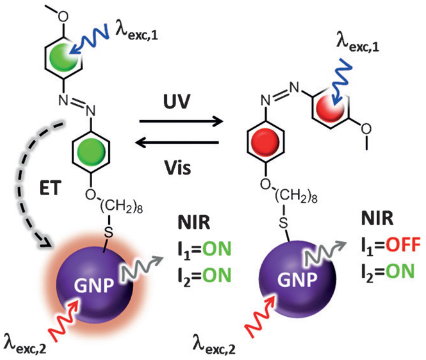
Gas-phase reactions: The influence of dopant atoms on the carbon monoxide adsorption on small platinum clusters was studied by mass spectrometry (see picture) in combination with density functional calculations. The results show a correlation of the dopant coordination and the dopant-dependent charge transfer with the CO adsorption energy.



Molecular Switches

S. Bonacchi, A. Cantelli, G. Battistelli,
G. Guidetti, M. Calvaresi, J. Manzi,
L. Gabrielli, F. Ramadori, A. Gambarin,
F. Mancin, M. Montalti* **11064 – 11068**

Photoswitchable NIR-Emitting Gold Nanoparticles



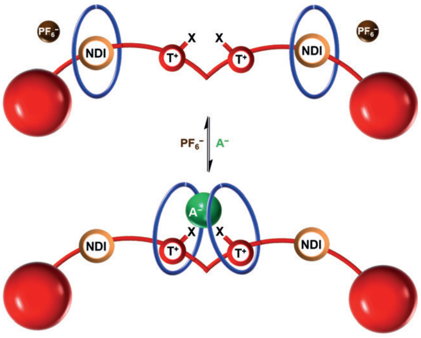
Reversible photo-isomerization of azobenzene ligands bound to the surface of gold nanoparticles (GNP) induces ON/OFF switching of the metal core NIR luminescence. An excitation energy transfer process from the ligands to the GNP, which produces sensitized NIR emission, is shown to be the basis of the phenomenon.

Molecular Shuttles

T. A. Barendt, A. Docker, I. Marques,
V. Félix, P. D. Beer* ——— **11069 – 11076**

Selective Nitrate Recognition by a Halogen-Bonding Four-Station [3]Rotaxane Molecular Shuttle

Anion sandwich is a pincer cake: The synthesis of the first halogen-bonding (XB) [3]rotaxane host system containing a four-station axle is reported. Anion-binding titration experiments reveal that the rotaxane is selective for nitrate and operates through a dynamic pincer mechanism in which both macrocycles shuttle to the central XB anion recognition sites to form a 1:1 stoichiometric oxoanion–rotaxane sandwich complex.

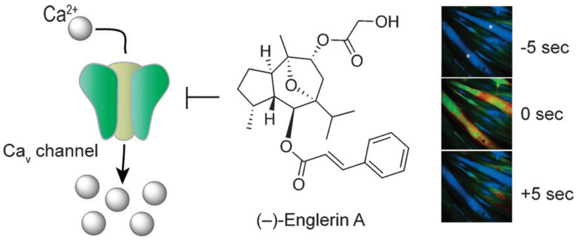


A^- = oxoanion, NDI = naphthalene diimide, T^+ = triazolium and X = I or H.

Target Prediction

T. Rodrigues,* F. Sieglitz, V. J. Somovilla,
P. M. S. D. Cal, A. Galione, F. Corzana,*
G. J. L. Bernardes* ——— **11077 – 11081**

Unveiling (−)-Englerin A as a Modulator of L-Type Calcium Channels

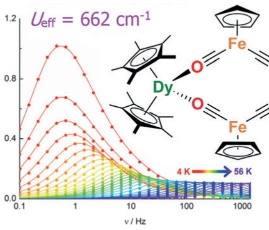


Target acquired: The L-type calcium channel was discovered to be a macromolecular target of the cancer-selective natural product (−)-englerin A through a ligand-based target-prediction method. The results suggest that cross-natural-product target inference can be used in the discovery of targets for complex natural products, and to support the understanding of polypharmacology networks in chemical biology and molecular medicine.

Single-Molecule Magnets

T. Pugh, N. F. Chilton,
R. A. Layfield* ———— 11082 – 11085

A Low-Symmetry Dysprosium Metallocene Single-Molecule Magnet with a High Anisotropy Barrier



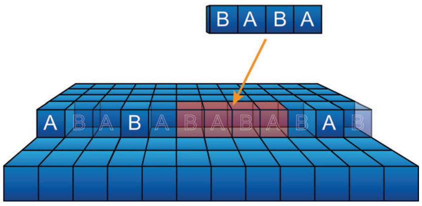
Kramers vs. Kramers: An isocarbonyl-ligated dysprosium metallocene single-molecule magnet (SMM) is designed and synthesized using a magnetostructural correlation. The SMM has a very large barrier of 662 cm^{-1}, with magnetization reversal occurring via the fourth-, fifth-, and sixth-excited Kramers doublets.

Mineral Growth

M. P. Andersson,* S. Dobberschütz,
K. K. Sand, D. J. Tobler, J. J. De Yoreo,
S. L. S. Stipp ———— 11086 – 11090

A Microkinetic Model of Calcite Step Growth

A robust model: A microkinetic model is presented that accurately reproduces calcite growth over a wide range of experimental parameters for solution composition, saturation index, pH and impurities. Polynuclear complexes play a central role at high supersaturation and a classical complexation model is sufficient to reproduce measured rates.

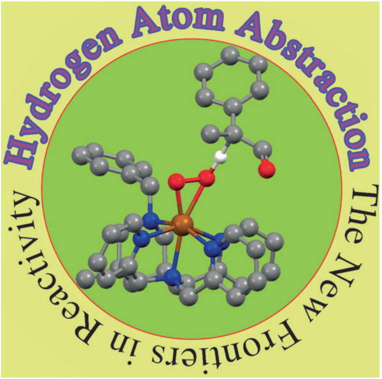


Biomimetic Models

VIP

P. Barman, P. Upadhyay, A. S. Faponle,
J. Kumar, S. S. Nag, D. Kumar,*
C. V. Sastri,*
S. P. de Visser* ———— 11091 – 11095

Deformylation Reaction by a Nonheme Manganese(III)–Peroxo Complex via Initial Hydrogen-Atom Abstraction

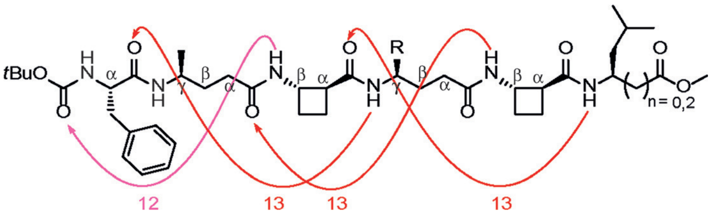


Grab the hydrogen first: A combined spectroscopic, kinetic, and computational modeling study gives first evidence of a rate-determining hydrogen-atom abstraction reaction for aldehyde deformation reactions by nonheme manganese(III)–peroxo complexes (see picture: Mn brown, C gray, O red, N blue, H white).

Peptidomimetics

C. M. Grison, J. A. Miles, S. Robin,
A. J. Wilson,*
D. J. Aitken* ———— 11096 – 11100

An α-Helix-Mimicking 12,13-Helix: Designed α/β/γ-Foldamers as Selective Inhibitors of Protein–Protein Interactions



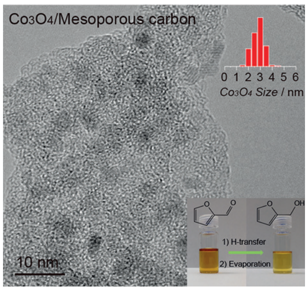
Match and mimic: α/β/γ-Peptides featuring *trans*-2-aminocyclobutanecarboxylic acid (*t*ACBC) as the "structuring" β-amino acid component adopt a 12,13-helical conformation and can behave as selective inhibitors of the p53/*h*DM2 interaction.

Supported Catalysts

G.-H. Wang, X. Deng, D. Gu, K. Chen, H. Tüysüz, B. Spliethoff, H.-J. Bongard, C. Weidenthaler, W. Schmidt, F. Schüth* ———— 11101–11105

Co_3O_4 Nanoparticles Supported on Mesoporous Carbon for Selective Transfer Hydrogenation of α,β-Unsaturated Aldehydes

A particularly good transfer: Co_3O_4 nanoparticles (ca. 3 nm) dispersed on mesoporous carbon have been prepared by a simple and scalable method. The product shows excellent catalytic performance in transfer hydrogenation of furan-based α,β-unsaturated aldehydes to unsaturated alcohols with selectivity higher than 95% at full conversion.

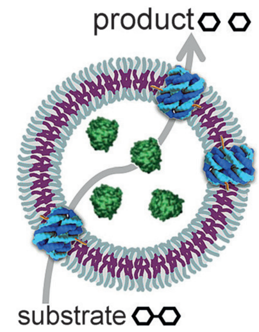


Nanotechnology

L. Messager, J. R. Burns, J. Kim, D. Cecchin, J. Hindley, A. L. B. Pyne, J. Gaitzsch, G. Battaglia,* S. Howorka* ———— 11106–11109

Biomimetic Hybrid Nanocontainers with Selective Permeability

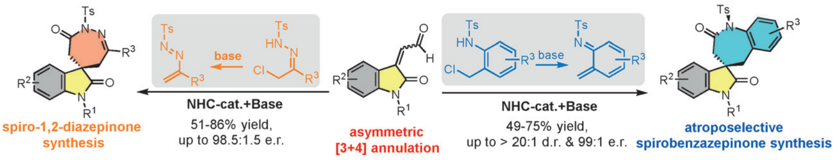
Functional hybrid nanocontainers composed of polymersomes (purple/gray) and DNA nanopores (blue) exhibit size-selective permeability and permit the transport of enzyme substrates and products through the DNA nanopores while bioactive encapsulated enzymes (green) are retained.



Organocatalysis

L. Wang, S. Li, M. Blümel, A. R. Philipps, A. Wang, R. Puttreddy, K. Rissanen, D. Enders* ———— 11110–11114

Asymmetric Synthesis of Spirobenzazepinones with Atroposelectivity and Spiro-1,2-Diazepinones by NHC-Catalyzed [3+4] Annulation Reactions

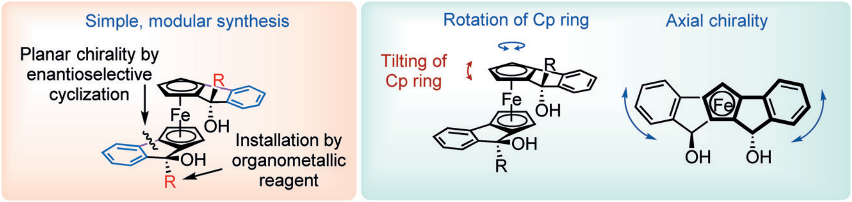


Spiro via [3+4]: The asymmetric NHC-catalyzed [3+4] annulation of isatin-derived enals and aryl sulfonamides or tosyl hydrazones leads to spirobenzazepinones with atroposelectivity, or to spiro-1,2-diazepinones bearing an oxindole moiety in high yields and excellent enantioselectivities with a wide variety of substrates.

Planar Chirality

C. Nottingham, H. Müller-Bunz, P. J. Guiry* ———— 11115–11119

A Family of Chiral Ferrocenyl Diols: Modular Synthesis, Solid-State Characterization, and Application in Asymmetric Organocatalysis

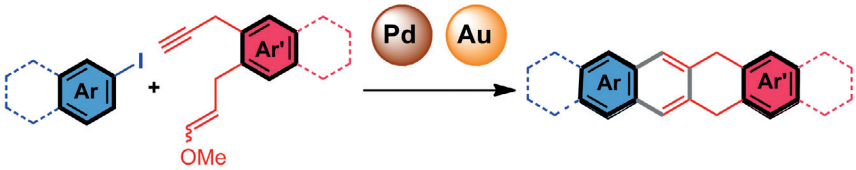


Triple crown of chirality: Reported is the synthesis of a novel family of chiral ferrocenyl diols possessing planar, central, and axial chirality. X-ray crystallography reveals dense intra- and intermolecular hydrogen-bond networks. The potential of these diols as organocatalysts was demonstrated in an asymmetric hetero-Diels–Alder reaction, thus providing cycloadducts in up to 84% yield with *ee* values ranging from −92 to +72%.

Cycloaddition Reactions

R. Dorel, P. R. McGonigal,
A. M. Echavarren* ——— 11120 – 11123

Hydroacenes Made Easy by Gold(I) Catalysis

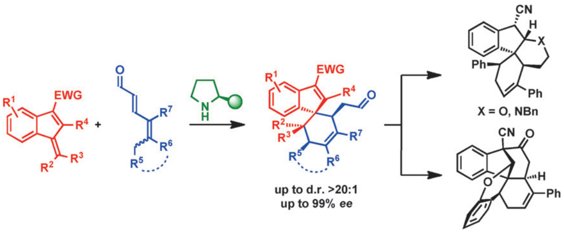


Gold lines them up! A straightforward annulation based on a Sonogashira coupling and a gold(I)-catalyzed cyclization of aryl-tethered 1,7-enynes leads to partially saturated acenes such as dihydropentacene, tetrahydroheptacene, and tetrahydrononacene.

Asymmetric Organocatalysis

B. S. Donslund, R. P. Nielsen,
S. M. N. Mønsted,
K. A. Jørgensen* ——— 11124 – 11128

Benzofulvenes in Trienamine Catalysis: Stereoselective Spiroindene Synthesis

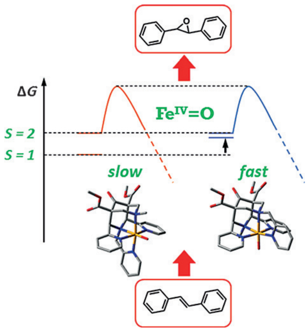


High fidelity: The benzofulvene core was found to be an excellent starting point for the asymmetric synthesis of spiroindenes with up to four contiguous stereocenters under trienamine catalysis. The product scaffold can be diversified by further manipulations of the chiral spiroindenes, as demonstrated by three intramolecular ring-closing reactions resulting in highly complex polycyclic systems (see scheme).

Iron Complexes

P. Comba,* S. Fukuzumi,* C. Koke,
B. Martin, A.-M. Löhr,
J. Straub ——— 11129 – 11133

A Bispidine Iron(IV)–Oxo Complex in the Entatic State

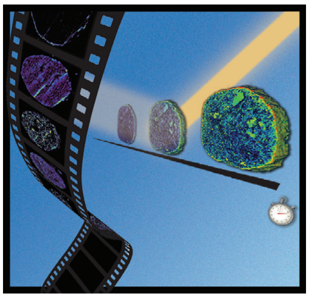


Fe^{IV}=O complexes with tetra- and pentadentate bispidine ligands were studied regarding the correlation of redox potentials with reactivity for substrates in alkane hydroxylation, alkene epoxidation, and thioether oxygenation. The redox potentials span about 350 mV and reaction rates over 8 orders of magnitude. The reactivity difference of two isomeric pentadentate bispidine systems is due to destabilization of the $S=1$ ground state of one of the ferryl isomers.

Heterogeneous Catalysis

S. Kalirai, P. P. Paalanen, J. Wang,
F. Meirer,
B. M. Weckhuysen* ——— 11134 – 11138

Visualizing Dealumination of a Single Zeolite Domain in a Real-Life Catalytic Cracking Particle

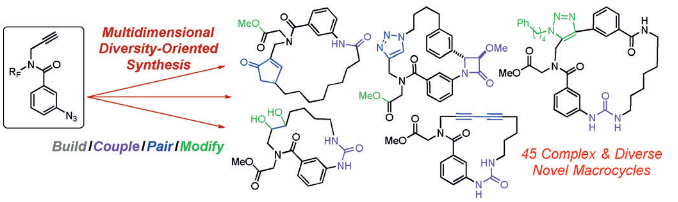


New light on catalyst deactivation: Real-life catalytic cracking particles of different catalytic age were studied with scanning transmission X-ray microscopy (see picture). By localizing individual zeolite domains on the basis of lanthanum mapping, zeolite dealumination could be tracked at the level of an individual zeolite domain.

Synthetic Methods

F. Nie, D. L. Kunciw, D. Wilcke,
J. E. Stokes, W. R. J. D. Galloway,
S. Bartlett, H. F. Sore,
D. R. Spring* ______ **11139 – 11143**

A Multidimensional Diversity-Oriented Synthesis Strategy for Structurally Diverse and Complex Macrocycles



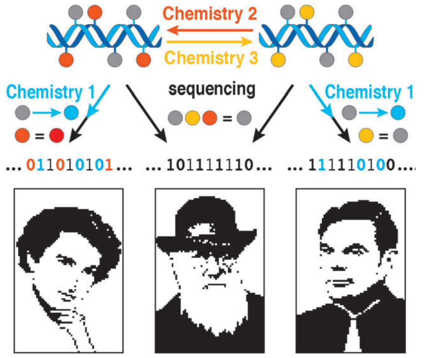
A diversity-oriented synthesis: A four-stage multidimensional strategy for the synthesis of complex, highly functionalized and structurally diverse macrocycles is reported (see picture). The synthesis exploits the diverse reactivity of aza-ylides and imines and features eight different macrocyclization methods, two of which are novel.

Epigenetics

C. Mayer, G. R. McInroy, P. Murat,
P. Van Delft,
S. Balasubramanian* ______ **11144 – 11148**

An Epigenetics-Inspired DNA-Based Data Storage System

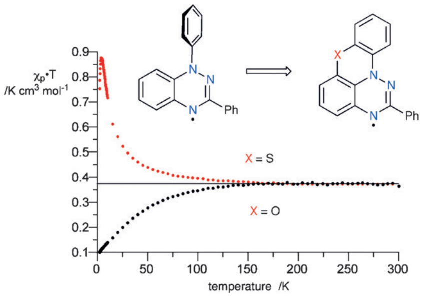
Information storage: Inspired by the epigenetic regulation of genomic information in cells, it is shown how digital data can undergo controlled changes when encoded in synthetic DNA strands. Chemical transformations were used to alter naturally occurring cytosine derivatives, which enabled the reversible recovery of multiple data layers from a single DNA template (see portraits).



Radicals

P. Kaszyński,* C. P. Constantinides,
V. G. Young, Jr. ______ **11149 – 11152**

The Planar Blatter Radical: Structural Chemistry of 1,4-Dihydrobenzo[*e*][1,2,4]triazin-4-yls

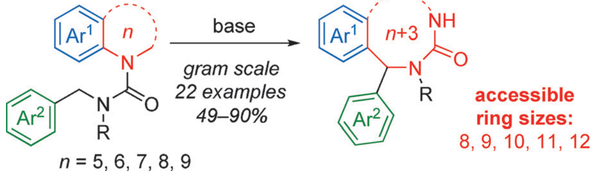


Plane away: The planarized Blatter radical offers expanded spin delocalization, near-IR absorption, and a new tool for controlling supramolecular assembly, and hence magnetic behavior. The structure provides a new platform for molecular and supramolecular engineering, and for tuning the electronic and magnetic properties of the radical.

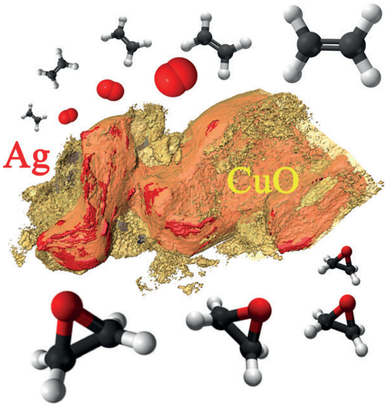
Heterocycles

J. E. Hall, J. V. Matlock, J. W. Ward,
K. V. Gray, J. Clayden* ______ **11153 – 11157**

Medium-Ring Nitrogen Heterocycles through Migratory Ring Expansion of Metalated Ureas



Ringing in ureas: Simple benzo-fused nitrogen heterocycles (indolines, tetrahydroquinolines, and their homologues) undergo migratory ring expansion under basic conditions to generate a range of medium-ring nitrogen heterocycles with ring sizes of 8–12. Considerable complexity is rapidly generated in an efficient synthesis of these otherwise difficult-to-obtain rings.



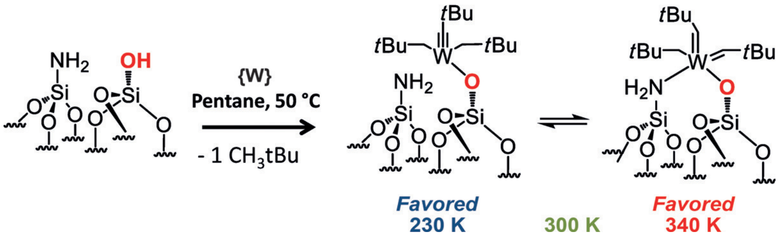
When silver meets copper oxide: A catalyst composed of silver nanostructures dispersed within a nanotubular copper oxide support was found to be an excellent catalyst for the selective epoxidation of ethylene at temperatures below 250 °C. The catalyst can accommodate chlorine promoters in a single pretreatment step with the CuO acting essentially as a Cl sponge, thus avoiding, for the most part, irreversible catalyst poisoning.

Heterogeneous Catalysis

A. Ramirez, J. L. Hueso,* H. Suarez, R. Mallada, A. Ibarra, S. Irusta, J. Santamaria* ———— **11158 – 11161**

A Nanoarchitecture Based on Silver and Copper Oxide with an Exceptional Response in the Chlorine-Promoted Epoxidation of Ethylene

Inside Cover



O brave HETCOR! Look how it binds! Solid-state NMR was used to demonstrate the tautomerization of the alkyl alkylidyne and bis(alkylidene) forms of a tungsten complex on a SBA15 silica surface. Such equilibrium is possible through the coordination of W to the surface-adjacent [(≡Si−OH) (≡Si−NH$_2$)] groups, which behave as a [N,O] pincer ligand. {W} = W(≡C*t*Bu)(CH$_2$*t*Bu)$_3$.

Heterogeneous Catalysis

A. Bendjeriou-Sedjerari, J. Sofack-Kreutzer, Y. Minenkov, E. Abou-Hamad, B. Hamzaoui, B. Werghi, D. H. Anjum, L. Cavallo, K. W. Huang, J. M. Basset* ———— **11162 – 11166**

Tungsten(VI) Carbyne/Bis(carbene) Tautomerization Enabled by N-Donor SBA15 Surface Ligands: A Solid-State NMR and DFT Study

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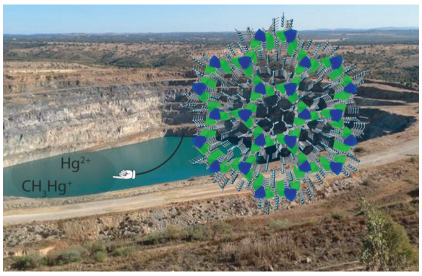
A highly flexible bioMOF was developed for the selective and efficient capture of the most harmful forms of mercury, CH_3Hg^+ and Hg^{2+}, from aqueous solutions. These ions were efficiently immobilized by specific conformations adopted by the flexible thioether "claws" decorating the pores of the bioMOF.

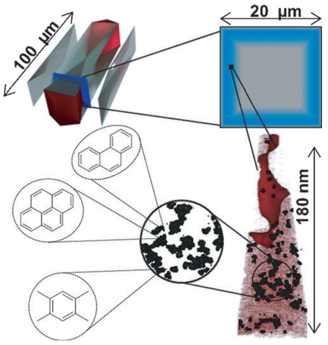


Mercury

M. Mon, F. Lloret, J. Ferrando-Soria,* C. Martí-Gastaldo, D. Armentano,* E. Pardo* ———— **11167 – 11172**

Selective and Efficient Removal of Mercury from Aqueous Media with the Highly Flexible Arms of a BioMOF

Al have a coke: Atom probe tomography (APT) has been used for the first time to probe the nanoscale distribution of coke deposits within a single zeolite ZSM-5 crystal used in the methanol-to-hydrocarbons reaction. Cluster analysis of the ^{13}C, Al, and Si APT data has identified isolated clusters of approximately 30–60 ^{13}C atoms that are intimately correlated with sub-nm increases in Brønsted acid site density. Possible coke species present in the ^{13}C clusters are shown.

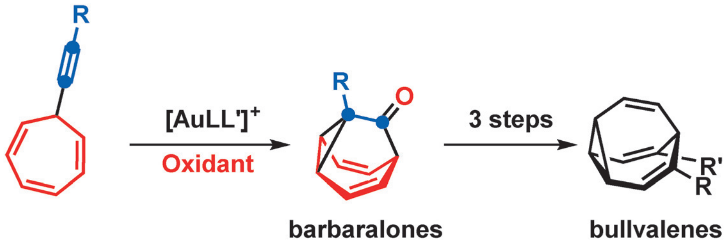


Zeolite Catalysis

J. E. Schmidt, J. D. Poplawsky, B. Mazumder, Ö. Attila, D. Fu, D. A. M. de Winter, F. Meirer, S. R. Bare,* B. M. Weckhuysen* ———— **11173 – 11177**

Coke Formation in a Zeolite Crystal During the Methanol-to-Hydrocarbons Reaction as Studied with Atom Probe Tomography

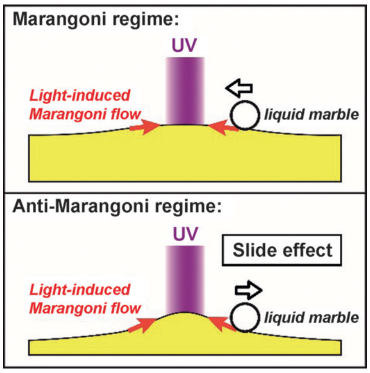
Fluxional Molecules



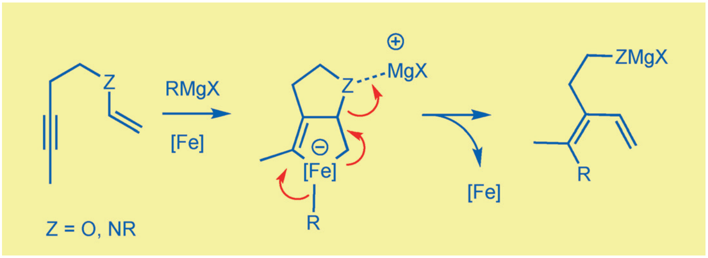
Take the bull by the horns: A method that accomplishes the shortest known syntheses of bullvalene and other substituted bullvalenes has been developed. Gold(I)-catalyzed oxidative cyclization of 7-(substituted ethynyl)-1,3,5-cycloheptatrienes yields 1-substituted barbaralones, allowing easy access to other fluxional molecules.

Liquid Marbles

Sliding marbles: Floating liquid marbles can be transported by light-induced Marangoni flows. Liquid marbles move in the direction of these flows at a large liquid-layer thickness (Marangoni regime) but show a remarkable upstream motion at a low substrate thickness (anti-Marangoni motion). The upstream motion occurs as a result of deformation of the surface of the liquid, a behavior termed the "slide effect".



Reaction Cascades

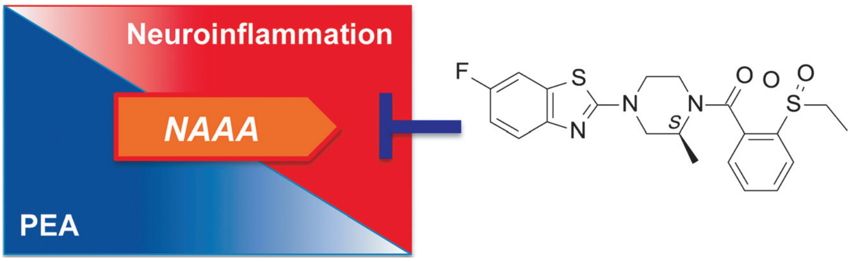


Cut and paste: Iron catalysis allows cycloisomerization chemistry and cross-coupling to be merged into a new reaction cascade. This manifold engenders formation of two new C–C bonds at the expense of a C–Z bond in the substrate backbone, which is cleaved while the tetrasubstituted alkene product is forming.

Medicinal Compounds

M. Migliore, S. Pontis,
A. L. Fuentes de Arriba, N. Realini,
E. Torrente, A. Armirotti, E. Romeo,
S. Di Martino, D. Russo, D. Pizzirani,
M. Summa, M. Lanfranco, G. Ottonello,
P. Busquet, K.-M. Jung,
M. Garcia-Guzman, R. Heim,
R. Scarpelli,*
D. Piomelli* ——— **11193–11197**

Second-Generation Non-Covalent NAAA Inhibitors are Protective in a Model of Multiple Sclerosis

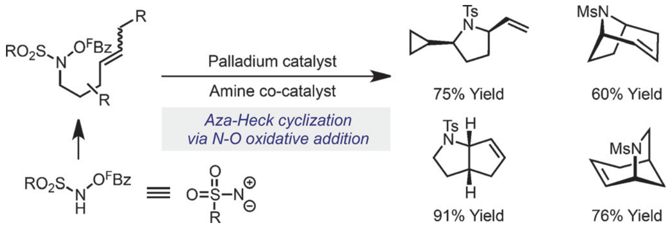


Treating neuroinflammation: The cysteine amidase *N*-acyl ethanolamine acid amidase (NAAA) promotes inflammation by degrading endogenous anti-inflammatory lipid amides such as palmitoylethanolamide (PEA). A new class of non-covalent, orally available NAAA inhibitors (see example) interrupt NAAA-mediated lipid amide degradation in the brain, and are strongly protective in a mouse model of neuroinflammation.

N-Heterocycles

I. R. Hazelden, X. Ma, T. Langer,
J. F. Bower* ——— **11198–11202**

Diverse *N*-Heterocyclic Ring Systems via Aza-Heck Cyclizations of *N*-(Pentafluorobenzoyloxy)sulfonamides

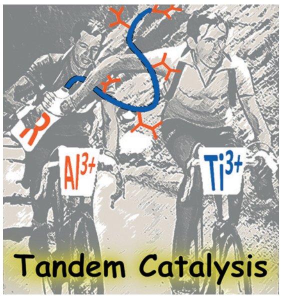


Aza-Heck cyclizations initiated by oxidative addition of Pd^0 catalysts into the N−O bond of *N*-(pentafluorobenzoyloxy)sulfonamides are described. These studies, which are only the second class of aza-Heck reaction developed to date, provide direct access to diverse *N*-heterocyclic ring systems (18 examples, 42–91 % yield).

Heterogeneous Catalysis

A. Piovano, K. S. Thushara, E. Morra,
M. Chiesa, E. Groppo* ——— **11203–11206**

Unraveling the Catalytic Synergy between Ti^{3+} and Al^{3+} Sites on a Chlorinated Al$_2$O$_3$: A Tandem Approach to Branched Polyethylene



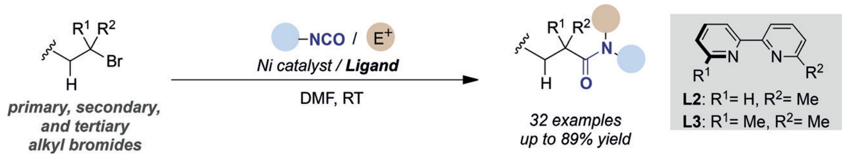
Working side by side: Branched polyethylene was synthesized using a catalyst consisting of Ti^{3+} and Al^{3+} sites on chlorinated alumina. Spectroscopic and physicochemical characterization showed that the catalytic sites act synergistically to promote the olefin conversion.

Reductive Coupling

E. Serrano, R. Martin* ——— **11207–11211**

Nickel-Catalyzed Reductive Amidation of Unactivated Alkyl Bromides

Back Cover

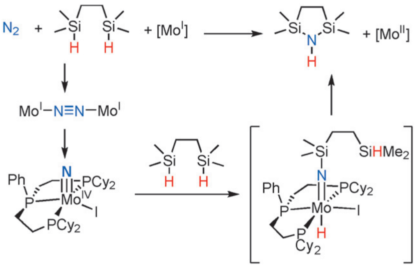


Mild and selective: A versatile Ni-catalyzed reductive amidation of unactivated primary, secondary, and tertiary alkyl bromides with isocyanates gives access to a wide range of aliphatic amides. The reaction proceeds under mild conditions, has excellent chemoselectivity, and avoids the use of stoichiometric and sensitive organometallic reagents.

Nitrogen Fixation

Q. Liao, A. Cavaillé, N. Saffon-Merceron, N. Mézailles* ______ **11212 – 11216**

Direct Synthesis of Silylamine from N_2 and a Silane: Mediated by a Tridentate Phosphine Molybdenum Fragment

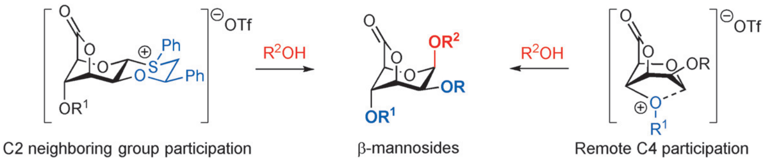


Split up: Reaction of N_2 with an in situ generated molybdenum(I) fragment stabilized by a tridentate phosphine ligand results in direct N_2 splitting and formation of the nitrido complex. Functionalization of the nitrido all the way to the formation of bis(silyl)amine can be achieved under mild reaction conditions with bis(silane).

Glycosylation

H. Elferink, R. A. Mensink, P. B. White, T. J. Boltje* ______ **11217 – 11220**

Stereoselective β-Mannosylation by Neighboring-Group Participation

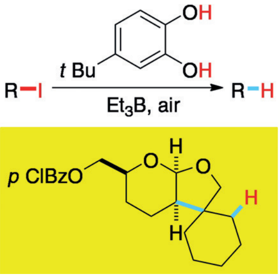


Borrowing from next door: Reported herein is the design and synthesis of novel mannosyl donors which provide 1,2-*cis*-mannosides through neighboring-group participation by thioether auxiliaries. By using conformationally locked mannuronic acid lactone donors, neighboring-group participation from C2 and C4 could be exploited to prepare β-mannosides.

Hydrogen-Atom Donors

G. Povie, L. Ford, D. Pozzi, V. Soulard, G. Villa, P. Renaud* ______ **11221 – 11225**

Catechols as Sources of Hydrogen Atoms in Radical Deiodination and Related Reactions



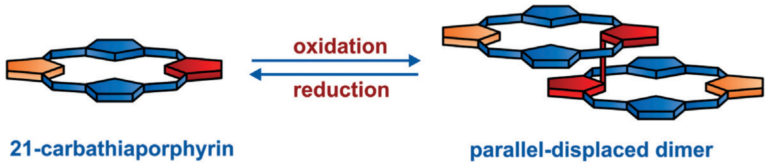
Simple catechols, when used with triethylborane, are excellent hydrogen-atom donors for radical chain reactions involving alkyl iodides and related radical precursors. As a concequence, highly efficient radical cyclizations leading to the formation of quaternary centers can be performed in a concerted process (no slow addition of the hydrogen atom donor) at standard concentrations.

Hypervalent Compounds

G. L. Tolnai, U. J. Nilsson, B. Olofsson* ______ **11226 – 11230**

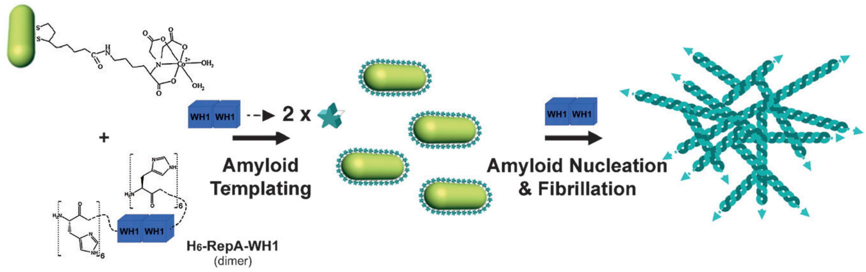
Efficient O-Functionalization of Carbohydrates with Electrophilic Reagents

Salty sweet! A novel method for O-functionalization of carbohydrate derivatives has been established using bench-stable, easily prepared iodonium(III) reagents. Both electron-withdrawing and electron-donating aryl groups were introduced under ambient conditions and without precautions to exclude air or moisture. The reaction has been extended to trifluoroethylations and to full arylation of cyclodextrin.



A reactive cyclopentadiene ring in 21-carba-23-thiaporphyrin enables the formation of a dimer with a direct covalent bond between internal carbon atoms and a unique parallel-displaced arrangement of the two macrocyclic π planes. The dimer shows exceptional reactivity towards acids, which cause its cleavage and formation of the asymmetric carbathiaporphyrin–carbatichlorin dyad or 2,3-dihalo-21-carba-23-thiachlorin depending on the acid used.

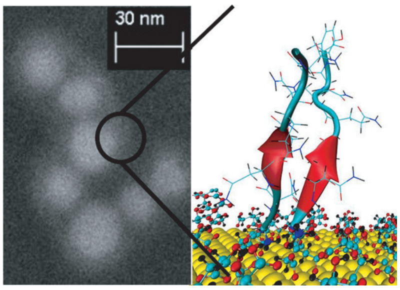
Carbaporphyrinoids



Amyloid oligomerization of the RepA-WH1 prionoid was promoted by monomerization of the protein dimer precursor in the presence of metal chelate-functionalized gold nanorods. Such oligomers were used as seeds to grow characteristic amyloid fibers. SERS spectral changes of H6-RepA-WH1 confirmed the expected gradual increase in β-sheet structure.

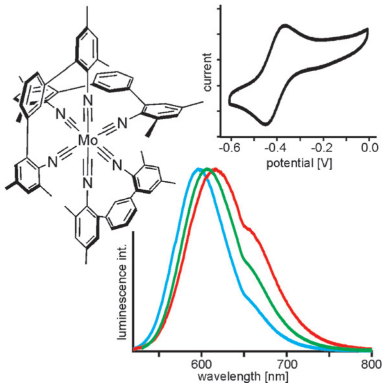
Amyloid-β Peptides

The corona is the key: Electron microscopy and molecular dynamics simulations are used to study the mechanism of accelerated fibril formation near gold nanoparticles. The molecular dynamics simulations reveal that partial physisorption to the surface results in the formation of aligned monolayers, which stimulate the formation of parallel, critical oligomers.



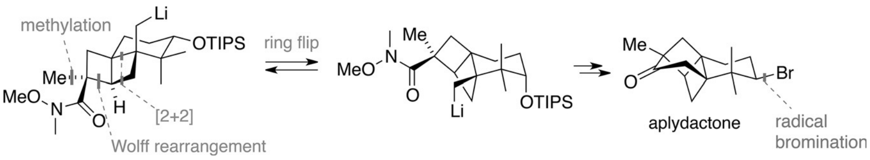
Protein Aggregation

A homoleptic Mo^0 complex with chelating isocyanide ligands was investigated. This chemically robust complex exhibits long-lived ^{3}MLCT luminescence, and it is a far stronger photoreductant than d^6 metal diimines made from precious metals. The utility of this complex as a photoredox sensitizer is demonstrated by its successful application in the rearrangement of an acyl cyclopropane to a 2,3-dihydrofuran.



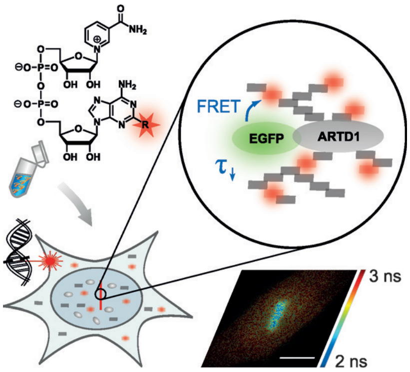
Photoredox Catalysis

Natural Product Synthesis



The unusual sesquiterpenoid aplydactone was obtained by total synthesis. The core skeleton was constructed by two non-biomimetic photochemical reactions, a diastereoselective [2+2] cycloaddition, a photochemical Wolff rearrangement, and a Barbier reaction. New radical conditions were developed for installing the sterically hindered secondary bromide.

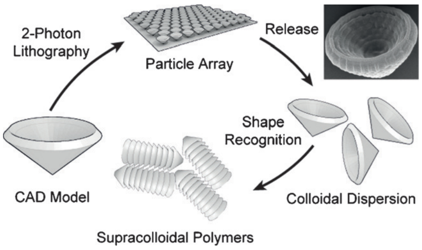
Bioimaging



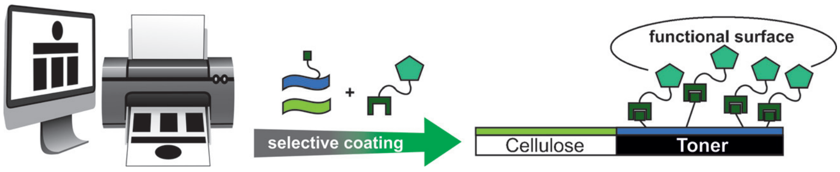
PARylation live: A fluorescent NAD$^+$ analogue was developed that enables the direct observation of poly(ADP-ribose) (PAR) turnover in living cells in response to DNA damage induced by microirradiation. In combination with FLIM-FRET microscopy, this analogue provides a powerful tool for the protein-specific monitoring of both covalent and non-covalent interactions with the nucleotide-based PAR biopolymer.

Self-Assembly

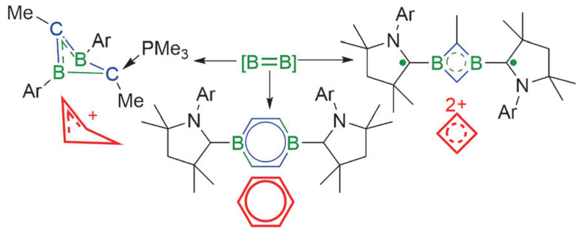
Designer colloids: Direct 3D laser writing opens new ways for the preparation of shape-anisotropic colloidal lock-and-key building blocks, which hierarchically self-assemble to form colloidal polymers and nematic liquid-crystalline domains.



Peptide Coatings



Stick to print: Selective coating of laser-printed patterns was achieved by material-specific adhesion of peptides to cellulose or toner. The peptide sequences were obtained using phage display. Functionalization of the immobilized peptides was realized by selective modification of tyrosine residues present on the printed-pattern coatings, offering new ways towards low-cost printed devices.



B_2-aromatic: Uncatalyzed cycloaddition of nonpolar alkynes with B–B multiple bonds provides facile and selective access to novel 2π- and 6π-aromatic and 2π-homoaromatic diboron analogues of C_6H_6, $C_4H_4^{2+}$, and $C_4H_5^+$.

Cycloaddition

M. Arrowsmith, J. Böhnke, H. Braunschweig,* M. A. Celik, C. Claes, W. C. Ewing, I. Krummenacher, K. Lubitz, C. Schneider ———— **11271–11275**

Neutral Diboron Analogues of Archetypal Aromatic Species by Spontaneous Cycloaddition

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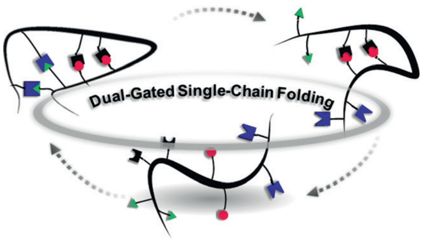

One step at a time: A single-chain nanoparticle based on a well-defined high-molecular-weight tetrablock copolymer equipped with mutually orthogonal folding elements undergoes order-independent and highly orthogonal unfolding in response to simple chemical triggers.

Supramolecular Chemistry

T. S. Fischer, D. Schulze-Sünninghausen, B. Luy, O. Altintas,* C. Barner-Kowollik* ———— **11276–11280**

Stepwise Unfolding of Single-Chain Nanoparticles by Chemically Triggered Gates

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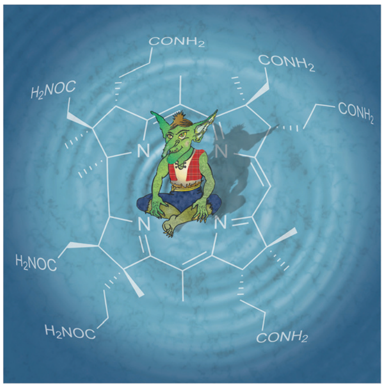
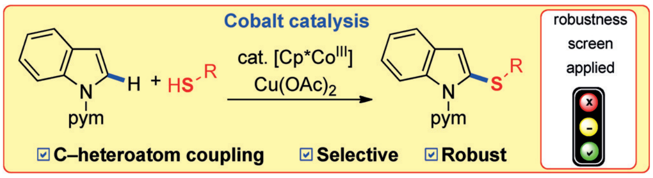


The rhodium homologue (AdoRbl) of coenzyme B_{12} (AdoCbl) was obtained by total synthesis using a strategic combination of biosynthetic and chemical synthetic steps, and was found to be inactive as a cofactor. Its crystal structure revealed a strikingly better fit for the Rh^{III} ion than for Co^{III} in AdoCbl, raising the question of the presumed structural adaptation of the corrin ligand for cobalt, the "goblin" element.

Vitamin B_{12}

F. J. Widner, A. D. Lawrence, E. Deery, D. Heldt, S. Frank, K. Gruber, K. Wurst, M. J. Warren,* B. Kräutler* ———— **11281–11286**

Total Synthesis, Structure, and Biological Activity of Adenosylrhodibalamin, the Non-Natural Rhodium Homologue of Coenzyme B_{12}



Co-laboration! A new method for the dehydrogenative cross-coupling of thiols and indoles features a novel mode of action for the cobalt-catalyzed formation of a C–heteroatom bond. Mechanistic studies indicate a sequence of C–H activation, thiolate transfer, and reductive elimination.

Dehydrogenative Cross-Coupling

T. Gensch, F. J. R. Klauck, F. Glorius* ———— **11287–11291**

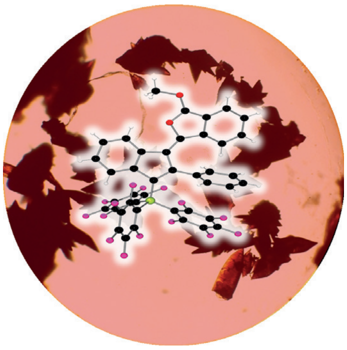
Cobalt-Catalyzed C–H Thiolation through Dehydrogenative Cross-Coupling

Heteroannulation

L. C. Wilkins, B. A. R. Günther, M. Walther, J. R. Lawson, T. Wirth, R. L. Melen* ____________ **11292 – 11295**

Contrasting Frustrated Lewis Pair Reactivity with Selenium- and Boron-Based Lewis Acids

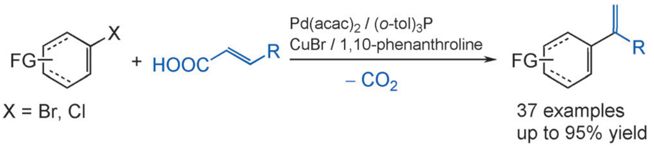
Making a difference: The activation of π-bonds in diynyl esters by soft and hard Lewis acids has been investigated in a one-pot reaction. The soft selenium reagent PhSeCl affords a salt containing three distinct selenium environments, while the hard Lewis acid borane $B(C_6F_5)_3$ yields a complex conjugated zwitterionic system in a domino reaction.



Cross-Coupling

J. Tang, D. Hackenberger, L. J. Goossen* ____________ **11296 – 11299**

Branched Arylalkenes from Cinnamates: Selectivity Inversion in Heck Reactions by Carboxylates as Deciduous Directing Groups



Directors cut: A palladium/copper-catalyzed Mizoroki–Heck coupling of aryl halides with cinnamic acids has been developed in which the carboxylate group directs the arylation into its β-position before being tracelessly removed through protodecarboxylation. 1,1-Disubstituted alkenes are selectively obtained in this transformation, which ideally complements traditional 1,2-selective Heck reactions of styrenes.

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