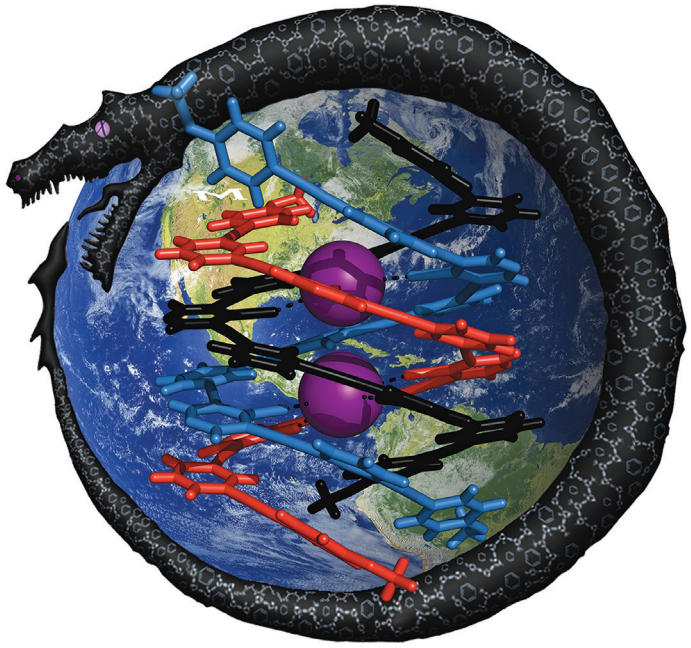
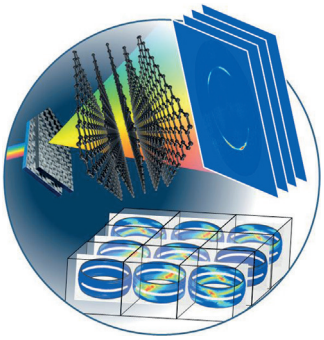
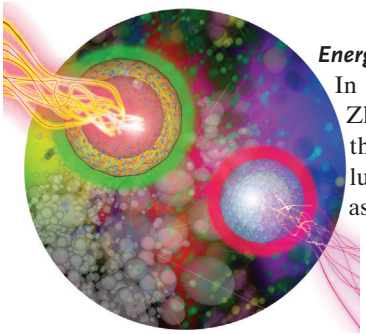


... of Norse mythology that encircled Midgard—arylethynyl oligomers envelop their guests with halogen bonds. In their Communication on page 12398 ff., O. B. Berryman et al. present the first halogen-bond-induced triple helicate to encapsulate iodide in solution and the solid state. Strong and linear halogen bonds promote this intricate and robust self-assembly. Garron Hale (Univ. of Oregon) is gratefully acknowledged for assisting with preparation of the cover artwork.



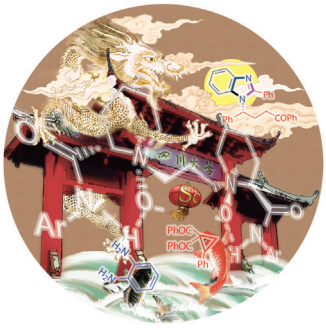
Crystallographic Texture

H. C. Lichtenegger et al. describe in their Communication on page 12190 ff. a method to determine crystallographic texture. The method is based on energy-dispersive Laue diffraction and enables 3D information to be obtained without sample rotation.



Energy Transfer

In their Communication on page 12356 ff., B. Zhou, Q. Y. Zhang, Y. H. Tsang et al. demonstrate the realization of both up- and down-conversion luminescence of lanthanides by using gadolinium as energy donor in a core–shell nanostructure.



Asymmetric Synthesis

The first asymmetric ring-opening/cyclization/retro-Mannich reaction of cyclopropyl ketones with aryl-1,2-diamines is described by X. M. Feng, X. H. Liu et al. in their Communication on page 12228 ff.

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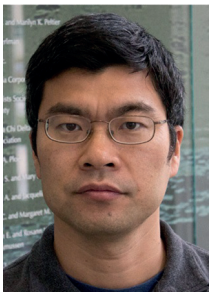
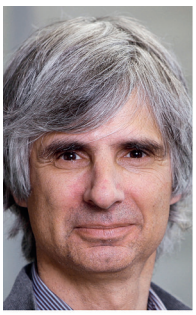


"If I were not a scientist, I would be a chef. My greatest achievement has been volunteering in my son's kindergarten class for nearly one year. …"
This and more about Weiping Tang can be found on page 12142.

News



B. H. Meier

H.-P. Steinrück

H. Braunschweig

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Books

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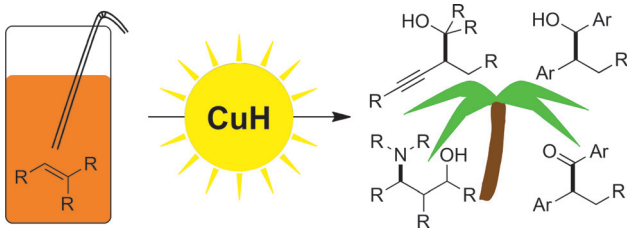
Highlights

Asymmetric Catalysis

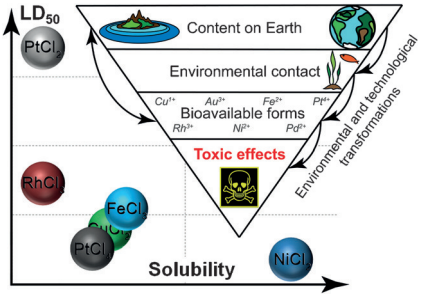


Coppercabana: The copper(I) hydride catalyzed functionalization of unactivated alkenes has been shown to be compatible with conventional carbonyl reduction. Through the combination of both pathways or complete suppression of C=O reduction in favor of C=C functionalization, methods for the stereoselective synthesis of a variety of chiral molecules have been developed.

Minireviews

Sustainable Chemistry

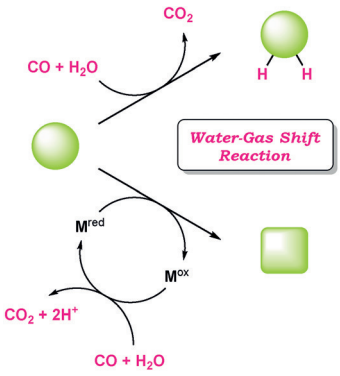
Heavy weights versus the light weights: A comparison of available data on biological activity of metals commonly used in catalysis suggests that the assumption of toxic heavy metals and benign lighter metals should be re-evaluated. The available experimental data are insufficient for accurate evaluation of biological activity of these metals. Therefore, without dedicated experimental measurements, toxicity should not be used as a "selling point" when describing new catalysts.



Reviews

Synthetic Methods

New directions for a classic: In addition to its fundamental role in the production of hydrogen, the water-gas shift reaction has found application in a multitude of reductive transformations in organic synthesis. These include hydrogenation-type reactions, as well as catalytic, overall-reductive processes wherein the CO/H_2O couple can act as the terminal reductant.



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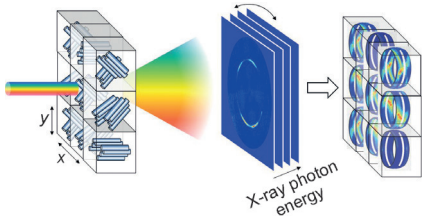
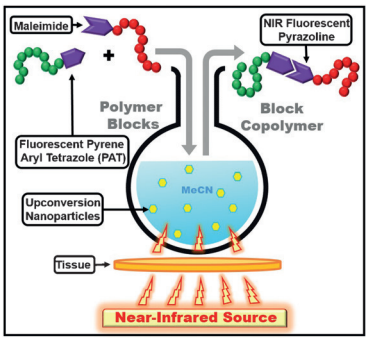
Communications



In full view: A new method to determine crystallographic texture based on energy-dispersive Laue diffraction exploits the curvature of the Ewald sphere to obtain 3D information in one shot without sample rotation, which opens up unprecedented spatial resolution. The principle was demonstrated on a complex carbon fiber system as well as the biomineralized exocuticle tissue of the American lobster.

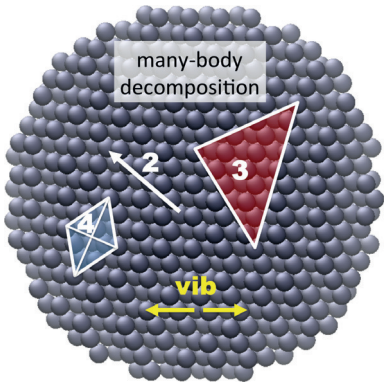
Crystallographic Texture

Gently does it: The first example of upconversion photoinduced coupling chemistry based on the established tetrazole–ene cycloaddition system induced by near-infrared light is introduced. The power of the technique, including tissue penetration, is demonstrated for small-molecule ligation, macromolecular end-group modification as well as polymer–polymer ligation.



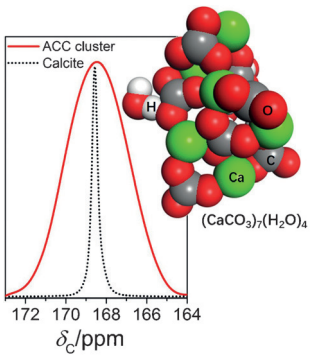
Photochemistry

Testing theory at the very limit: The cohesive energy for solid argon is obtained from a many-body decomposition into static and dynamic contributions by application of relativistic coupled cluster theory. The deviation from experimental findings is in the J mol^{-1} range.



Computational Chemistry

Proto-calcite short-range order was found in ligand-stabilized amorphous calcium carbonate clusters with a very small $CaCO_3$ core 1.4 nm in diameter consisting of only seven $CaCO_3$ units. This supports the notion of a structural link between prenucleation clusters and the postnucleation amorphous phase.



Crystallization

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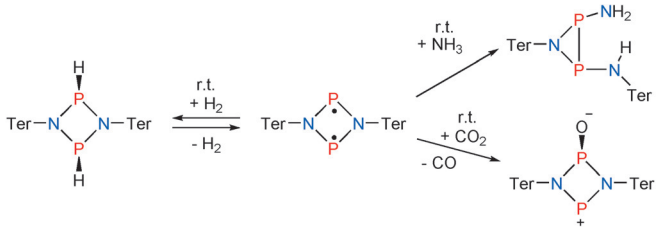
Environmental Chemistry

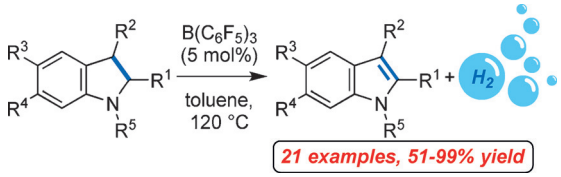
Take it away: DNA nanogels were developed as a biomimetic scavenging agent by exploiting the generic complexation of DNA with polycyclic aromatic hydrocarbons (PAHs). Up to 720 μg of PAH per gram of DNA nanogel are taken up and the uptake is rapid, reaching 50% loading after 15 minutes. Beyond PAHs, DNA nanogels may be useful for the generic removal of genotoxins from water, since most known molecules that strongly associate with DNA are mutagenic.

Main-Group Chemistry



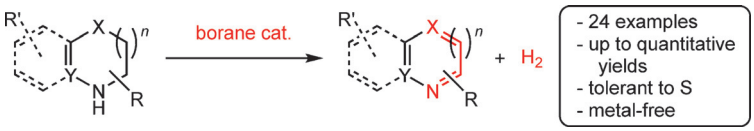
Don't wait for activation: The singlet biradicaloid [P(μ-NTer)]$_2$ readily reacts with H_2, CO_2, or NH_3 at ambient temperature. The addition of H_2 is reversible whereas CO_2 is reduced to CO with formation of "biradicaloid monoxide". Activation of ammonia causes the P_2N_2 scaffold to rearrange to give an azadiphosphiridine.

Dehydrogenation



The acceptorless dehydrogenation of N-protected indolines and other heterocycles is catalyzed by frustrated Lewis pairs. Mechanistic as well as quantum-mechanical studies revealed the liberation of molecular hydrogen to be the rate-determining step. The addition of a weaker Lewis acid as a hydride shuttle increased the reaction rate by a factor of 2.28.

Heterocycles



B-side of borane: A metal-free acceptorless dehydrogenation of N-heterocycles was realized by using an electrophilic borane. This protocol affords synthetically important N-heteroarenes in high yield. The borane catalyst exhibits unprecedented chemoselectivity as it is tolerant to sulfur functionalities and demonstrates superior reactivity in the synthesis of benzothiazoles compared to the conventional metal-catalyzed methods.

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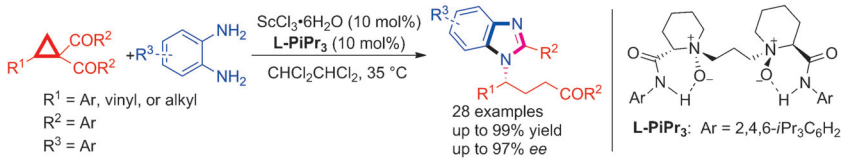
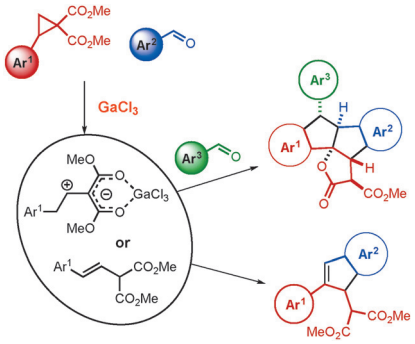


Scandalous Sc: The title reaction proceeds in the presence of a chiral *N*,*N*′-dioxide/Sc^{III} catalyst. A variety of benzimidazoles bearing chiral side chains were obtained with excellent results. This method provides novel access to chiral benzimidazole-substituted amide and cycloheptene derivatives.

Heterocycle Synthesis

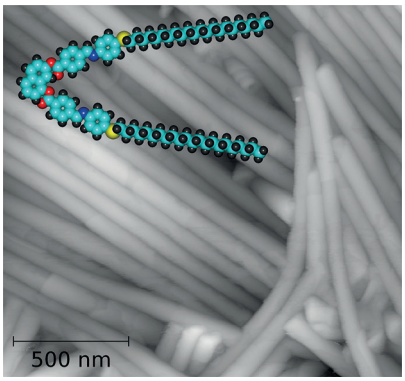
Back Cover

Old reagents, new products: A new strategy for the cascade assembly of substituted indenes and polycyclic lactones based on reactions of donor–acceptor cyclopropanes and styrylmalonates with aromatic aldehydes has been developed. Use of $GaCl_3$ makes it possible to change the direction of the reaction and to perform the process in a multicomponent version (27 examples).



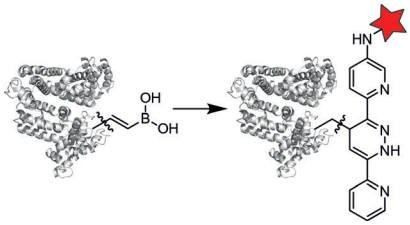
Cascade Reactions

The lamellar crystal phase (B_4) made of acute-angle bent-core mesogens exhibits an unusual, highly porous sponge-like morphology. However, if grown in the presence of low-weight mesogenic molecules, the same crystal forms nanotubes with a very high aspect ratio.



Crystalline Phases

Bioorthogonal iEDDA reagents: Vinylboronic acids (VBAs) were studied as non-strained, synthetically accessible, and water-soluble bioorthogonal reagents in the Carboni–Lindsey reaction with dipyridyl-*s*-tetrazines. The VBAs were shown to be biocompatible, non-toxic, and highly stable in aqueous media and cell lysate. Furthermore, VBAs were used orthogonally to the strain-promoted alkyne–azide cycloaddition for protein modification.



Bioorthogonal Reactions

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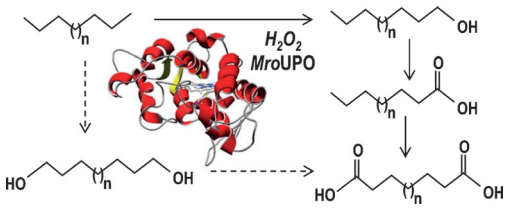
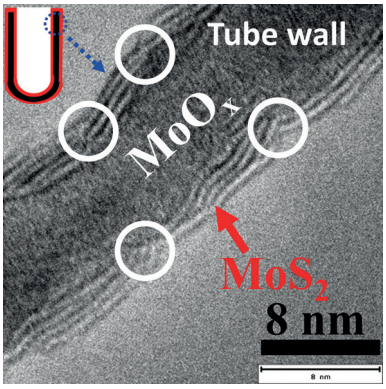
Enzyme Catalysis



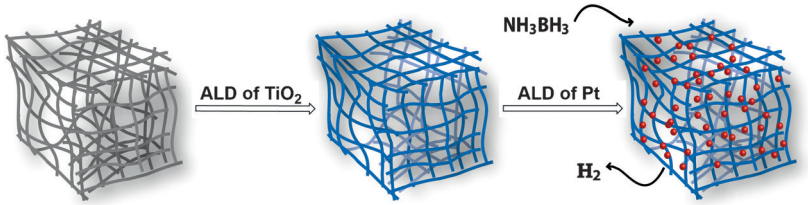
A peroxygenase from the fungus *Marasmius rotula* was found to catalyze a cascade of mono- and diterminal oxygenation reactions of long-chain *n*-alkanes to carboxylic acids in the presence of H_2O_2 as the sole cosubstrate (see scheme). This peroxygenase type has great advantages for the mild activation of alkanes, with its self-sufficient monooxygenase activity and its ability to hydroxylate the most unreactive terminal positions.

Electrocatalysis

Anodic molybdenum oxide nanotube arrays were formed. These MoO_x nanotube layers can be converted into a MoO_x/MoS_2 nanotubular core–shell structure with bent MoS_2 nanosheets consisting of stacks of typically four S-Mo-S layer units, which are discordantly grown on the MoO_x substrate, exposing catalytically active end planes to the surrounding. These structures are highly promising for applications in electrocatalysis.

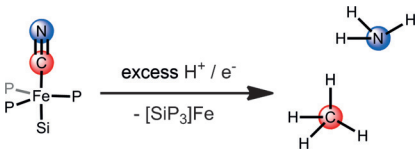


3D Nanomaterials



A 3D peptide nanofiber aerogel was coated with TiO_2 by atomic layer deposition (ALD) with angstrom-level thickness precision. This nano-network was further decorated with Pt nanoparticles (Pt NPs; see picture; red) using ozone-assisted ALD. The 3D Pt-TiO_2 nano-network shows superior catalytic activity in hydrolysis of ammonia–borane, generating 3 equivalents of H_2.

Nitrogen Fixation



Reductive cleavage of cyanide: A trigonal bipyramidal iron cyanide complex is shown to evolve methane and ammonia upon exposure to proton and electron equivalents at low temperature (see picture). Terminally bound Fe(CNH) and $Fe(CNH_2)$ complexes are characterized as possible intermediates in this CN^- cleavage reaction.

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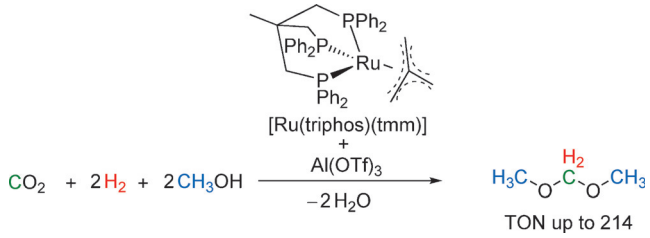
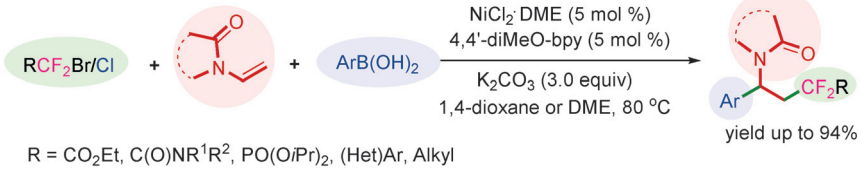


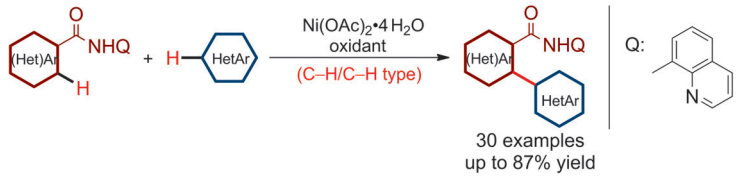
Come together! The molecular catalyst [Ru(triphos)(tmm)] in combination with the Lewis acid $Al(OTf)_3$ enables the synthesis of dimethoxymethane from carbon dioxide, molecular hydrogen and methanol. This new catalytic reaction provides the first synthetic example for the selective conversion of carbon dioxide and hydrogen into the formaldehyde oxidation level, thus opening access to new molecular structures using this important C_1 source.

CO_2 Utilization



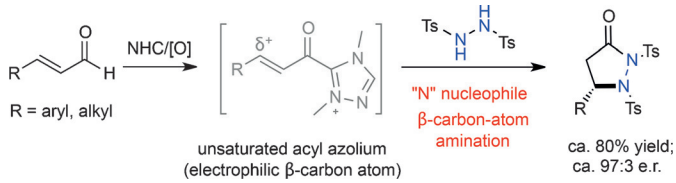
All about efficiency: The title reaction tolerates a variety of arylboronic acids and widely available difluoroalkyl bromides, and even the relatively inert substrate chlorodifluoroacetate. The protocol provides a highly efficient method for the catalytic synthesis of difluoroalkylated compounds.

Cross-Coupling



An odd couple: The title reaction with the aid of the 8-aminoquinoline group gives biheteroaryl structural motifs. The reaction exhibits high functional-group compatibility and broad substrate scope, and the silver oxidant can be recycled to reduce costs and waste.

Homogeneous Catalysis



Focus on the β-C: The aza-Michael addition of protected hydrazine to a catalytically generated unsaturated acyl azolium intermediate provides a highly efficient approach for enantioselective β-carbon-atom amination of enals. The heterocyclic products, prepared by using this method, are common scaffolds found in bioactive molecules, and can be readily transformed into β^3-amino-acid derivatives. NHC = N-heterocyclic carbene.

Heterocycle Synthesis

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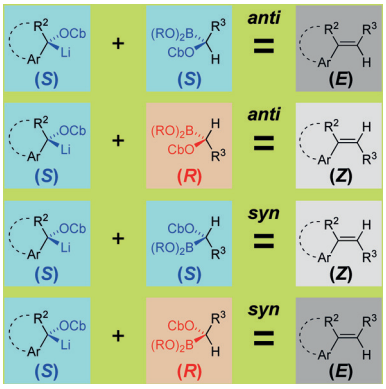
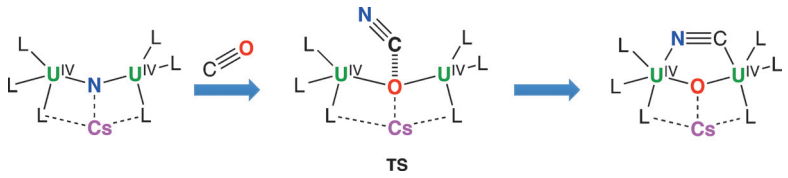
Alkene Synthesis

3D to 2D: Stereochemical information encoded in a pair of scalemic carbenoid reagents controls the geometry of the alkene products formed by their eliminative cross-coupling. The configuration of the alkene is determined by the carbenoid stereochemical pairing (*like* or *unlike*) and the elimination mechanism (*syn* or *anti*), but not by the nature of the substituents.

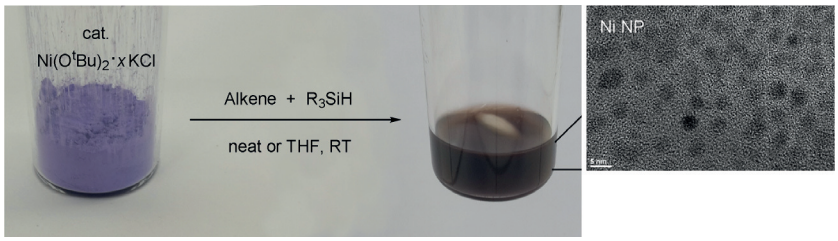


CO Cleavage



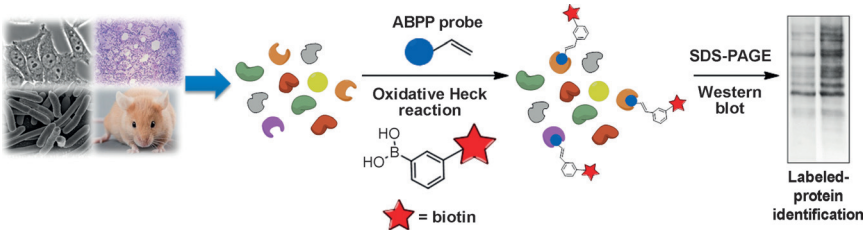
The power of cooperation: A heteropolymetallic uranium nitride with a CsU^{IV}–N–U^{IV} core effected complete cleavage of the strong C≡O bond of carbon monoxide under ambient conditions (see scheme). The reaction led to the formation of a CN^- ligand, which could be alkylated readily to afford organic nitriles. The important role of multimetallic cooperativity in these reactions was identified by computation of the reaction mechanisms.

Hydrosilylation



A nickel nanoparticle catalyst is an efficient and non-precious catalyst for alkene hydrosilylation with commercially relevant tertiary silanes. 28 examples of silanes were formed by this method.

Enzyme Labeling



A villain meets its match: An activity-based probe was developed for human 15-lipoxygenase-1 (15-LOX-1), which plays an important role in various diseases. The probe mimicked the natural enzyme substrate and was able to bind covalently to the active enzyme. It included a terminal alkene as a chemical reporter for the bioorthogonal linkage of a detectable functionality by the oxidative Heck reaction (see scheme).

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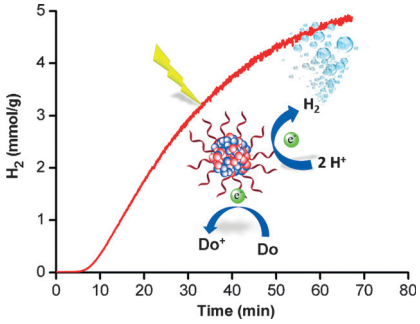
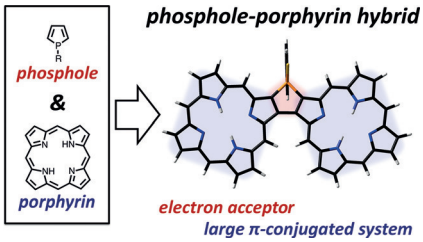


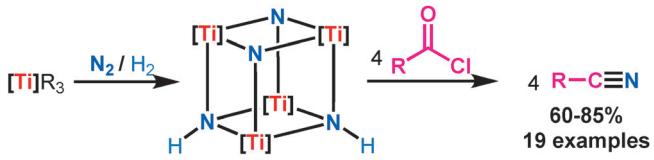
Organic polymer dots were used as a photocatalyst for visible-light-driven hydrogen generation for the first time and showed impressive activity with an initial hydrogen generation rate of 8.3 mmol h^{-1} g^{-1} without the assistance of any co-catalysts. Do = donor.

Photocatalysis

A phosphole-fused porphyrin dimer as a representative of a new class of phosphorus-containing porphyrins was synthesized. This structure exhibits remarkably broadened absorption as well as unique optoelectronic properties and is a good electron acceptor owing to the unique phosphole-fused structure.

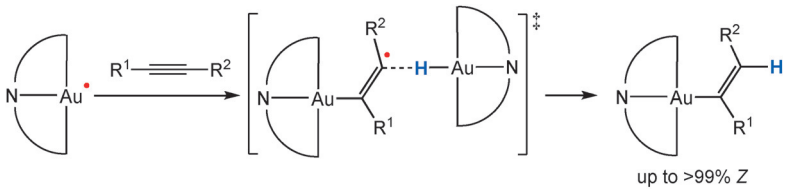


Porphyrinoids



Activation and functionalization of N_2: A mixed diimide/dinitride tetranuclear titanium complex formed by activation of dinitrogen served as a unique platform for the synthesis of nitriles (see picture). Functional groups such as aromatic C–X (X = Cl, Br, I) bonds, nitro groups, and ammonia-sensitive aldehyde and chloromethyl moieties were compatible with the synthetic method.

Nitrogen Fixation



Gold(II) provides a helping hand: Gold(III) pincer complexes overcome their lack of substrate binding sites by participating in a radical-mediated bimolecular pathway. Gold(III) hydrides react with acetylenes in the presence of a radical source in a kinetically controlled reaction to give *trans*-hydroauration products with high regio- and stereoselectivity.

Reaction Mechanisms

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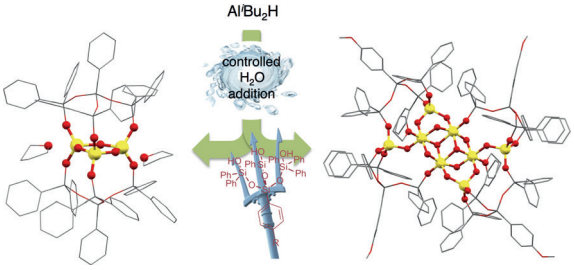
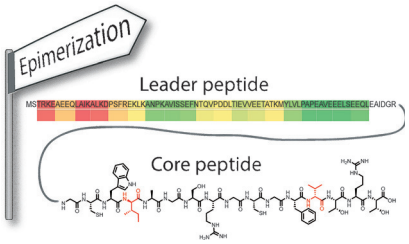
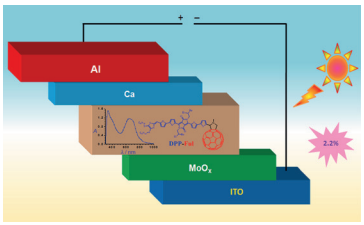


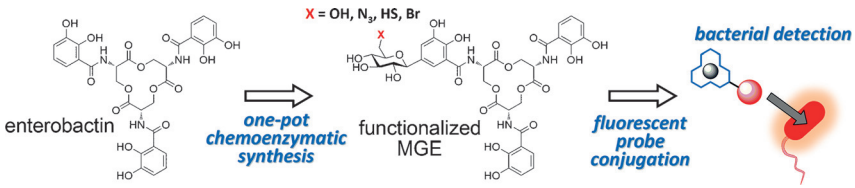
Picking out early aggregates: Tripodal trisilanols stabilize aluminum hydroxide aggregates formed during the hydrolysis of Al^{i}Bu$_2$H with different sizes dependent on the amount of water added.

To guide an epimerase: Radical *S*-adenosyl-methionine peptide epimerases from proteusin biosynthetic pathways introduce D-amino acids into ribosomal peptides. A region in proteusin peptide precursors is identified that is important for epimerization. This region and other shared features in precursors of proteusins, lanthipeptides, and other peptide classes suggest a common evolutionary origin with nitrile hydratase-like enzymes as ancestors.



Climbing alone: The combination of dithiafulvalene-functionalized diketopyrrolopyrrole (DPP) as donor with fullerene (Ful) as acceptor has been successfully explored. Its utilization in single-component organic solar cells (SC-OSCs) was investigated, and it was shown to have a record power-conversion efficiency. ITO = indium tin oxide.





Siderophore-based bacteria labeling: A one-pot chemoenzymatic synthesis approach that is capable of functionalizing enterobactin with different reactive groups is developed. The functionalized enterobactin can be further conjugated with fluorophores to perform specific detection of bacteria. This strategy can serve as a convenient way to deliver cargos into bacteria with selectivity.

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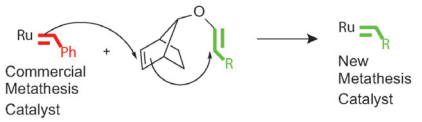
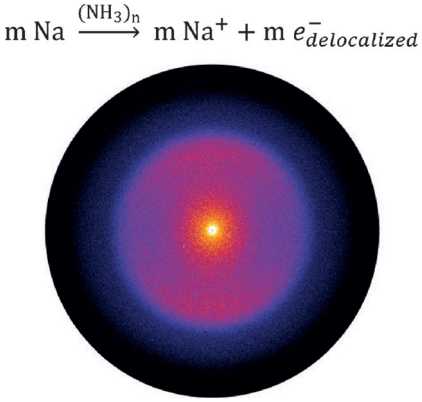


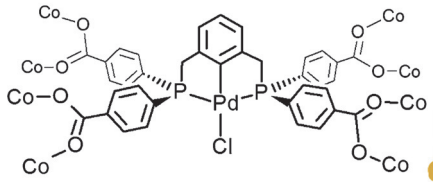
The preferred reaction of a commercial ruthenium benzylidene complex with a highly strained norbornene, followed by a fast intramolecular cyclization, yields new ruthenium carbene complexes in excellent yields. These complexes are ready for functional initiation of polymerization reactions without the need of purification.

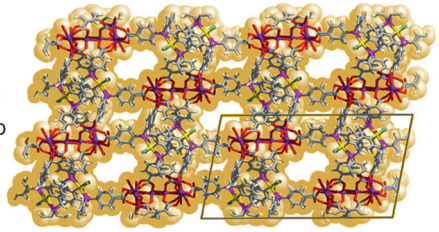
Olefin Metathesis



When is a metal not a metal? For more than a century, chemists have been struggling for a detailed understanding of the intriguing concentration-dependent color change of metal–ammonia solutions from deep blue to copper-gold. Indications for the underlying nonmetal-to-metal transition have now been found in photoelectron images of sodium–ammonia nanodroplets, paving the way for an atomistic description.

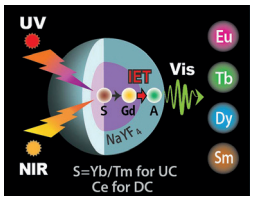
Metal–Ammonia Solutions





Poly-PCP-pincers: A new synthetic strategy for the formation of crystalline, porous versions of PCP-pincer complexes is presented. These complexes can selectively activate gas molecules, such as CO_2 over CO, in the solid state. PCP = Porous Coordination Polymer

Coordination Polymers



Up, down, flying around: Photon up- and down-conversion (UC and DC, respectively) have been realized through Gd^{3+}-mediated interfacial energy transfer (IET) in a core–shell nanoarchitecture. This finding offers a simple, efficient approach for photon management, and enables a fundamental understanding of the interactions between lanthanide ions at nanometer length scale.

Up- and Down-Conversion

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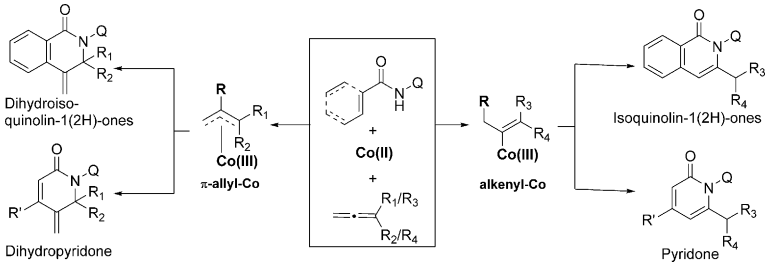
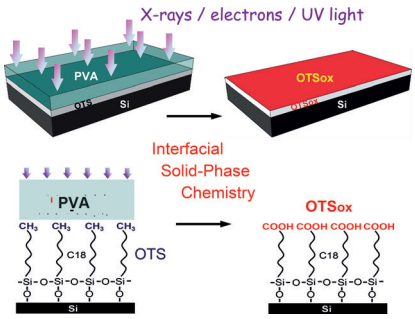
C–H Activation



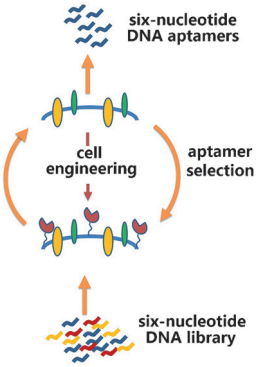
Two paths to ring formation: Heterocyclization reactions of aryl and alkenylamides with allenes at room temperature are reported. The reactions, which involve C–H activation using a Co catalyst, feature a high regioselectivity and impressive substrate scope for both coupling partners.

Surface Functionalization

Novel interfacial chemistry is induced by electromagnetic radiation or electrons at the boundary between two solid materials, one of which acts as a removable thin film reagent/catalyst. This approach offers a variety of viable routes for nondestructive surface functionalization and patterning over length scales extending from centimeters to nanometers.



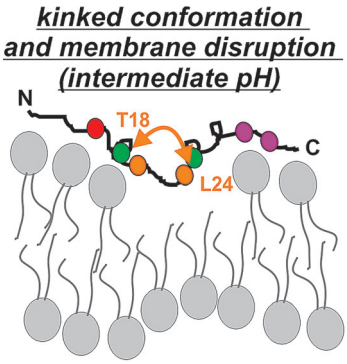
Laboratory Evolution



Six nucleobases: An expanded genetic information system and laboratory in vitro evolution were used to generate six-nucleotide aptamers that target cells engineered to overexpress a particular cell-surface protein. These aptamers could be used to distinguish cells that display that protein from those that do not.

Peptides

Showing backbone: The pH-low insertion peptide (pHLIP) inserts into membranes and forms a transmembrane (TM) α-helix in response to acidity changes. Tracing backbone conformations revealed that the TM helix spans from A10 to D33 with a break at T19 to P20. Residue-specific pK_a values of D31, D33, D25, and D14 were determined to be 6.5, 6.3, 6.1, and 5.8, respectively, and define the sequence of protonations which lead to insertion. Furthermore, possible intermediate states which disrupt membranes at pH 6.4 are proposed.



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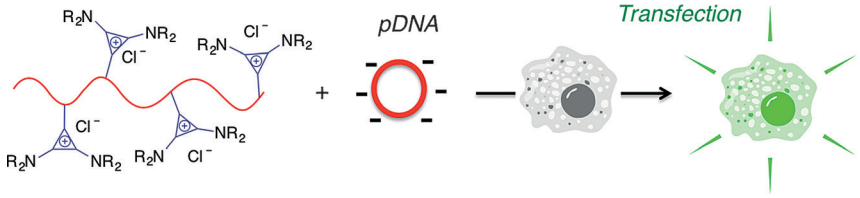
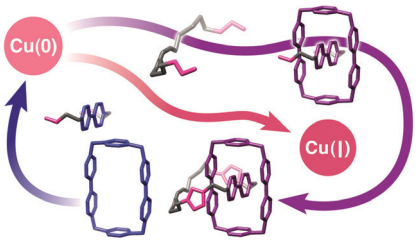
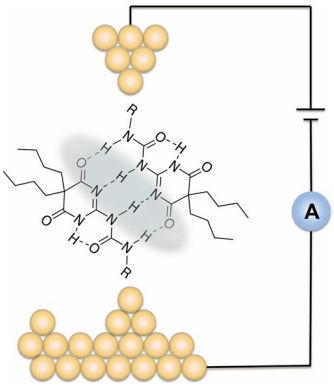


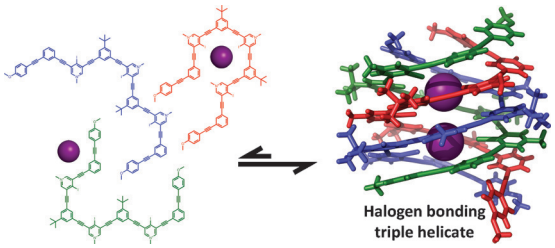
They just clicked: A stable bis(dialkylamino)cyclopropenium chloride salt can efficiently react with polymers containing secondary amines to yield cationic polyelectrolytes. The dialkylamino groups in this click transformation can be modulated to yield various polyelectrolytes bearing soft cationic moieties. Some of these cyclopropenium-based polymers give high transfection efficiencies and are less cytotoxic than linear polyethyleneimine (PEI).



A user-friendly technique for the construction of positively charged catenanes and rotaxanes, templated by radical-pairing interactions in a convenient and efficient manner, has been conceived and implemented. This method opens up the possibility of producing integrated systems with Coulombically challenged catenanes and rotaxanes and of fabricating devices based on these systems.



Electron transport through multiple hydrogen bonds: Supramolecular junctions bridged with quadruple hydrogen bonds have been constructed and characterized using the scanning tunneling microscopy break junction method. This noncovalent interaction exhibits conductivity comparable to that of covalently conjugated molecular devices and can also be manipulated by the polarity of the solvent environment.



Bond, halogen bond: Three tricationic arylethynyl strands self-assemble to form a tubular anion channel lined with nine halogen-bond donors in solution and the solid state. Eight strong iodine···iodide halogen bonds and numerous buried π-surfaces endow the triplex with remarkable stability, even at elevated temperatures. The stringent linearity of halogen bonding could be a powerful tool for the synthesis of multi-strand anion helicates.

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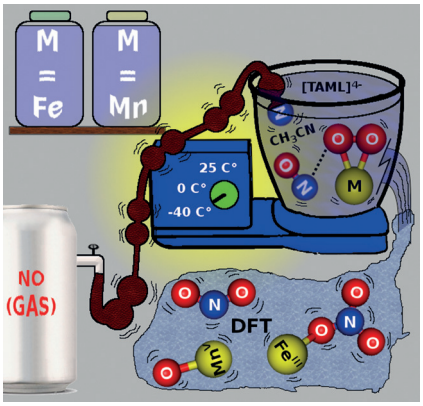
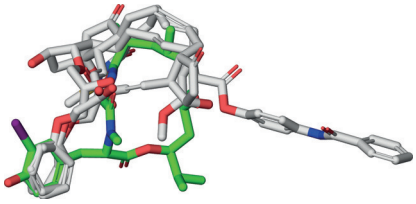
Nitric Oxide Chemistry

By NO means: Reactions of nonheme Fe^{III}–superoxo and Mn^{IV}–peroxo complexes bearing a common tetraamido macrocyclic ligand (TAML), namely $[(TAML)Fe^{III}(O_2)]^{2-}$ and $[(TAML)Mn^{IV}(O_2)]^{2-}$, with nitric oxide (NO) afford the Fe^{III}–NO_3 complex $[(TAML)Fe^{III}(NO_3)]^{2-}$ and the Mn^{V}–oxo complex $[(TAML)Mn^{V}(O)]^{-}$ plus NO_2^-, respectively.



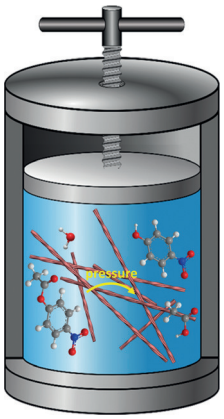
Natural Products

Computational adoption services: Macromolecular targets of the marine natural product doliculide were successfully identified using a chemocentric computer-based prediction method. This study reveals this cyclodepsipeptide as a potent antagonist of the human prostanoid receptor EP3.

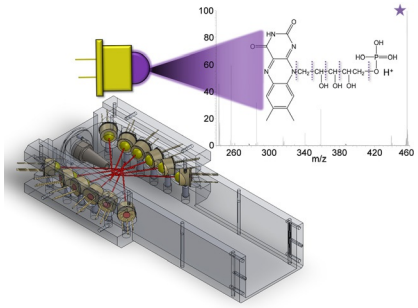


Pressure and Temperature

Negative + positive = better catalysis: Studying the combined effects of pressure and temperature on the hydrolysis of *p*-nitrophenyl acetate catalyzed by designed amyloid fibrils using high-pressure stopped-flow techniques with rapid UV/Vis absorbance detection showed that both pressure and temperature effectively enhance the catalysis as a consequence of a negative activation volume and a positive activation energy.



Analytical Chemistry



LEDs as an ultraviolet photodissociation light source: The latest ultraviolet LEDs are interfaced with a mass spectrometer to perform gas-phase ultraviolet photodissociation of cations and anions.

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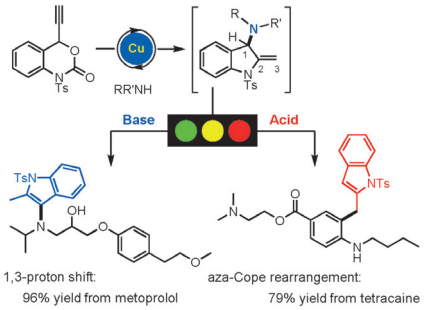
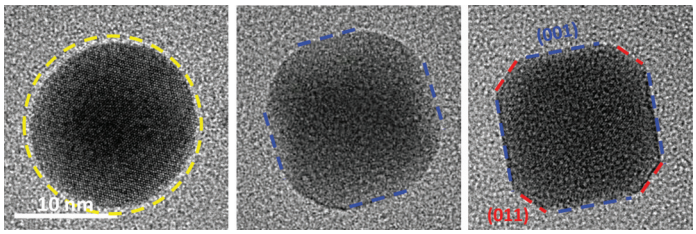


Switch-hitter: This work describes a copper-catalyzed decarboxylative amination/hydroamination sequential reaction. The one-pot treatment of an indoline intermediate with either an acid or a base enables the switchable synthesis of two types of functionalized indoles in generally high yields and with complete chemoselectivities (36 examples and up to 99% yield).

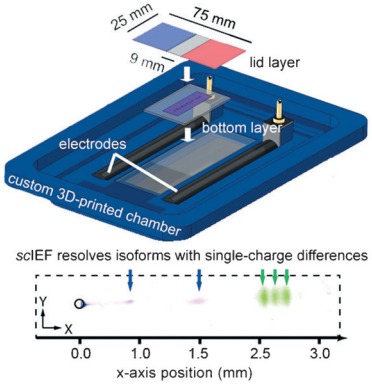
Heterocycles



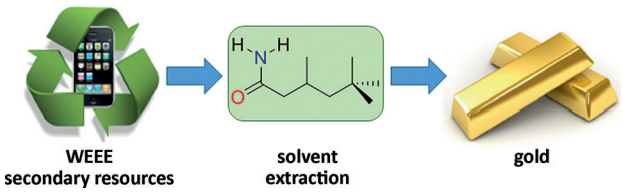
In good shape: Deliberate surface faceting of palladium–copper alloyed nanocrystals was achieved by simple post-synthetic treatment in atmospheric pressure hydrogen. Microscopic insight is provided for tailoring of the physical and chemical properties of catalytically significant palladium alloys.

Nanoparticle Morphology

Electrophoretic cytometry: A multilayer, patterned hydrogel device supports isoelectric focusing to separate protein isoforms from single cells (scIEF). All preparative and analytical steps, including cell isolation, lysis, protein separation, UV-actuated blotting, and immunoprobing, are performed on the device. Protein isoforms with single-charge differences are resolved, blotted, and detected by immunoprobing.



Single-Cell Analysis



Going for gold: A simple primary amide is shown to be an effective reagent for the selective recovery of gold by solvent extraction from a mixture of metals representative of those in waste electrical and electronic equipment (WEEE). The recovery is achieved through the formation of dynamically assembled hydrogen-bonded amide/$AuCl_4$ clusters.

Recovery of Gold

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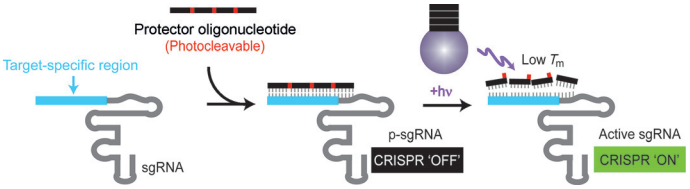
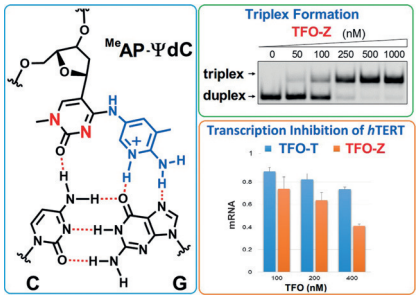
Gene Technology



Turn "ON" CRISPR with light: CRISPR can be brought under the control of light simply by hybridizing a single chimeric guide RNA (sgRNA) with a complementary oligonucleotide containing photocleavable groups (protector oligonucleotide). The protected sgRNA (p-sgRNA) remains inactive, blocking CRISPR activity, until the protector oligonucleotide is cleaved with a remote light trigger.

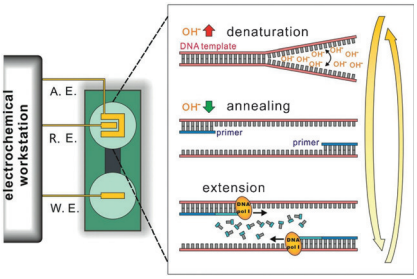
DNA Recognition



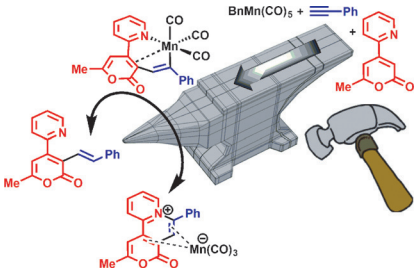
Pseudo-deoxycytidine (ΨdC) derivatives were developed for the selective recognition of the CG base pair to expand the triplex-forming sequence. The ΨdCs formed a stable triplex with the promoter of the hTERT gene containing four CG inversion sites, and effectively inhibited its transcription in human cancer cells, and may lead to the development of new triplex-forming oligonucleotides.

DNA Replication

A pH-legmatic approach to PCR: Polymerase chain reactions were triggered at room temperature by using automatic pH alternation with a microfabricated device.



C–H Activation



Look left, look right: A highly reactive seven-membered manganese(I) intermediate has been detected and characterized that is effective for H-transfer or reductive elimination to deliver alkenylated or pyridinium products, respectively. The two pathways are determined at Mn^{I} by judicious choice of an electron-deficient 2-pyrone substrate containing a 2-pyridyl directing group, which undergoes regioselective C–H activation.

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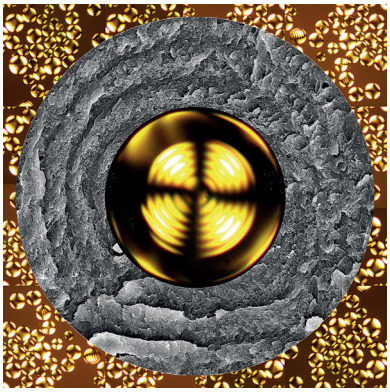
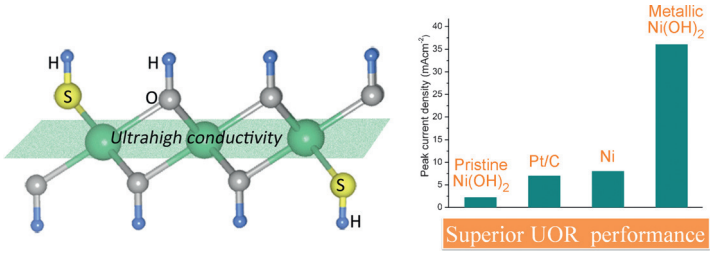
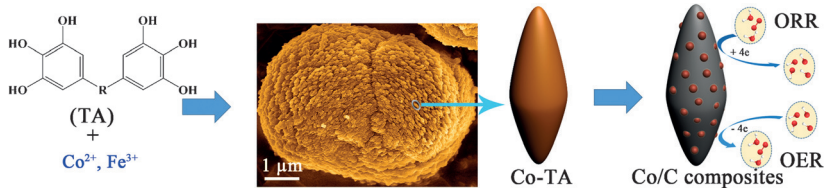
Polymer microspheres with chiral nematic order were obtained through photopolymerization of acrylamide in the presence of cellulose nanocrystals (CNCs). Using this approach, silica microspheres with chiral nematic structures were also fabricated for the first time.



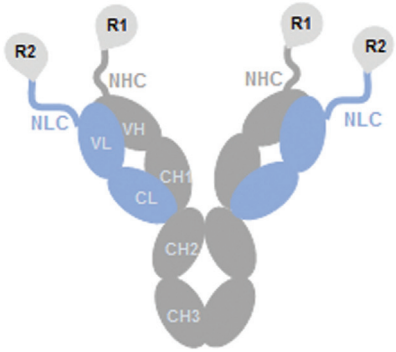


Metal as anything: Surface sulfur incorporation into β-Ni(OH)$_2$ nanosheets gives the first metallic configuration of a transition-metal hydroxide. The resulting metallic Ni(OH)$_2$ nanosheets have more exposed active sites and metallic electrical conductivity, giving rise to greatly enhanced performance for the urea oxidation reaction (UOR) for direct urea fuel cells.



Coordination crystals (see SEM image) obtained from a polyphenol (tannic acid; TA) and cobalt or iron were synthesized by a hydrothermal synthesis route. The crystals are a renewable source for the fabrication of metal/carbon composites as a nonprecious metal catalyst for the oxygen reduction and evolution reactions.

Mono- and multifunctional antibody agonists of the receptors GLP-1R, GCGR, and GIPR were generated by N-terminal fusion of the exendin-4, glucagon-like peptide-1, glucagon, GIP, and ZP peptides to the heavy chains (HC) and/or light chains (LC) of the humanized monoclonal antibody Synagis. The resulting antibody fusions show excellent activity in sustaining blood glucose control and reducing body weight in rodent models.



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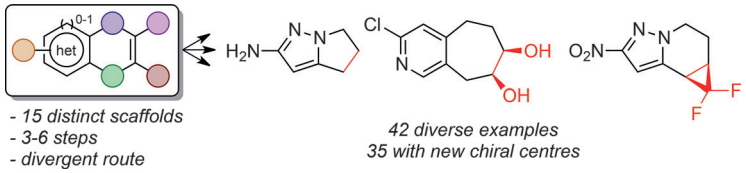
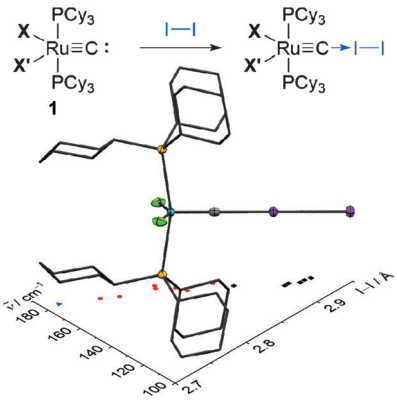
Drug Discovery



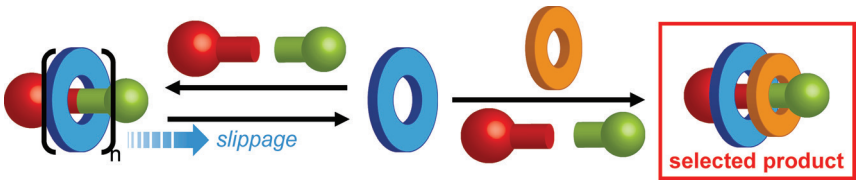
2D or not 2D: A collection of partially saturated bicyclic pyridine- and pyrazole-based fragments, derived from a diverse set of readily accessible branch-point scaffolds, is presented. Their enhanced sp^3 content, compared to typical fragment libraries, allows excellent control of 3D growth vectors in drug development applications.

Iodine Adducts

To give and take: terminal ruthenium carbide complexes $[(Cy_3P)_2X_2Ru{\equiv}C]$ (**1**; X = halide or pseudohalide), form charge-transfer adducts with I_2 exhibiting large variation in bond lengths and stretching frequencies. This shows that the auxiliary ligand sphere on ruthenium enables control over the σ-donor properties of carbide ligands, elucidating their isolobal relationship with carbon monoxide.

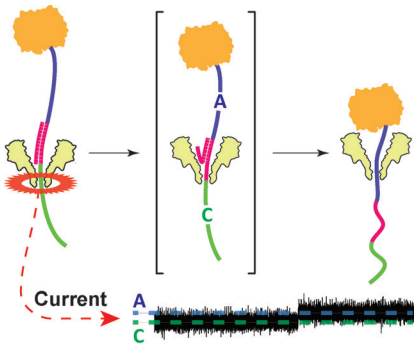


Supramolecular Chemistry



If at first you don't succeed, fall apart: A novel self-sorting approach is described in which the kinetic stability of the desired [3]rotaxane isomer determines the reaction outcome. All other threaded structures derived from the larger ring are kinetically unstable, allowing the yield of the target to be amplified at the expense of other possible products.

Biosensors



A biological nanopore with a deformable alpha-helical transmembrane region allows discrimination between homopolymeric single-stranded DNA and permits double-stranded DNA analysis.

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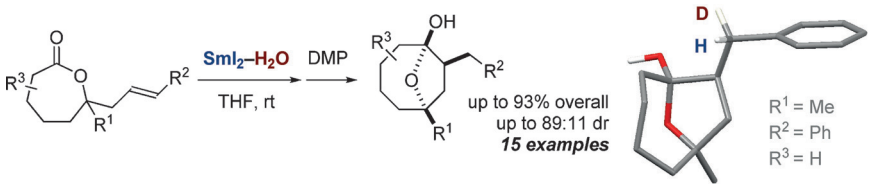
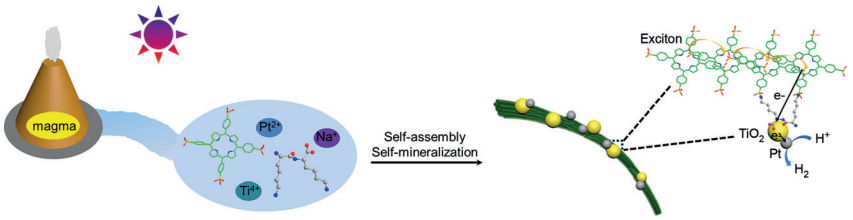


Radical Cyclization

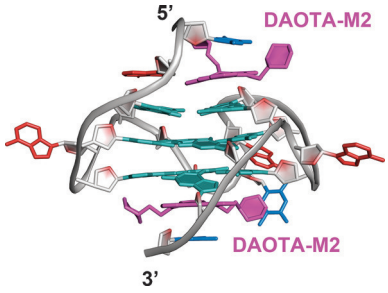
Seven-membered lactones undergo selective SmI_2–H_2O-promoted radical cyclization to form substituted cyclooctanols. The products arise from an *exo*-mode of cyclization rather than the usual *endo*-attack. A labeling experiment and neutron diffraction study have been used for the first time to probe the configuration and highly diastereoselective deuteration of a chiral organosamarium intermediate.



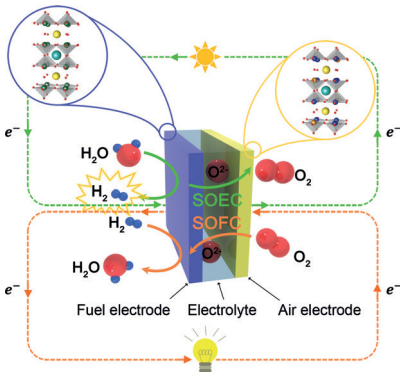
Biomimetic Self-Organization

Mimicking primitive photosystems: Self-organization, dynamic evolution, and sustainable utilization of components in a "prebiotic soup" are conceptually and experimentally validated through simple but well-functioning peptide–porphyrin co-assemblies, which support a new type of primitive hydrogen producing photobacteria model.

Playing the triangle in a quartet: A small-molecule optical probe (DAOTA-M2) based on a triangulenium core binds to G-quadruplexes in a 1:2 stoichiometry. Binding of DAOTA-M2 occurs mainly through π–π stacking between the triangulenium core and the guanine residues of the outer G-quartets. Interestingly, the binding affinities of DAOTA-M2 for the two outer G-quartets differ by a factor of two.



G-Quadruplexes



A solid oxide electrolysis cell using layered perovskites as both-side electrodes is shown to possess outstanding performance, reversible cycling, and long-term stability during hydrogen production.

Hydrogen Productions

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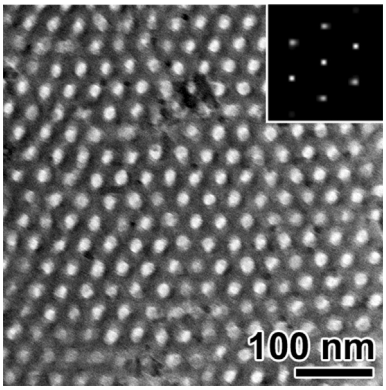
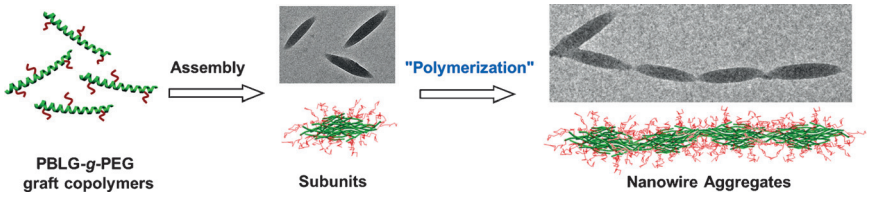
Conducting Polymers



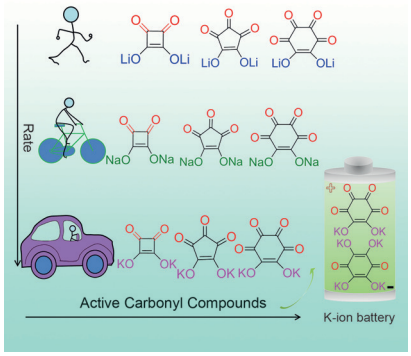
Ultrathin conducting polymer nanosheets were achieved by synergistically manipulating the self-assembly of perfluorocarboxylic acids and polystyrene-*b*-poly(ethylene oxide) diblock copolymers. The nanosheets feature mesoscale-ordered hexagonal pore arrays, tunable morphologies and pore sizes, large specific surface area as well as anisotropic and record-high electrical conductivity.

Hierarchical Assembly



Connect the dots: Anisotropic spindle-like micelles, self-assembled from polypeptide graft copolymers with rigid backbones, can serve as ideal pre-assembled subunits for constructing hierarchical nanowires. The growth of the nanowires follows a hierarchical process that resembles step polymerization.

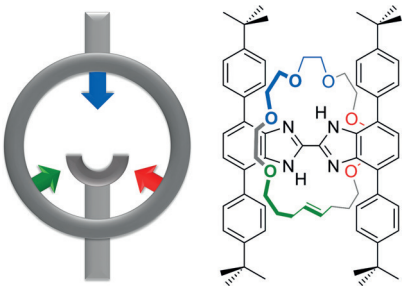
Energy Storage



Organic electrode material: Oxocarbon salts ($M_2(CO)_n$) with different metal ions (M = Li, Na, K) and frameworks (n = 4, 5, 6) were rationally designed and used as electrodes for rechargeable Li, Na, and K-ion batteries. A first example of a renewable and sustainable K-ion battery based on $K_2C_6O_6$ and $K_4C_6O_6$ with a rocking-chair reaction mechanism is shown.

Supramolecular Chemistry

A rigid, H-shaped [2]rotaxane ligand with different sets of donor atoms on the axle and wheel components was prepared. The dynamics of the rotaxane and the orthogonal arrangement of the donors allows access to different co-conformations by simple rotation of the wheel about the axle. Three different rotational isomers were observed and structurally characterized for the neutral ligand and coordination complexes with Li^+ and Cu^+ ions.



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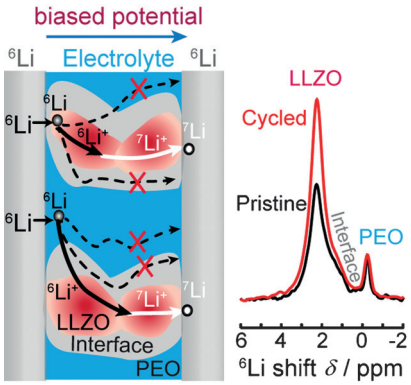
Where do they go? The first experimental evidence was obtained for lithium ions diffusing through composite ceramic electrolytes (LLZO and PEO) in an all-solid-state battery. Lithium ion diffusion was determined using ^{6,7}Li NMR and isotope exchange, and indicated that Li ions mainly pass through the LLZO ceramic phase instead of the LLZO-PEO interface or the PEO phase.



Batteries

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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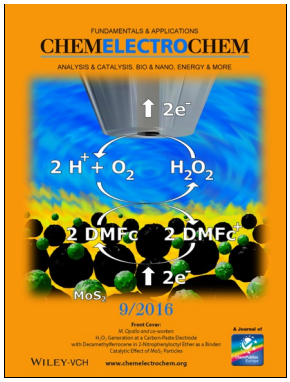

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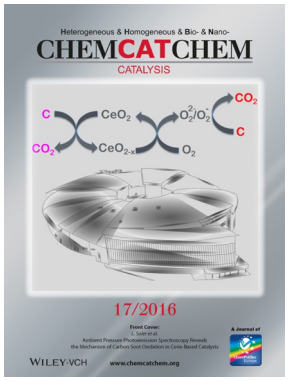

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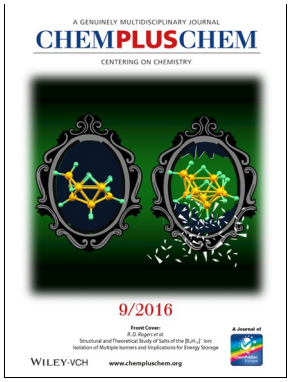

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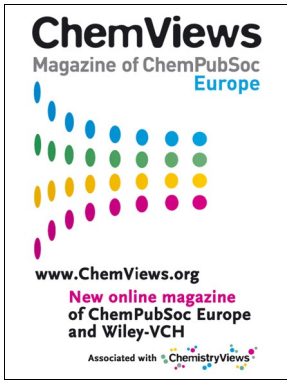

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Angewandte Corrigendum

Substrate-Controlled Product Divergence: Conversion of CO_2 into Heterocyclic Products

J. Rintjema, R. Epping, G. Fiorani, E. Martín, E. C. Escudero-Adán, A. W. Kleij* ——— **3972–3976**

Angew. Chem. Int. Ed. **2016**, *55*

DOI: 10.1002/anie.201511521

Figure 2 of this Communication needs to be revised as shown below. Specifically, compounds **18** and **19** were erroneously exchanged from their position. The authors wish to apologize for this error.

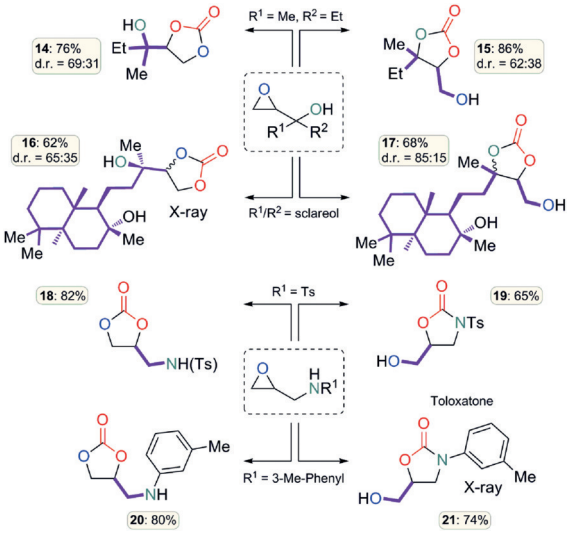

Figure 2. Product divergence from four epoxy alcohols/amines, thus giving access to the compounds **14**–**21**. For all reactions 2 mol% [Al^{tBu}] and $p(CO_2)° = 10$ bar were used unless indicated otherwise. Details: **14**, 5 mol% TBAB, 25 °C, 60 h, conv. 95%, sel. 85%; **15**, 80 °C, 40 h, 30 bar, conv. >99%, sel. 93%; **16**, 5 mol% TBAB, 50 °C, 14 h, 30 bar, conv. >99%, sel. 79%; **17**, 10 mol% TBACl, 75 °C, 14 h, conv. >99%, sel. 79%; **18**, 5 mol% TBAB, 75 °C, 14 h, conv. >99%, sel. 97%; **19**, 10 mol% DIPEA, 50 °C, 40 h, 30 bar, conv. >99%, sel. 77%; **20**, 5 mol% TBAB, 30 °C, 40 h, conv. >99%, sel. 81%; **21**, 2 mol% TBAB, 75 °C, 14 h, conv. >99%, sel. 81%.[13] Ts = 4-toluenesulfonyl.

Angewandte Corrigendum

Benzimidazobenzothiazole-based Bipolar Hosts to Harvest Nearly All of the Excitons from Blue Delayed Fluorescence and Phosphorescent Organic Light-Emitting Diodes

L.-S. Cui, J. U. Kim, H. Nomura, H. Nakanotani, C. Adachi* **6864–6868**

Angew. Chem. Int. Ed. **2016**, *55*

DOI: 10.1002/anie.201601136

The authors of this Communication wish to cite an additional contribution. For this reason, reference [13] must be added on page 6864, right column, at the end of the second sentence of the second paragraph: "The benzimidazo[2,1-*b*]benzothiazole backbone was synthesized though cyclization of 2-mercaptobenzimidazole with *o*-nitrophenyl bromide.[13]"

[13] The synthesis of benzimidazobenzothiazole backbone was reported by Lv et al. and Schäfer et al.: a) J. Gao, J. Zhu, L. Chen, Y. Shao, J. Zhu, Y. Huang, X. Wang, X. Lv, *Tetrahedron Lett.* **2014**, *55*, 3367; b) T. Schäfer, P. Murer, U. Heinemeyer, J. Kohlstedt, H. Wolleb, A. Wolleb, S. Watanabe, H. Nagashima, T. Sakai, C. Lennartz, G. Wagenblast, Patent WO, 2015014794, 2015.

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