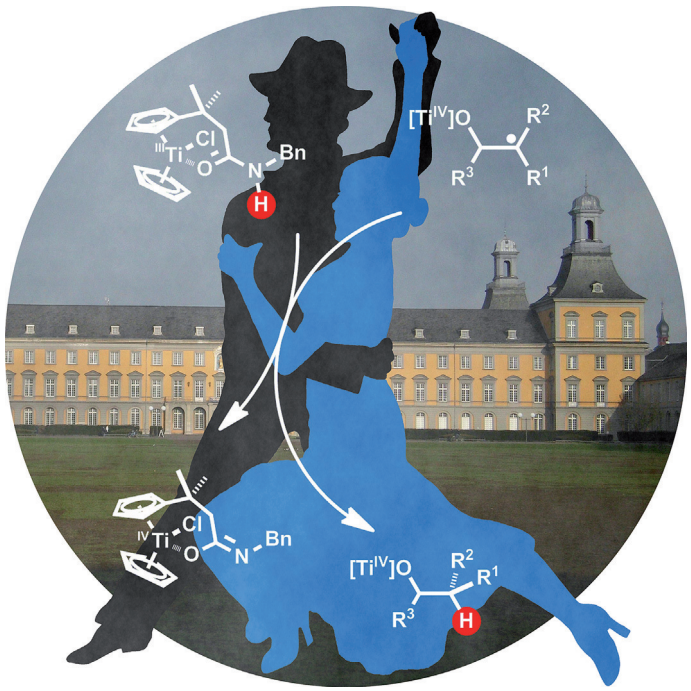
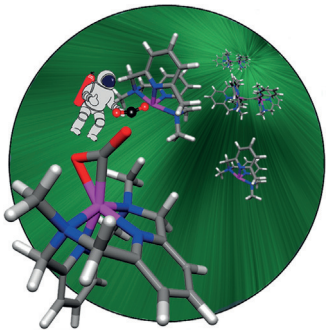
Angewandte International Edition Chemie

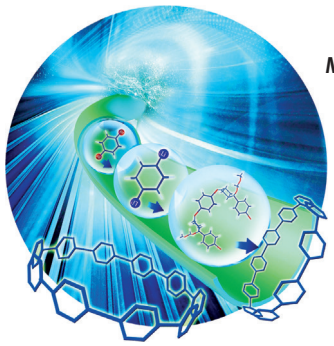


… through metal–ligand bifunctional catalysis or cooperative catalysis is like dancing the tango. In their Communication on page 1523 ff., A. Gansäuer and co-workers show that amides can be activated for radical reduction by amide-substituted titanocene(III) catalysts or through cooperative catalysis with titanocenes and Crabtree's catalyst (graphic design by Dina Schwarz G. Henriques).



CO_2 Activation

The activation of CO_2 by a cationic mononuclear nickel(I) complex is described by M. A. Johnson et al. in their Communication on page 1282 ff. The resulting complex features a bent CO_2 molecule (148°) bound to the metal center in an η^2 arrangement.



Microreactors

In their Communication on page 1422 ff., D.-P. Kim and co-workers describe a flow-assisted system for the efficient synthesis of the cyclo-paraphenylene (CPP) derivative [10]CPP under mild reaction conditions.

Magnetic Resonance Imaging

The imaging of cell-surface glycans in live mice, following metabolic labeling and subsequent bioorthogonal reaction, by magnetic resonance imaging is described by A. A. Neves et al. in their Communication on page 1286 ff.

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Editorial

"... Solvents are often considered to be an inert media, in which reactions occur. A molecular-level, bottom-up description of solvation that is able to predict the properties of new solvent systems, also for industrial applications has come within reach. Solvents are now increasingly recognized as playing an active role in their own right in various processes ...
Read more in the Editorial by Martina Havenith.

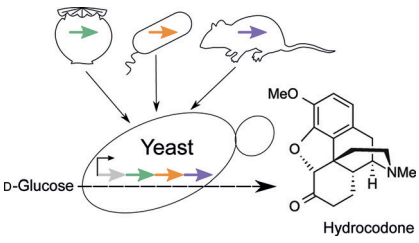
Service

Author Profile

"My biggest motivation is unexpected results. I lose track of time when I am doing experiments ..."
This and more about Akira Harada can be found on page 1244.

Highlights

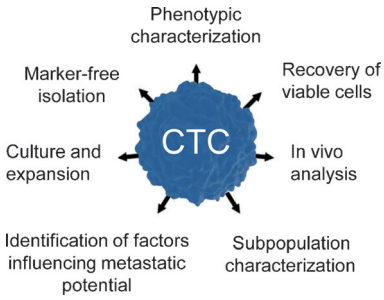
Home brew: Biotechnological modification of the yeast *Sacharomyces cerevisiae* enabled the production of opioids from glucose. This challenging extension of yeast metabolism, the result of ten years of work, involves the artificial expression of 23 genes originating from yeast, plants, and rats. This breakthrough was achieved by applying the design principles of synthetic biology, systems biology, and protein engineering.



Synthetic Biology

Minireviews

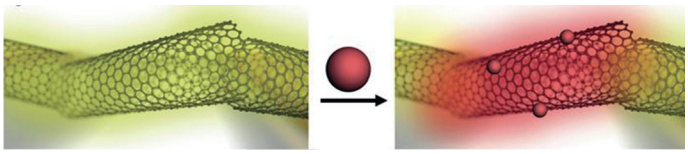
Tumor Profiling



Deadliest catch: Over the last decade, significant progress has been made towards the capture of rare circulating tumor cells (CTCs) from the blood of cancer patients, a critical capability for noninvasive tumor profiling. This Minireview summarizes recent breakthroughs and focuses on how new devices and materials have allowed this rapidly advancing field to move beyond enumeration and towards comprehensive characterization of CTCs.

Reviews

Sensors

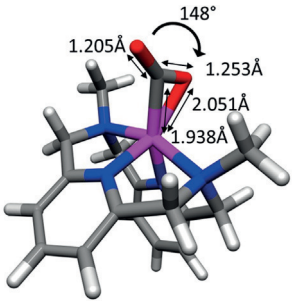


Down to the wire: Sensors based on chemiresistance can be readily integrated into electronic devices and are low priced compared to conventional analytical devides. This Review illustrates the advantages of such sensors, which transduce the binding or action of an analyte on a nanowire or nanowire arrangement into a signal.

Communications

CO_2 Activation

Highly distorted: A CO_2 molecule is activated in the gas phase by a cationic mononuclear nickel(I) complex containing a tetraazamacrocyclic ligand. The resulting complex was structurally characterized by mass-selected vibrational predissociation spectroscopy, which indicated that this complex features a highly distorted CO_2 molecule bound to the metal center in an η^2-C,O coordination mode.



Frontispiece

For the USA and Canada:
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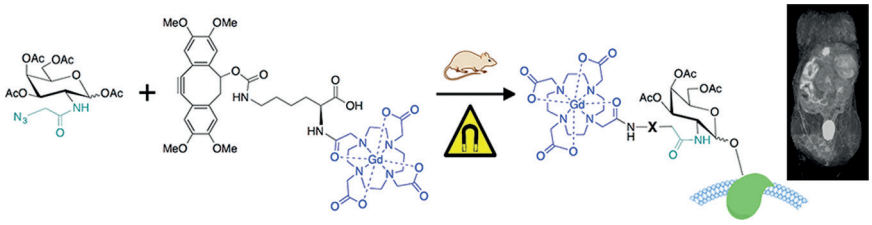
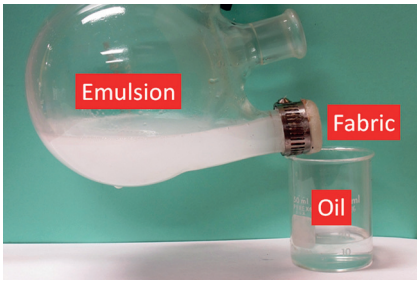


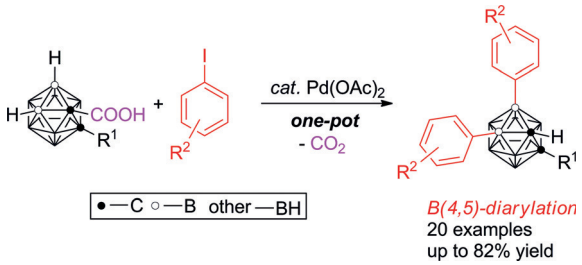
Magnetic Resonance Imaging

Glycans were imaged in live mice by magnetic resonance imaging, following metabolic labeling with an azido sugar and subsequent administration of a strained cyclooctyne linked to a gadolinium contrast agent. Significant azido sugar dependent contrast was observed in various tissues two hours after administration of the contrast agent.



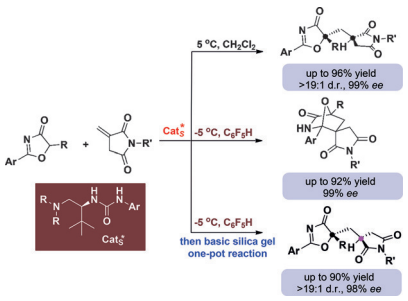
Oil/Water Separation

A superhydrophobic and a polyamine-bearing surface make up a Janus cotton fabric. When used as a filter, the polyamine-bearing side causes micrometer-sized oil droplets to coalesce and the hydrophobic side allows selective oil permeation. Oil separation using this method is rapid and the separated oil is very pure: hexadecane content in water after a separation can be reduced to less than 0.03 ± 0.03 vol%.



Carborane Functionalization

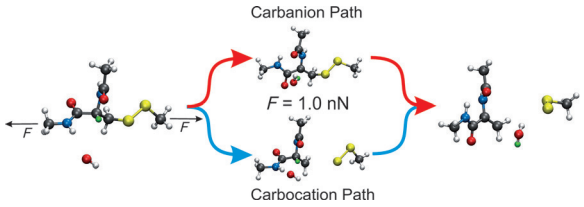
Palladium-catalyzed intermolecular coupling of *o*-carborane with aromatics by direct cage B–H bond activation has been achieved, leading to the synthesis of a series of cage B(4,5)-diarylated-*o*-carboranes in high yields with excellent regioselectivity. Traceless directing group -COOH plays a crucial role for site- and di-selectivity of such intermolecular coupling reactions.



Organocatalysis

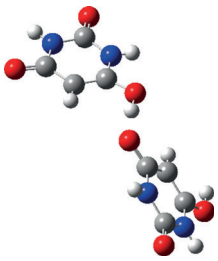
Divergent reaction paths: The first asymmetric reaction of 5*H*-oxazol-4-ones with itaconimides was developed by employing a chiral tertiary amine–urea catalyst. The substrates could go through either tandem conjugate addition–protonation or [4+2] cycloaddition with excellent enantio- and diastereoselectivities under controlled experimental conditions.

Mechanochemistry



Mechanical stress influences the pathway of disulfide cleavage by β-elimination. The rate-determining first step, the abstraction of the β-proton, is insensitive to external forces. Forces larger than about 1 nN reshape the free-energy landscape so that the order of the reaction steps is reversed, turning β-deprotonation into a barrier-free follow-up process to C–S cleavage.

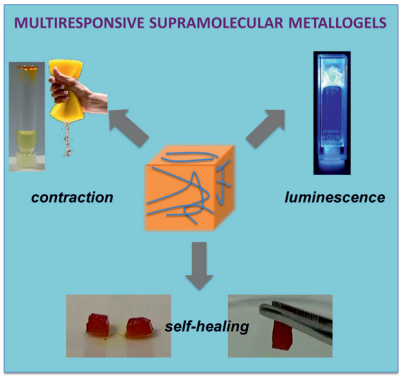
Polymorphism



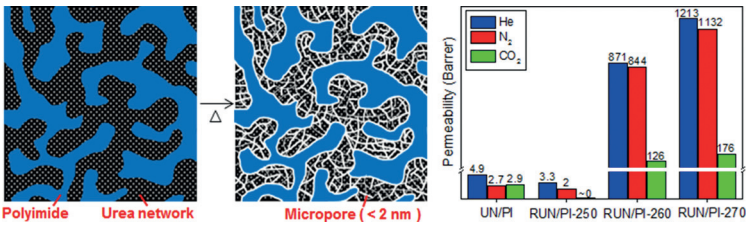
Tautomer lesson: The enol polymorph of barbituric acid has been crystallized and its structure determined at 95 K (N blue, O red, C gray, H white). The tri-keto tautomer of barbituric acid in solution and by computation is more stable than the enol by about 50 kJ mol^{-1}. However, the enol is the stable tautomer. Replacement of the four H atoms by D reverses the order of the stability of the tautomers.

Supramolecular Metallogels

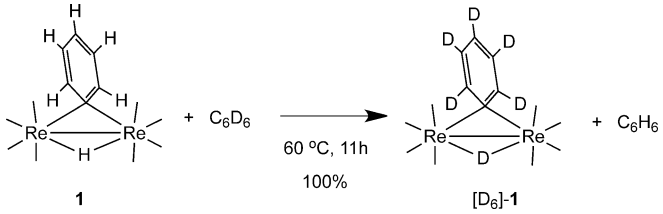
Lights, camera, action! A series of metallopolymers based on Zn^{II}–terpyridine coordination nodes and bearing photoisomerizable and/or luminescent moieties are reported. The polymers undergo gelation at ultralow critical concentrations. The resulting multiresponsive organogels are photoluminescent, display light-triggered mechanical actuation, and can rapidly self-heal.



Microporous Membranes

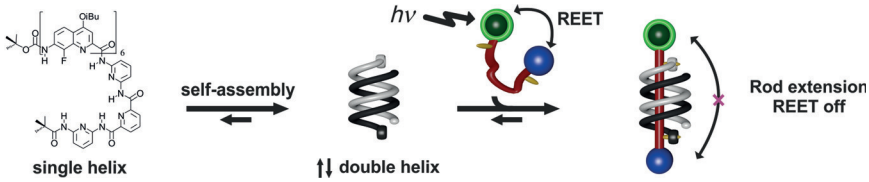


Selective networking: Reticular microporous channels are generated in situ throughout a urea-based network film by selective expulsion of molecular fragments during a thermal rearrangement. The nanocomposite membranes exhibited unusual reverse-selective gas-transport properties, rejecting carbon dioxide while transporting different gases.



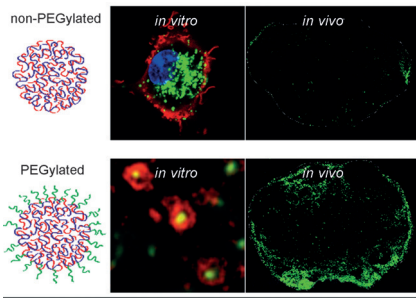
Two Rheniums are better than one: The electronically unsaturated dirhenium complex [$Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}Ph)$] (**1**) exhibits aromatic C–H activation upon reaction with [D_6]benzene to yield [D_6]-**1** in good yield. The mechanism has been elucidated by DFT analyses, and involves a binuclear C–H bond-activation process. *N*,*N*-Diethylaniline and naphthalene also react with **1** to generate [$Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^1\text{-}NEt_2C_6H_4)$] and [$Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}1,2\text{-}C_{10}H_7)$], respectively.

C–H Activation



A supramolecular abiotic double helix interpenetrated by a bichromophoric thread is described. While reversible interchromophore electronic energy transfer occurs in the excited free thread, giving prolonged emission, luminescence lifetime shortens when decoupled in the complex. The high sensitivity of emission decay to distance offers an approach to luminescence lifetime-based conformational probes.

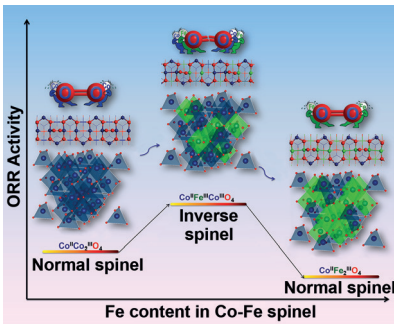
Foldamers



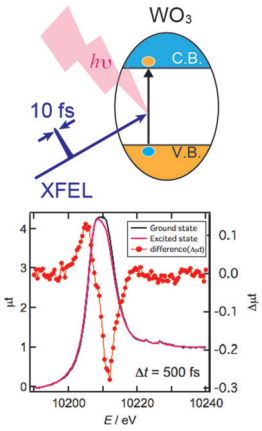
Lymphatic transportation: PEGylation is shown to be a key parameter for lymphatic transportation of hydrogel nanoparticles. The PEGylated nanoparticles result in a high association with dendritic cells and B cells as well as increased T cell responses in vivo, which can be potentially used to improve the delivery of vaccines and drugs to the lymph nodes.

Drug Delivery

Enhancing by reversing: The electrocatalytic performance of Co-Fe based spinel for the oxygen reduction reaction can be significantly promoted by reversing its structure from normal to inverse. The enhancement of activity originates from a dissimilarity effect of Fe and Co atoms at the octahedral sites, which modulates the oxygen adsorption energy (E_{ad}) and elongates the O–O bond compared to that on the normal spinel.

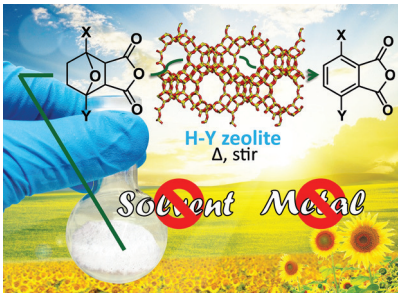


Electrocatalysis



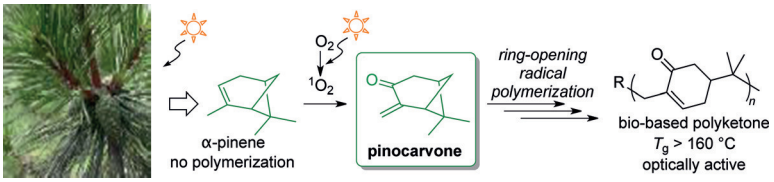
Caught on the "speed camera": Photoexcited states of WO_3 were observed by femtosecond X-ray absorption spectroscopy performed using an X-ray free electron laser (XFEL). The local structural transformation of W was found, which occurred after the change of the local electronic state and began within 200 ps after excitation.

Photoexcitation



Just heat and tumble: Furanics-derived hydrogenated Diels–Alder adducts can be conveniently converted, over acidic zeolites, into renewable aromatics using a solid-phase conversion strategy. The zeolite H-Y was found to perform the best and can be easily reused after calcination.

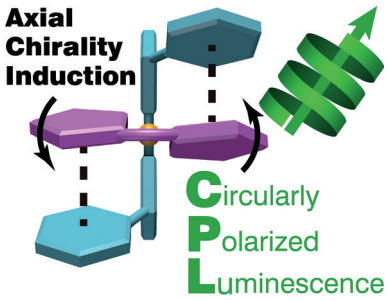
Arenes



Polymers from α-pinene: The most abundant naturally occurring terpene, α-pinene, was quantitatively converted into pinocarvone, which contains a reactive *exo* methylene group, under visible-light irradiation. The bicyclic vinyl ketone was quantitatively polymerized by selective ring-opening radical polymerization, resulting in novel bio-based polymers with good thermal properties, optical activities, and reactive groups.

Polymerization

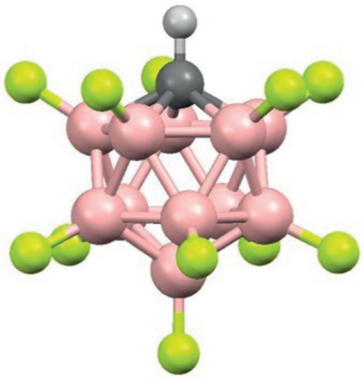
The odd couple: Heteroleptic zinc(II) complexes synthesized using achiral dipyrrinato (shown in magenta) and chiral bis(oxazoline) ligands (turquoise) show bright fluorescence from the dipyrrinato moiety with quantum efficiencies of up to 0.70. The luminescence is circularly polarized, which results from axial chirality induction to the dipyrrinato ligand by the bis(oxazoline) ligand.



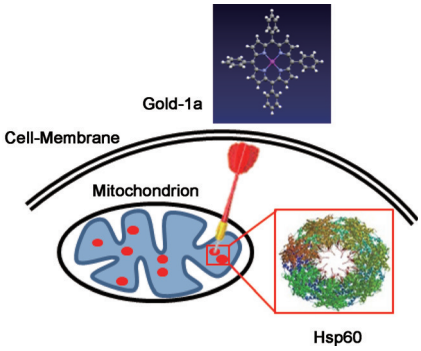
Photophysics

Superacids

Acid test: The fluorinated carborane acid $H(CHB_{11}F_{11})$ protonates CO_2 forming the proton disolvate $H(CO_2)_2^+$. Traditional mixed superacids do not, so carborane acids are the strongest known acids.

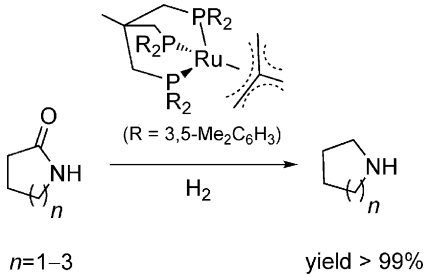


Metallodrugs



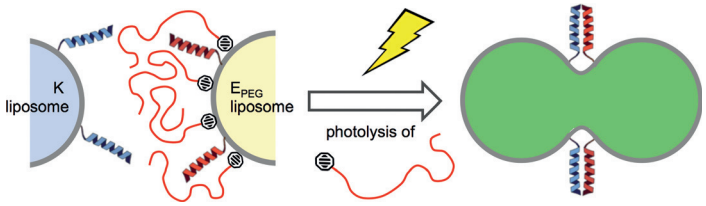
Golden gun: Hsp60 is a direct molecular target of the anticancer compound gold(III) *meso*-tetraphenylporphyrin (**gold-1a**) under both in vitro and cellular conditions, as revealed by chemical biology studies employing photo-affinity labeling, click chemistry, proteomic identification, cellular thermal shift, saturation-transfer difference NMR, protein fluorescence quenching, and protein chaperone assays.

Hydrogenation Catalysts

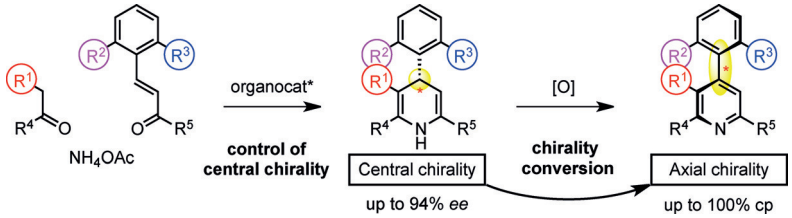


Bulky catalysts: A tailored sterically demanding tridentate ligand enabled the synthesis of a novel molecular ruthenium-triphos catalyst, which eliminates dimerization as the major deactivation pathway. The novel catalyst design showed increased performance and facilitated the hydrogenation of highly challenging lactam substrates with unprecedented activity and selectivity.

Photoactivation

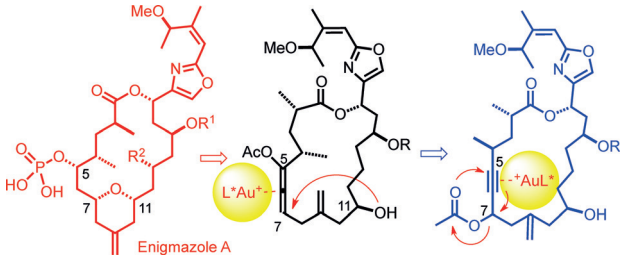


Membrane fusion was temporally controlled by photolabile steric shielding of fusogenic liposomes. An analogous method also enabled spatiotemporal control of liposome accumulation at cellular membranes in vitro. This general approach represents a non-invasive, user-defined route towards vector-based drug and gene delivery both in vitro and in vivo.



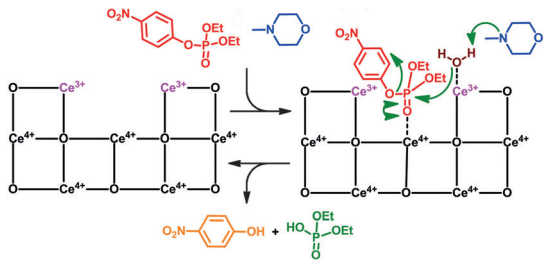
Enriched atropisomers: Substituted enantioenriched 4-aryl-1,4-dihydropyridines were prepared by an enantioselective Michael addition reaction, and then oxidized with MnO_2 into axially chiral 4-arylpyridines with central-to-axial chirality conversion. Moderate to complete conversion percentages (cp) were observed, and a model for the conversion of chirality is discussed.

Enantioselective Reactions



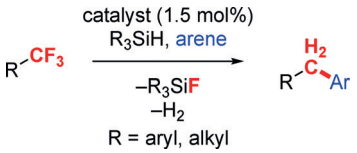
Within reach: A gold-catalyzed cascade of remarkable complexity paved the way to the parent phosphorylated macrolide of the enigmazole family, which exhibits a highly promising but not yet well-understood biological profile. Only if the π-acid itself is chiral, however, was the [3,3]-sigmatropic rearrangement complete before the hydroxy group reached across the macrocyclic ring.

Natural Products



Catalytic hotspots: Vacancy-engineered cerium dioxide nanoparticles provide potential enzyme mimetic hotspots for the rapid degradation of nerve agents. This study presents the first example of hydrolytic activity of a vacancy-engineered nanomaterial, where the dual oxidation states of the metal ions play a crucial role.

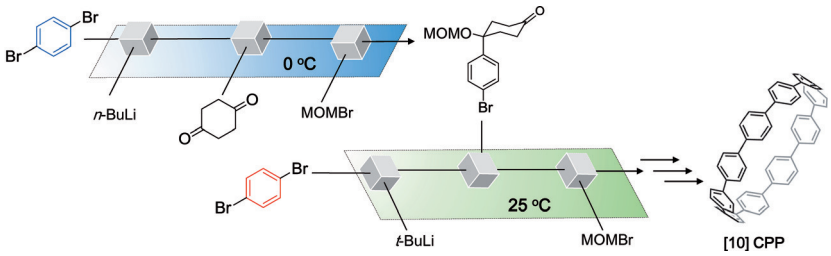
Nanocatalysis



Do the job and get outta here! A range of arenes underwent benzylation or alkylation with trifluoromethyl-substituted aryl and alkyl substrates in the presence of the electrophilic organofluorophosphonium catalyst $[(C_6F_5)_3PF][B(C_6F_5)_4]$ and a silane. Hydrodefluorination occurred rapidly to complete the net transformation of the CF_3 group into a CH_2–aryl fragment (see scheme).

Synthetic Methods

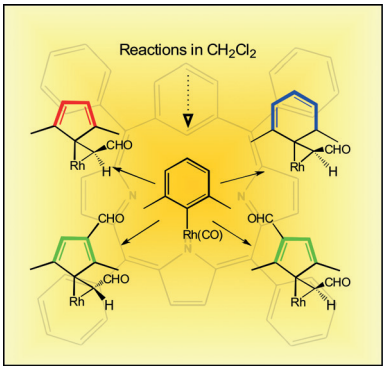
Microreactors



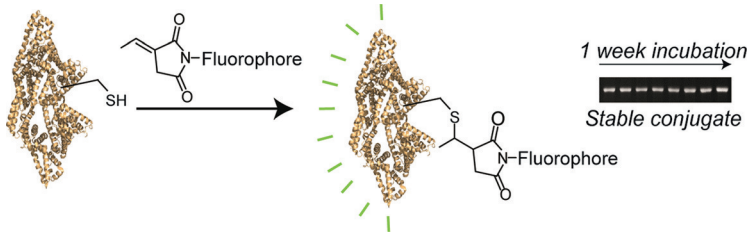
Go with the flow: The cycloparaphenylene (CPP) derivative [10]CPP was synthesized in four steps under mild conditions using a flow-assisted synthetic method by precise control of the reaction time and flow rate. Selective nucleophilic addition of a lithiated benzene derivative to a diketone could be achieved in high yield without a protection/deprotection step.

Porphyrins

Casting out a carbon: The *m*-phenylene ring in rhodium(III) *m*-benziporphyrin is demonstrated to undergo ring contraction to a cyclopentadienyl fragment, ultimately forming a unique rhodium(III) 21-carbaporphyrin derivative. The unusual coordination environment in this system facilitates the stabilization of peculiar structural motifs, specifically a rhodacyclopropane substituted by a formyl unit.

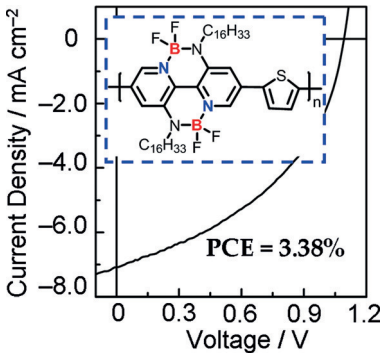


Bioconjugation

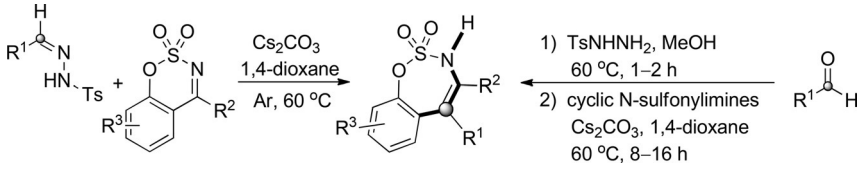


In stable bioconjugation: A variety of exocyclic olefinic maleimides have been prepared from endocyclic olefinic maleimides under solvent-free conditions by 4-nitrophenol-mediated catalysis. These scaffolds were found to react selectively with thiols at physiological conditions to form linkages that resist thiol-exchange-mediated breakdown, thus demonstrating their potential for stable thiol bioconjugation.

Conjugated Polymers

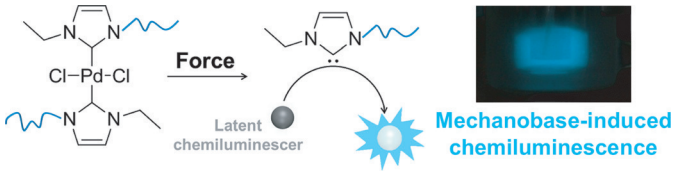


A bridge too far: An electron-deficient building block comprises a double B←N bridged bipyridyl (BNBP) moiety. The polymer constructed from the BNBP units exhibits high electron mobility, low-lying LUMO/HOMO energy levels, and strong absorbance in the visible range, and shows excellent device performance as polymer electron acceptor for all-polymer solar cells.



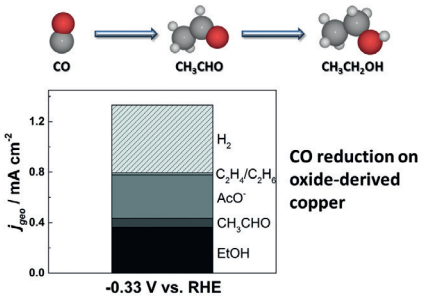
Diazo Compounds

A diazo thing: The title reaction between cyclic N-sulfonylimines and diazo compounds generated in situ from the N-tosylhydrazones is simple and functional-group tolerant. It thus delivers valuable seven-membered sulfonamides in up to 95% yield. Moreover, this reaction can be carried out in one-pot starting from the aryl aldehydes, without the need to isolate the N-tosylhydrazone (right).



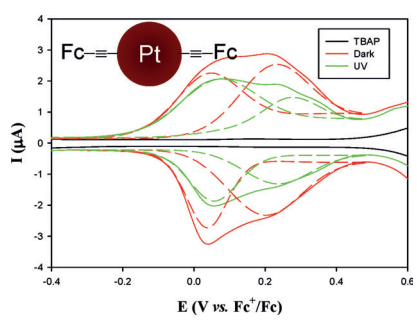
Mechanochemistry

Mechanophores capable of releasing N-heterocyclic carbene are combined with triggerable chemiluminescent substrates to give a novel system for mechanically induced chemiluminescence. The mechanophores are palladium bis-NHC complexes centrally incorporated in poly(tetrahydrofuran). Chemiluminescence is induced upon sonication of dilute solutions of the polymer complex and either APD or a coumaranone derivative.



Electrochemistry

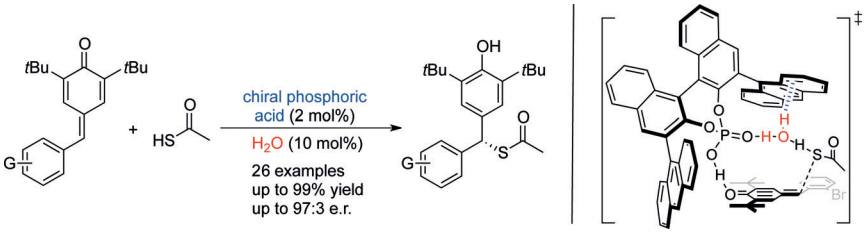
An unappreciated intermediate: Acetaldehyde is identified as a product and key intermediate in CO reduction to ethanol on oxide-derived copper. It is also shown that the detection of acetaldehyde with NMR spectroscopy in alkaline solution is challenging, requiring utilization of complementary techniques.



Platinum Nanoparticles

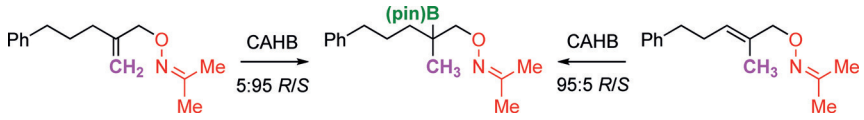
UV photoirradiation leads to markedly enhanced intervalence charge transfer (IVCT) between ferrocene moieties on a subnanometer-sized Pt cluster surface. TBAP = tetra-*n*-butylammonium perchlorate.

Organocatalysis



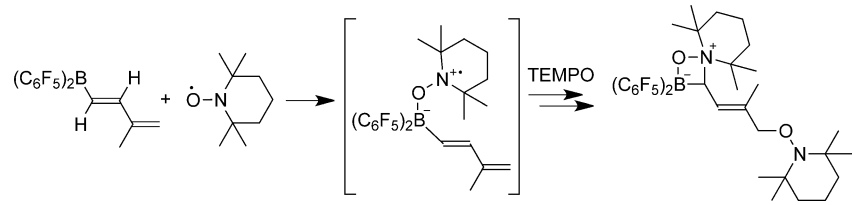
Building bridges: The title reaction was realized in the presence of water, and successfully solved the challenge of remote stereocontrol for the *para*-quinone methide substrates. Theoretical studies indicated that the water-bridged proton transfer and an unprecedented O–H···π interaction, between water and the aromatic nucleus of the chiral phosphoric acid, play important roles in the transition state.

Asymmetric Catalysis



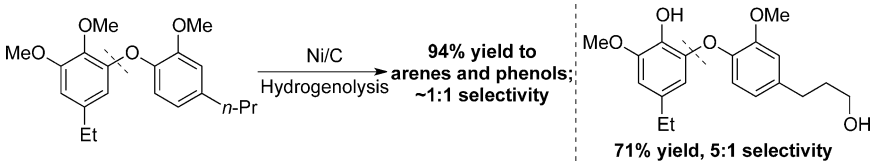
Take a CAHB, but give good directions: Methylidene and trisubstituted alkene substrates were converted into chiral tertiary boronic esters (up to 87% yield and 96:4 e.r.) by oxime-directed catalytic asymmetric hydroboration (CAHB) with a simple rhodium catalyst. Subsequent C–C coupling to form a quaternary stereocenter was demonstrated, as well as other transformations to give a chiral diol, O-substituted hydroxylamine, or isoxazoline.

Nitroxide Radicals

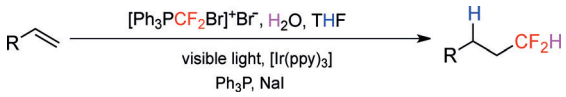


Things that go BONC... $B(C_6F_5)_2$-substituted dienes reacted with two molar equivalents of tetramethylpiperidine-1-oxyl (TEMPO) to give N,O-addition products containing a B,O,N,C four-membered heterocyclic ring (see example). The reaction is thought to involve the addition of TEMPO to the boron atom to give an N-centered radical that then undergoes rapid C–N bond formation.

C–O Bond Cleavage

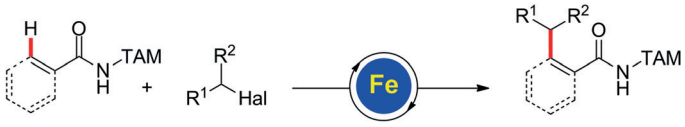


Nick's pillar of strength: A catalyst comprising heterogeneous nickel particles supported on activated carbon promoted the efficient chemo- and regioselective hydrogenolysis of C–O bonds in di-*ortho*-substituted diaryl ethers to give arenes and phenols without hydrogenation (see scheme). The high thermal stability of the embedded metal particles enabled C–O bond cleavage to occur in highly substituted diaryl ethers units akin to those in lignin.



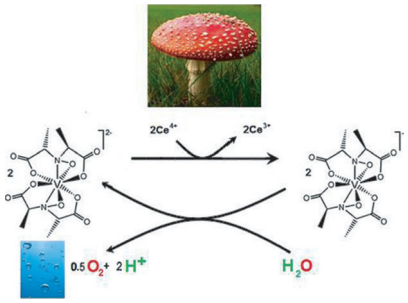
Getting involved: The visible-light photoredox catalysis of alkenes with a bromodifluoromethylphosphonium bromide using H_2O and THF as hydrogen sources afforded hydrodifluoromethylated alkanes in moderate to excellent yields. The in situ generated difluoromethylphosphonium salt and a CF_2H radical are involved in this transformation. ppy = 2-phenylpyridine.

Photochemistry



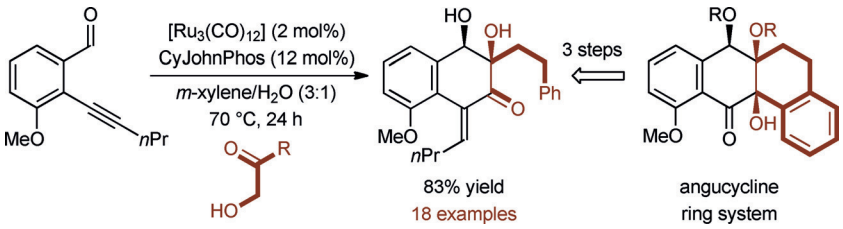
One for all: A unified strategy for iron-catalyzed C–H allylation and alkylation was developed by the use of a triazole directing group that could be cleaved under exceedingly mild conditions. The inexpensive catalyst promotes the site-selective functionalization of arenes, heteroarenes, and alkenes with a wide range of primary and secondary allyl and alkyl groups.

Iron Catalysis



Kept in the dark: Amavadin and related vanadium complexes are shown to be capable of promoting water oxidation under non-photochemical conditions through a mechanism involving cooperation between the mononuclear metal center and ligands.

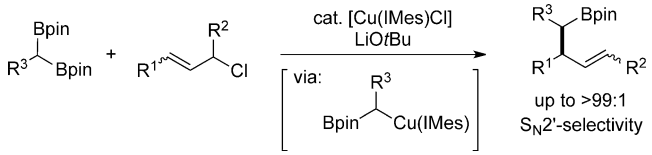
Transition-Metal Catalysts



Ringing with efficiency: Ruthenium(0) complexes modified by either CyJohnPhos or RuPhos catalyze the successive C–C coupling of acetylenic aldehydes with α-ketols to form [4+2] cycloadducts as single diastereomers. This method enables convergent construction of type II polyketide ring systems of the angucycline class.

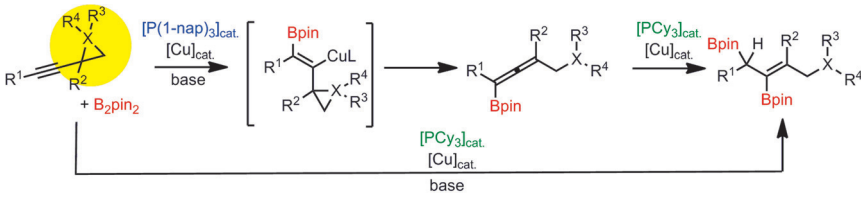
Cycloaddition

Allylic Compounds



Readily accessible 1,1-diborylalkanes are used as the alkyl source in the title reaction. The method has a wide substrate scope, is highly regioselective for the S_N2' product. IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene, pin = pinacolato.

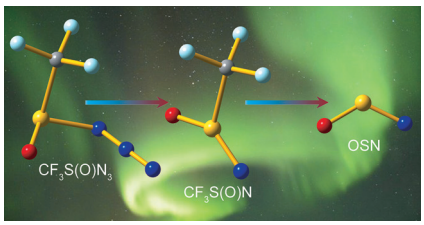
Homogeneous Catalysis



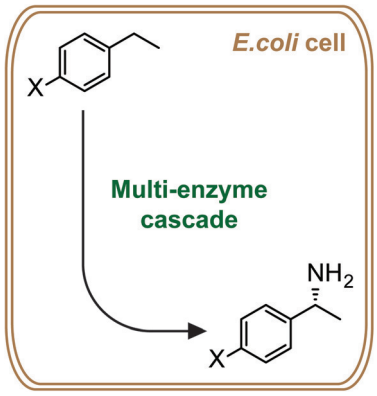
Strain-breaking: A copper-catalyzed reaction for the stereo- and regioselective synthesis of alkenyl diboronates and allenyl boronates is presented. In this process propargyl derivatives of strained three/four-membered rings were employed as substrates and B_2pin_2 was used as the boronate source. Selective formation of the alkenyl diboronate versus the allenyl boronate products was controlled by the choice of phosphine ligand.

IR Spectroscopy

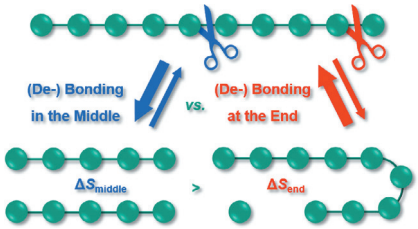
The triatomic molecule OSN was generated from the stepwise decomposition of gaseous $CF_3S(O)N_3$ via the novel sulfinyl nitrene $CF_3S(O)N$. Matrix IR spectroscopy and DFT calculations were employed to identify and characterize the matrix-isolated decomposition products and to elucidate the reaction mechanism.



Biocatalysis

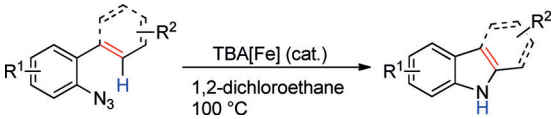


Enantiomerically pure chiral amines are ubiquitous chemical building blocks in bioactive pharmaceuticals and their synthesis from simple starting materials is of great interest. One strategy is the stereoselective installation of a chiral amine through formal C–H amination. A multienzyme cascade was constructed and applied in a single bacterial whole cell that can catalyze stereoselective benzylic aminations with 97.5% *ee*.



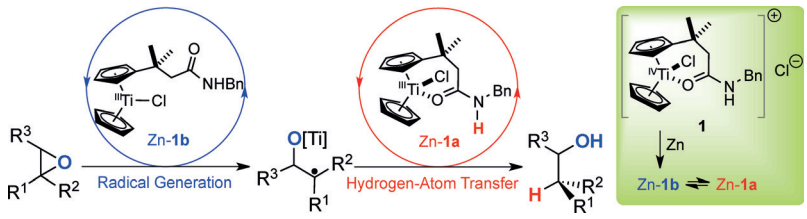
Middle versus end? When all other conditions are equal, bond cleavage in the middle of molecules is entropically much more favored than bond cleavage at the end. Experimental and theoretical approaches were used to study the selectivity of bond cleavage or dissociation of both covalent and supramolecular adducts. The findings have extensive implications for other fields of chemistry.

Polymer Chain Cleavage



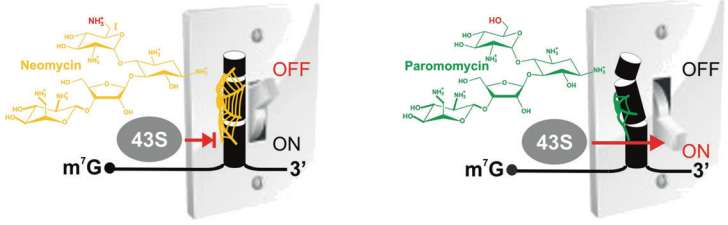
The nucleophilic iron complex $Bu_4N[Fe(CO)_3(NO)]$ (TBA[Fe]) catalyzes the selective intramolecular aryl/vinyl C(sp²)–H amination of aryl azides to give either substituted carbazole or indole derivatives in good to excellent yields. Kinetic isotope effects reveal a mechanistic similarity to the non-catalyzed thermal and rhodium-catalyzed variants.

Heterocycle Synthesis



It takes two to tango: The coupling of catalytic cycles to enable the activation of amide N–H bonds for radical reduction is reported. This can either be achieved by using a bifunctional amide-substituted catalyst or through cooperative catalysis with amide-substituted titanocenes and Crabtree's catalyst. The results lead the way for the use of peptides in HAT catalysis.

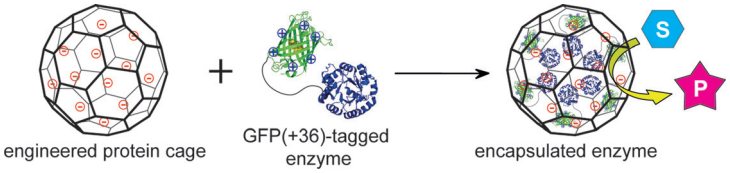
Radical Catalysis



Think local, act global: A synthetic neomycin riboswitch also binds paromomycin, which differs from neomycin only in the substitution of an amino group with a hydroxy group. Binding of paromomycin does not activate the switch, however, because the loss of key intermolecular interactions at one position of the paromomycin complex is translated through a defined network of intramolecular interactions into global changes in RNA conformational dynamics.

Riboswitches

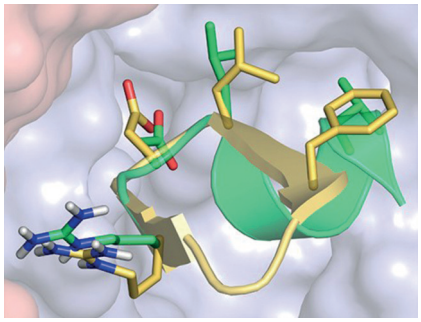
Nanoreactors



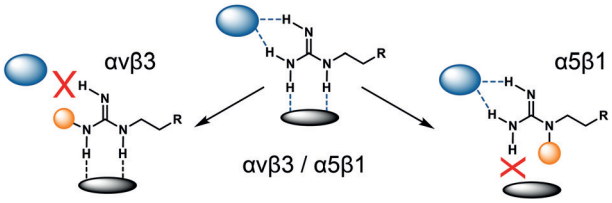
Caught in a trap: Genetic fusion of cargo proteins to a positively supercharged variant of green fluorescent protein enables their quantitative encapsulation by engineered lumazine synthase capsids possessing a negatively charged lumenal surface.

Integrin Ligands (1)

The search for binding: The αvβ6 integrin binds the RGD-containing peptide of the foot and mouth disease virus with high selectivity. The long binding helix of this ligand was downsized to an enzymatically stable cyclic peptide endowed with subnanomolar binding affinity toward the αvβ6 receptor and remarkable selectivity against other integrins.

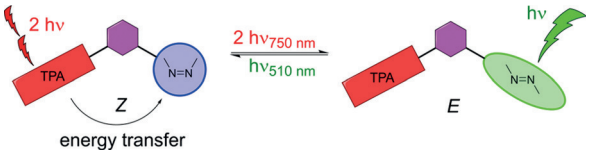


Integrin Ligands (2)

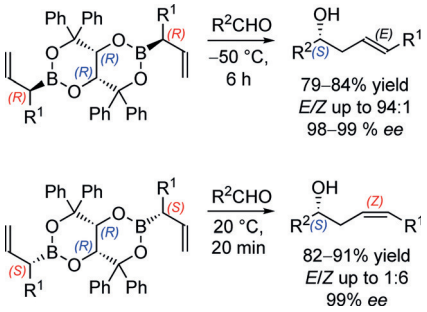


Simple modification of the guanidine group of the integrin ligand cilengitide can be used to tune integrin subtype selectivity in two directions. The two isomeric compounds obtained vary only in the position of a guanidine methyl group but have completely opposite selectivity properties for αv and α5 integrins.

Photoswitches

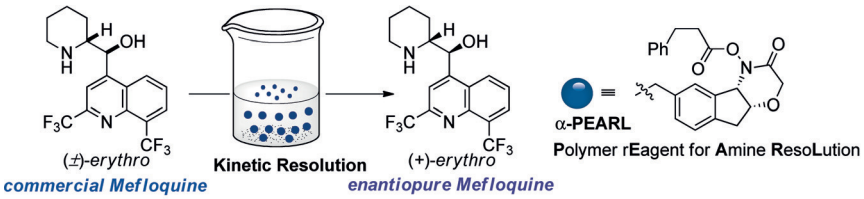


Red light, green light: Photoswitching with two NIR photons was accomplished by covalently linking a two-photon-harvesting triarylamine antenna (TPA) to a thermally stable azobenzene derivative. The new photoswitch is addressable with visible and NIR light through one-photon and two-photon excitation, respectively.



All isomers of homoallylic alcohols are readily accessible. The required enantiomerically pure allylboronates can be prepared by a short and convenient three-step sequence. The diboron compounds show unprecedented high reactivity. The observed selectivity as well as the relative reactivity were studied by computational methods.

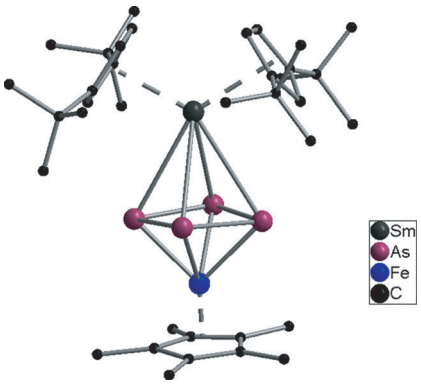
Asymmetric Synthesis



Pearl Jam: A novel ROMP-gel supported reagent allows the preparation of enantiopure (+)-*erythro*-mefloquine on a decagram scale from its racemate. The monomer synthesis does not require chromatographic purification, and polymerization can be carried out safely on a >30 gram scale. PEARL is readily recovered after each cycle and has been applied for resolution of a broad range of N-heterocycles.

Kinetic Resolution

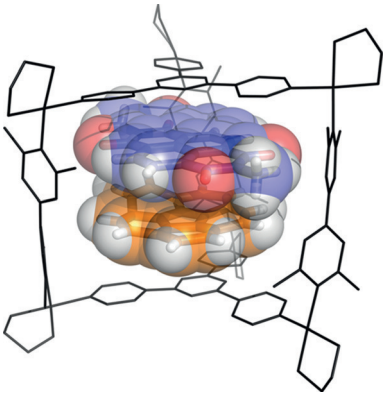
Sandwich with arsenic filling: $[(Cp''_2Sm)(\mu,\eta^4{:}\eta^4\text{-}As_4)(Cp^*Fe)]$ and $[(Cp''_2Sm)_2As_7(Cp^*Fe)]$, which are the first polyarsenides of the rare-earth metals, are reported. $[(Cp''_2Sm)(\mu,\eta^4{:}\eta^4\text{-}As_4)(Cp^*Fe)]$ is also the first d/f-triple decker sandwich complex with a purely inorganic aromatic middle deck.



Polyarsenides

Host–Guest Systems

Molecular compressor: Self-assembled coordination cages can compress the bowl-shaped guest corannulene when encapsulated in a pillared cage. Unsubstituted corannulene was pairwise included together with naphthalene diimide, while bromocorannulene formed a defined homodimer to be accommodated.



Supporting information is available on www.angewandte.org (see article for access details).

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

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The Hot Papers are articles that the Editors have chosen on the basis of the referee reports to be of particular importance for an intensely studied area of research.

Angewandte Corrigendum

Synthesis of 3,4,5-Trisubstituted Isoxazoles from Morita–Baylis–Hillman Acetates by an $NaNO_2/I_2$-Mediated Domino Reaction

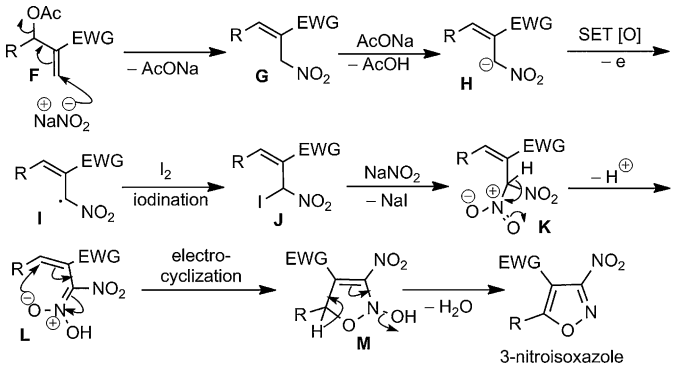
S. U. Dighe, S. Mukhopadhyay, S. Kolle, S. Kanojiya, S. Batra* ____ 10926–10930

Angew. Chem. Int. Ed. **2015**, *54*

DOI: 10.1002/anie.201504529

In this Communication, the statement "analogous nucleophilic addition on the C–H bond α to the nitro group is unprecedented" (page 10927, first paragraph, line 6–7) must be retracted. The authors inadvertently omitted citing two seminal publications[1,2] pertaining to oxidative nitration of nitroalkanes which were brought to their notice by an attentive reader.

In view of these publications, an alternate mechanism which appears to be more logical towards explaining the formation of the observed product is suggested (Scheme 3). This detail however has no bearing on the conclusions from the manuscript.



Schema 3. Plausible mechanism for the transformation of MBH acetates into 3,4,5-trisubstituted isoxazoles. SET = single-electron transfer.

[1] N. A. Petrova, M. B. Shcherbinin, A. G. Bazanov, I. V. Tselinskii, *Russian J. Org. Chem.* **2007**, *43*, 640 – 651.

[2] K. Baum, D. A. Lerdal, J. S. Horn, *J. Org. Chem.* **1978**, *43*, 203 – 209.

