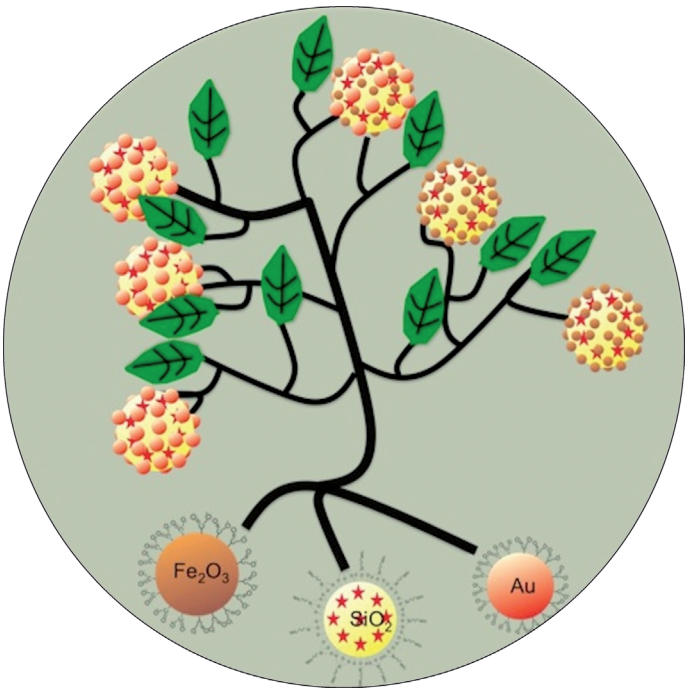
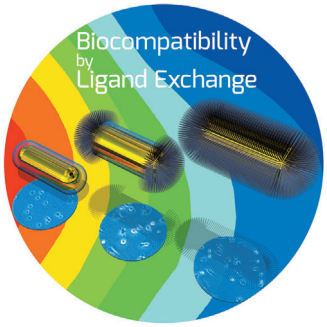
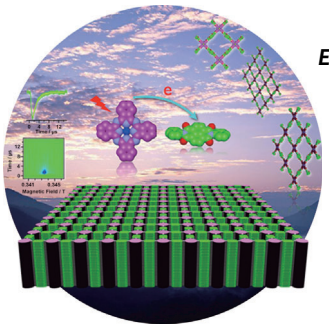


… occurs with perfection in nature (such as in trees) under laminar flows because these flows are symmetrical and continuous. In their Communication on page 1994 ff., A. Abou-Hassan and co-workers use laminar flow microreactors for the self-assembly of fluorescent, plasmonic, and magnetic nanoparticles for the preparation of different categories of assemblies with dual or triple functionalities.



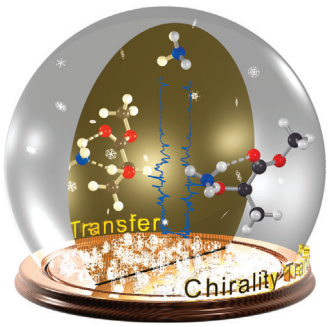
Nanochemistry

In their Communication on page 1934 ff., A. Petri-Fink et al. obtain complete control over the surface functionality of gold nanoparticles in both overall composition and spatial distribution.



Electron Transfer

D. Jiang et al. give mechanistic insights in their Communication on page 2017 ff. into the photochemical events and charge dynamics of a donor–acceptor covalent organic framework by using time-resolved spectroscopic methods.



Chirality Transfer

In their Communication on page 2073 ff., Y. Xu and C. Merten use matrix-isolation vibrational circular dichroism spectroscopy to measure the spectral signatures of chirality transfer from methyl lactate to ammonia.

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Editorial

"... From an international perspective, Sweden's research expenditure is high at 3.4% of the gross domestic product (GDP), compared to the average of 3.0% within the OECD countries. However, merely 24% of the funding in Sweden comes from the government ..."
Read more in the Editorial by Christina Moberg.

Service

Author Profile

"My favorite time of day is the night.
My favorite book is anything by Helmut Krausser ..."
This and more about Günter Mayer can be found on page 1870.

News

P. Mountford

N. Yabuuchi

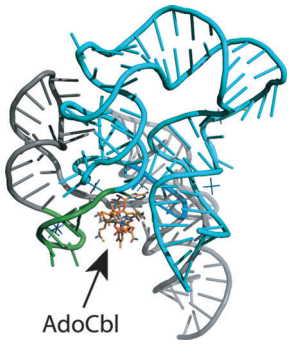
H. Kessler

Books

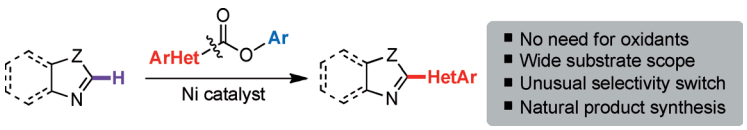
Highlights

Riboswitches

The complex class of cobalamin-sensitive riboswitches use a "kissing loop" to regulate gene expression. The molecular details of the recognition and folding mode of this riboswitch have been revealed by recent X-ray structures. These insights, together with the identification of RNA polymerase pause sites during transcription, have resulted in a more complete understanding of the response mechanism. AdoCbl = adenosylcobalamin.



C–H Arylation

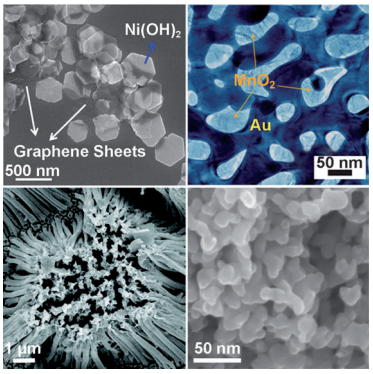


Activation à la carte: The direct arylation of heteroarenes was accomplished by employing aromatic esters as effective coupling partners under nickel catalysis (see scheme; Z = O, S). The key process implies an unconventional and unprecedent Ni-catalyzed decarbonylative coupling utilizing cost-efficient nickel catalysts.

Minireviews

Energy Storage

Three key parameters determine the performance of nanostructured electrodes for pseudocapacitor applications: pore structure, conductivity, and crystallinity. These parameters determine the utilization of electrode materials, especially at high power densities. Future progress can be seen in developing techniques that can simultaneously tailor those parameters and also be able to facilitate electrode production at large scales.



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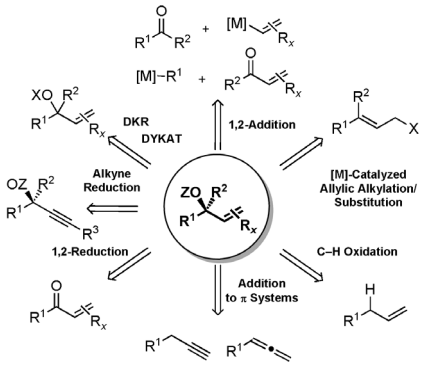
Reviews

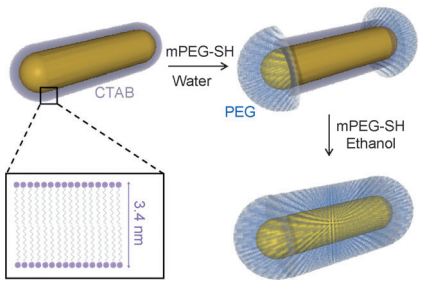
Synthetic Methods

Highly versatile: Allylic alcohols represent an important class of chiral building blocks for organic synthesis. This Review addresses the plethora of methods developed for the catalytic asymmetric synthesis of enantioenriched allylic alcohols and their many applications in further synthesis, including of natural products.



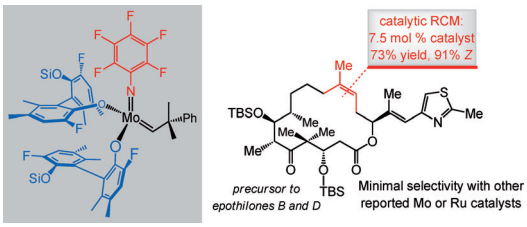
Communications

Bio-Nanomaterials



Surface functionalization: Complete detoxification of gold nanorods was achieved by manipulating the position in the stability map between surface-adsorbing polyethylene glycol (PEG) and destabilizing ethanol (see picture). This robust procedure complements studies related to the effects of shape when contemplating the nanoparticle–cell interaction.

Ring-Closing Metathesis



Olefin metathesis catalysts for controlling the formation of trisubstituted macrocyclic *Z* alkenes have been developed. The most effective complexes are Mo alkylidenes with a pentafluorophenylimido group and two large aryloxide ligands. The macrocyclic lactone precursor to anticancer agents epothilones B and D is obtained in 73% yield and 91% *Z* selectivity in less than 6 hours at room temperature.

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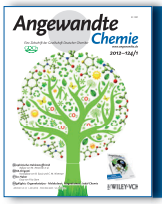

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Roald Hoffmann (Nobel Prize 1981)

Susumu Kitagawa

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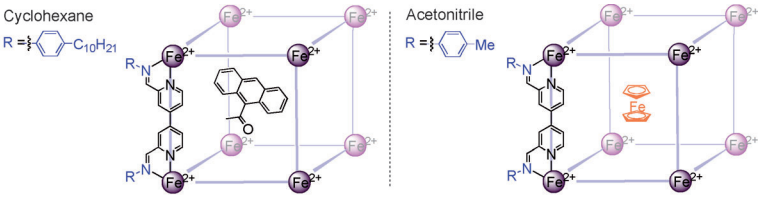
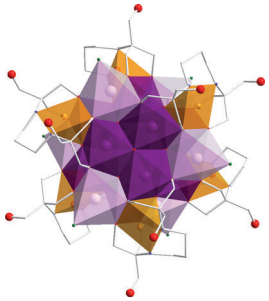


Cubes: The rational design of a simple set of organic subcomponents led to the formation of a $M_8L_{12}^{16+}$ cubic capsule upon their self-assembly with Fe^{II} ions. By altering the length of alkyl chains on these subcomponents, the solubility of the assembled structures was greatly increased in apolar solvents, such as cyclohexane, and the structures displayed solvent-dependent host–guest interactions.

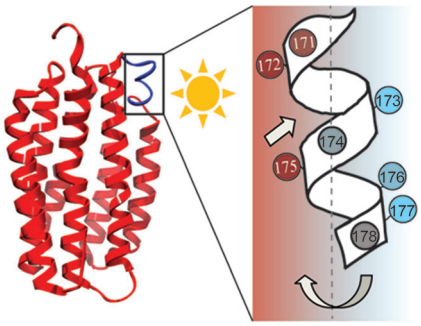
Supramolecular Chemistry

A two-step method for the directed synthesis of high-nuclearity Mn^{III}-Mn^{II}-Cu^{II} heterometallic transition metal complexes is described. The synthesis starts from a preformed copper(II) complex to trap an inner hexacapped cuboctahedral manganese oxide core.

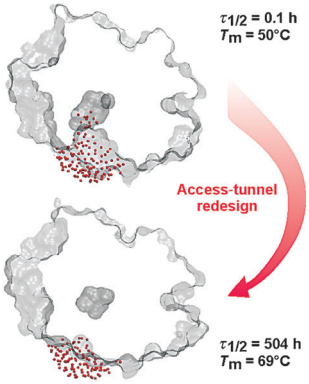


Heterometallic Complexes

Proteins on film: The Overhauser dynamic nuclear polarization method resolves hydration dynamics to an unprecedented level of detail for a transmembrane protein surface. The heterogeneous hydration landscape of proteorhodopsin rearranges upon photoactivation (see picture), thus providing an insight into how water contributes to protein function even for biological systems embedded in a hydrophobic membrane.



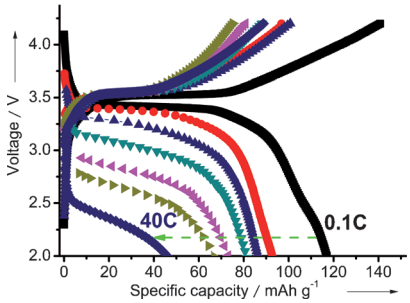
Membrane Protein Activation



Mutations targeting as few as four residues lining the access tunnel extended the half-life of an enzyme in 40% dimethyl sulfoxide from minutes to weeks and increased its melting temperature by 19°C. Protein crystallography and molecular dynamics revealed that the tunnel residue packing is a key determinant of protein stability and the active-site accessibility for cosolvent molecules (red dots).

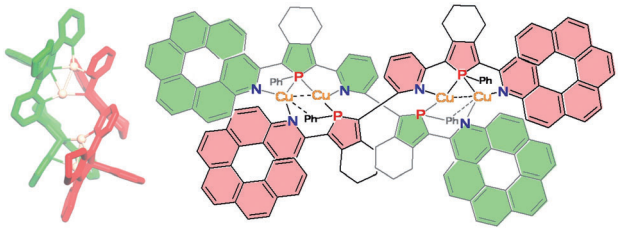
Protein Stability

Sodium-Ion Batteries



Sodium manganese hexacyanoferrates (NMHFCs) synthesized in aqueous solution at room temperature show high reversible capacity and outstanding rate capability as cathodes for a rechargeable sodium-ion battery (SIB). Earth-abundant elements and a low-cost synthesis route make these NMHFCs promising cathodes for SIBs, independent of natural lithium sources.

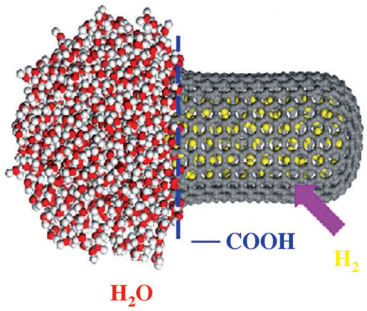
Supramolecular Helices



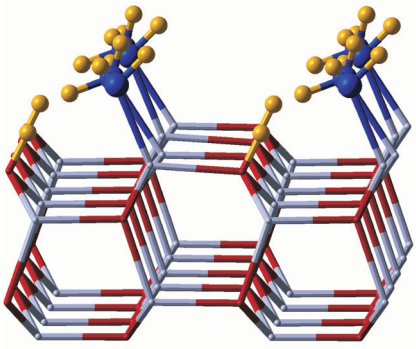
Combining helicate and helicene chemistry: Pentadentate phosphole-pyridine helicands (see scheme) coordinated to Cu^{I} or Ag^{I} centers afford configurationally stable double-stranded helicates bearing multiple bridging-phosphane coordination modes. Similarly enantiomerically pure helicene-grafted helicands afford enantiopure helicates.

Molecular Dynamics

Carbon nanotubes: The end section of a carbon nanotube, cut by acid treatment, contains hydrophilic oxygen groups, around which water molecules can assemble to block the entry of the tube. Hydrogen of pressures up to 10000 bar can be locked inside the tube by such an "aqueous valve" (see picture).

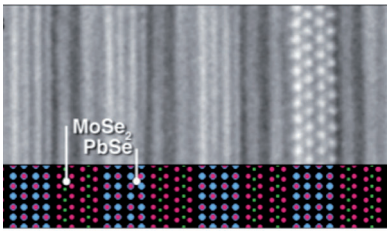


Surface Chemistry

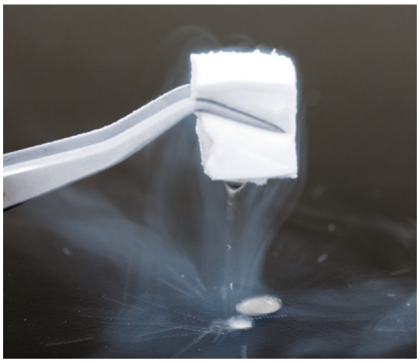


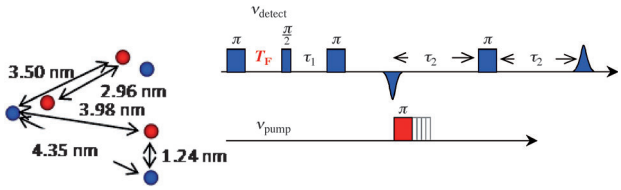
Deprotonating a base: High-resolution electron energy loss spectroscopy and ultrahigh-vacuum infrared spectroscopy have been used to determine that high surface coverage can induce proton transfer from adsorbed ammonia to surface oxygen atoms on both single crystals and nanoparticles of ZnO (see picture; Zn blue sticks, O red, N blue spheres, H yellow). These observations are supported by DFT calculations.

Inorganic nanocrystals: The structures of the compounds $[(PbSe)_{1.00}]_m(MoSe_2)_n$ and $[(PbSe)_{0.99}]_m(WSe_2)_n$ ($m \geq 1$ and $n \leq 5$) were investigated using X-ray diffraction and scanning transmission electron microscopy, which revealed a pairing distortion of the PbSe component that is dependent on m, the thickness of the PbSe layers, but independent of n, the thickness of the dichalcogenide.

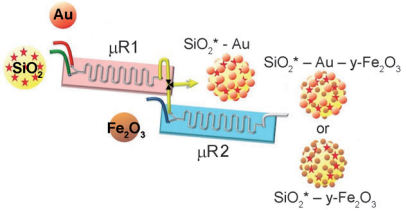


Soaking up s'more: Marshmallow-like flexible gels synthesized from organoalkoxysilanes by a facile process show superior oil/water separation properties. The gels are superhydrophobic and can be used to remove organic compounds from water through absorption; they can then be recovered by squeezing them out of the gel, as if it were a sponge. The gel retains flexibility over a wide temperature range, even in liquid nitrogen (see photo).



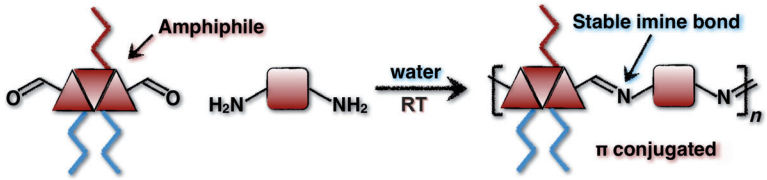


A new pulse sequence: The distances between copper sites of the homotrimeric Cu-containing nitrite reductase were determined by EPR spectroscopy (see picture). By exploiting the differences in the electron spin relaxation of the Cu ions, a filtering technique allows the selective removal of distances from a complex distance distribution. This filter technique combined with the PELDOR experiment promises to be useful for distance mapping by EPR spectroscopy.



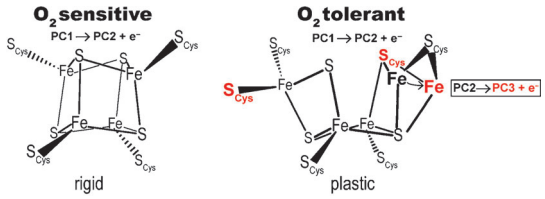
Lab-on-a-particle: Fluorescent, plasmonic, and magnetic SiO_2*-Au-γ-Fe_2O_3 nanostructures were assembled under continuous flow using two microfluidic devices (μR1 and μR2) connected in series. After assembling the SiO_2*-Au nanostructures by electrostatic interactions, γ-Fe_2O_3 nanoparticles were attached to the structures (see picture).

Self-Assembly



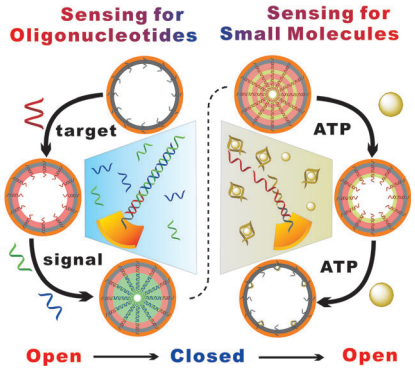
Come together: Self-assembly can drive the formation of conjugated imine polymers in water, and stabilization of otherwise unstable imine bonds is used to obtain fully π-conjugated, responsive dynamic covalent polyimines in aqueous environments. Both the optical properties and the aggregate morphology can be tuned by varying the aromatic monomers.

Hydrogenases



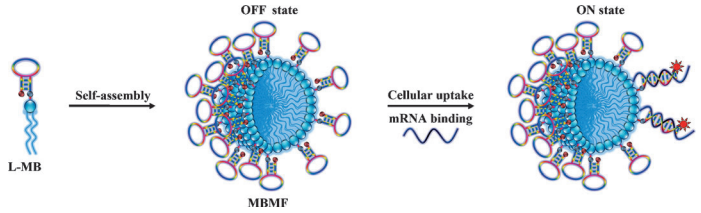
The main difference between O_2-sensitive and O_2-tolerant [NiFe] hydrogenases is the plasticity of the proximal [4Fe3S] cluster in the latter hydrogenase (see scheme). Deprotonation of a conserved glutamate residue initiates the movement of the iron atom, resulting in its binding to the amide nitrogen atom of one of the two supernumerary cysteine ligands and superoxidation of the proximal cluster.

Nanomaterials



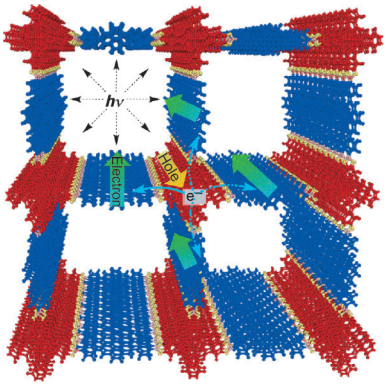
Pore me another one: Sub-nanomolar sequence-specific DNA detection and sub-micromolar small-molecule (ATP) detection was shown by way of self-assembly and disassembly of DNA superstructures within solid-state nanopores (see scheme). These DNA structures provide a built-in amplification mechanism to increase the signal strength and sensitivity. This sensor was also shown to work within complex mixtures, such as mammalian serum.

Molecular Beacons



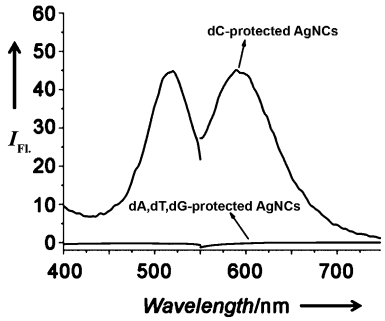
Lighting the way with DNA: Molecular beacon micelle flares (MBMFs), based on self-assembly of diacyllipid–molecular-beacon conjugates (L-MBs; see figure), have been developed for combined mRNA detection and gene therapy. These MBMFs were shown to inhibit a model gene in vitro and decrease the viability of cancer cells in culture.

Light works: Mechanistic insights into the photochemical events and charge dynamics of a donor–acceptor covalent organic framework were given by time-resolved transient absorption spectroscopy and time-resolved electron spin resonance spectroscopy (see picture). The organic framework triggers ultrafast electron transfer and enables long-distance charge delocalization and exceptional long-term charge separation.

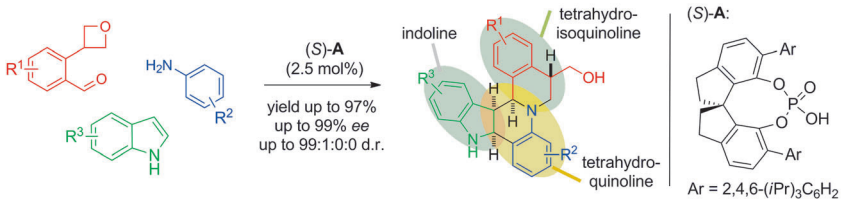


Electron Transfer

Basic evidence is provided for the benefits of using cytosine-rich DNA strands as scaffolds for fluorescent silver nanoclusters. The DFT-calculated fluorescence spectra of silver nanoclusters (AgNCs) protected by DNA monomers (dC, dA, dT, and dG) were in good agreement with the experimentally obtained spectra (see picture), showing that only the use of cytosine-rich DNA strands as scaffolds gives fluorescent nanoclusters.

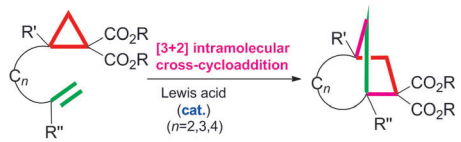


Nanotechnology



Starting from three achiral compounds, the title reaction provides rapid access to a variety of molecules that contain indoline, tetrahydroquinoline, and tetrahydroisoquinoline moieties (see scheme). The process features the efficient formation of multiple new bonds and chiral centers, excellent stereoselectivity, oxetane desymmetrization, and easy product purification through filtration.

Synthetic Methods

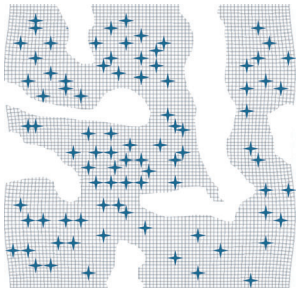


Carbon bridges: The title reaction has been successfully developed, and applied to the total synthesis of the tetracyclic diterpenoids phyllocladanol and phyllocladene. The method provides an efficient, general, and conceptually new strategy for the construction of structurally complex and diverse [*n*.2.1] carbocyclic skeletons (see scheme).

Synthetic Methodology

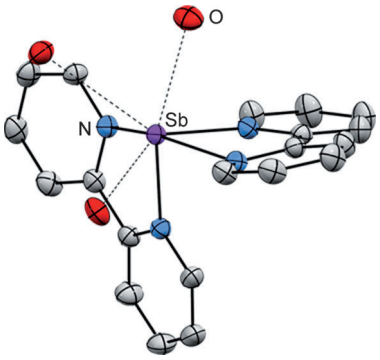
Microporous Materials

Shape-selective reactions: Highly selective catalysts are obtained by alkaline and subsequent acid leaching of conventionally prepared zeolites. Active sites that are located in the shape-selective environment of micropores and accessible through mesopores (see picture) provide high selectivity and activity in acid-catalyzed reactions.

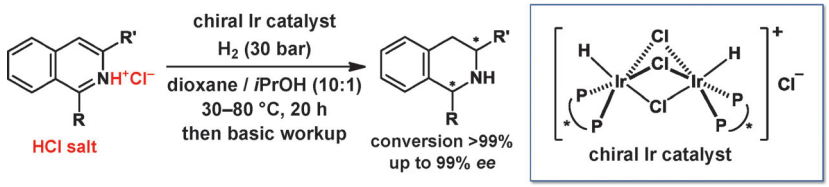


Main-Group Elements

Gas driven: A high-yield approach to sequential fluoride ion abstraction from SbF_3 in the presence of 2,2′-bipyridine gives a series of complexes containing $[SbF_2]^+$, $[SbF]^{2+}$, and $[Sb]^{3+}$ (see figure) acceptors. The thermodynamically favorable rapid elimination of gaseous Me_3SiF provides a potentially general approach to enhance the Lewis acidity and coordination chemistry of p-block centers.



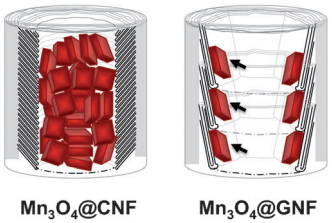
Asymmetric Synthesis

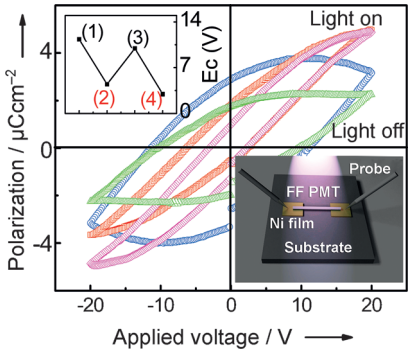


The salt makes the difference: In the presence of a chiral iridium catalyst, 1- and 3-substituted as well as 1,3-disubstituted isoquinolinium salts can be hydrogenated, giving the corresponding 1,2,3,4-tetrahydroisoquinolines in high enantiomeric excess after a basic workup (see scheme). This protocol is applicable to the synthesis of the prescription drug solifenacin.

Carbon Materials

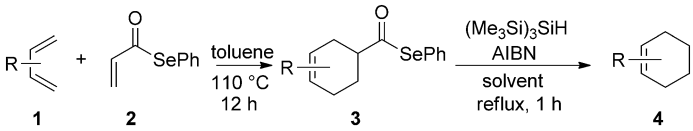
Effects of confinement: Magnetic nanoparticles are encapsulated within hollow carbon nanofibers. The density and orientation of the guest Mn_3O_4 nanoparticles depend crucially on the internal structure of the host carbon nanocontainer, which enables tuning functional magnetic properties of the composite material.





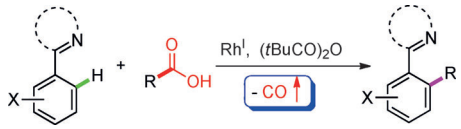
Spontaneous polarization reversal: Saturated polarization–electric field loops with a concave region were obtained from diphenylalanine peptide microtubes (FF PMTs) by combining the action of light during the hysteresis loop measurements (see picture; Ec = coercive field). The existence of ferroelectricity in FF peptide nanostructures was shown experimentally. The ferroelectricity of the FF PMTs is expected to extend their applications to biomedicine and microelectronics.

Ferroelectric Materials



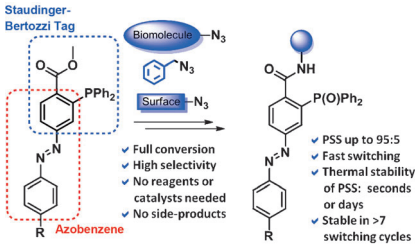
Reactive: *Se*-phenyl prop-2-eneselenoate (phenyl selenoacrylate) **2**, readily prepared from acryloyl chloride, is a very reactive dienophile in Diels–Alder reactions, and more reactive than acrylates. Its cycloadducts **3** with many dienes **1** can be easily reduced to the hydrocarbons **4** under radical conditions. This process works even in cases where there is an adjacent group that can be easily eliminated, e.g., an allylic ether.

Synthetic Methods



Marked absent: The pseudo-oxidative decarboxylative coupling of carboxylic acids and arenes using rhodium(I) in the absence of an oxidant is described. The study offers a new convenient method for the construction of C_{sp^2}–C_{sp^2}/C_{sp^3} bonds.

C–H Activation

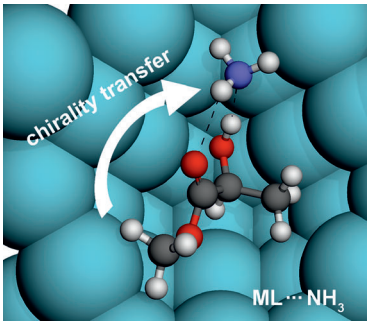


Click to switch: A novel family of azobenzenes containing residues needed for aqueous Staudinger–Bertozzi ligation to azides was designed (see scheme). The resulting photochromes show stable and reversible switching behavior in water, with a photostationary state (PSS) of up to 95:5 *cis/trans*. Applications in model systems include the modification of azide-bearing surfaces and proteins.

Photochromism

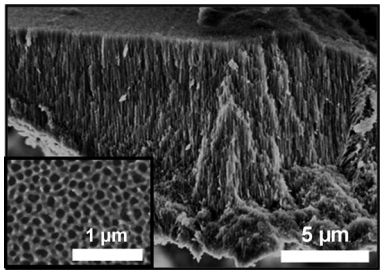
Chirality Transfer

Hand-me-down chirality: Chirality transfer from methyl lactate to ammonia has been investigated and the mirror-imaged vibrational circular dichroism (VCD) spectra of a pair of enantiomers of a flexible chiral molecular complex are presented. The distinct VCD spectral pattern provides decisive evidence for the existence of two dominant and subtly different conformers of the complex.

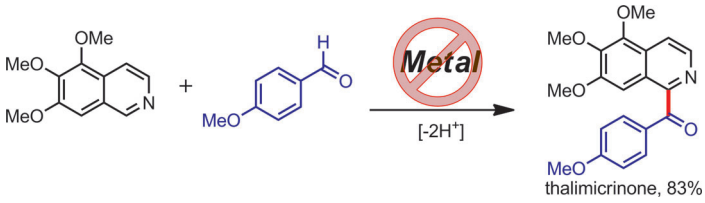


Electrochemistry

Nanoporous materials: High-aspect-ratio, ordered porous Co_3O_4 layers were formed by self-organizing anodization of a cobalt substrate and subsequent annealing. The key for successful formation of such layers is to sufficiently suppress competing oxygen evolution during anodization. The aligned Co_3O_4 channel layers behave as a highly efficient water oxidation catalyst (see picture).



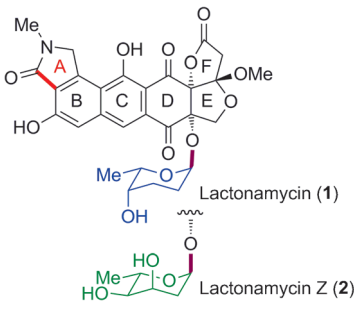
C–H Functionalization

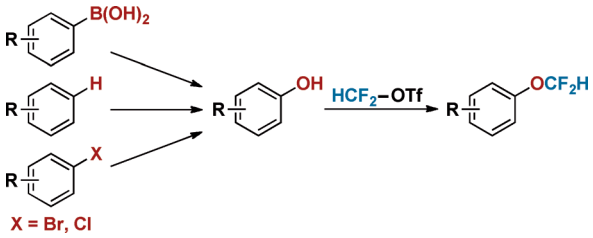


A range of heterocyclic compounds were synthesized by a novel, metal-free cross-dehydrogenative coupling between heterocycles and aldehydes under mild reaction conditions that are not sensitive to moisture. The products are formed smoothly and regioselectively at room temperature by a hypervalent iodine mediated transformation. This method has a broad substrate scope and was used in the highly efficient, one-step synthesis of natural products.

Natural Product Synthesis

The highly oxygenated polyketide antibiotics, lactonamycin and lactonamycin Z were synthesized. The BCDEF ring system was constructed by a cycloaddition and a palladium-catalyzed cyclization and a Bischler–Napieralski-type cyclization was used for the formation of the A ring. The glycosylation of the aglycon with the appropriate sugar gave lactonamycin and lactonamycin Z.

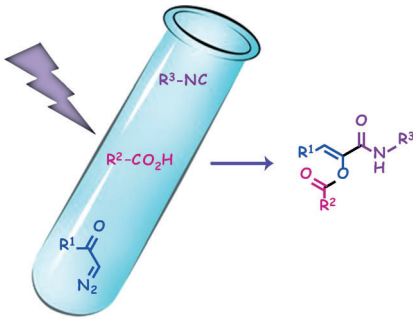




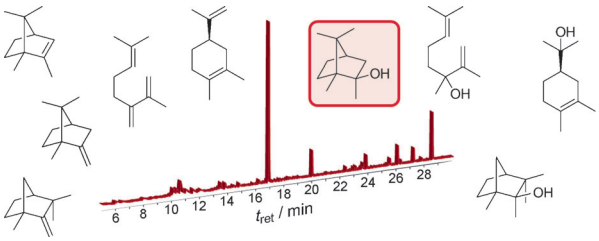
The difluoromethylation of phenols with a simple, non-ozone-depleting reagent is described. The reaction occurs within minutes at room temperature with exceptional functional-group tolerance, which makes possible tandem processes for the conversion of arylboronic acids, aryl halides, and arenes to difluoromethyl ethers.

Difluoromethylation

Three in the spotlight: Irradiation promotes a general, three-component reaction between diazoketones, carboxylic acids, and isocyanides. The highly functionalized captodative olefin products of this reaction are versatile synthons for organic synthesis.

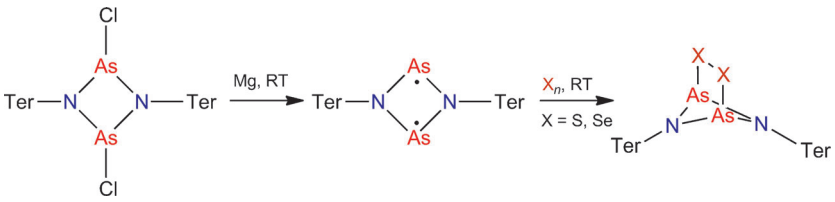


Synthetic Methods



Odor of earth: Several homomonoterpenes were identified in actinomycetes that produce 2-methylisoborneol (2-MIB, see scheme, which is responsible for an earthy odor in drinking water). Their occurrence clarifies the 2-MIB pathway, because they are derived from cationic intermediates that are otherwise difficult to detect. A highly sensitive method using feeding experiments with ^{13}C-labeled precursors gives detailed insights into 2-MIB biosynthesis.

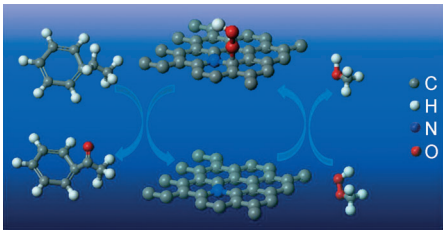
Terpene Biosynthesis



As you like it: The first reported four-membered heterocycle $[As(\mu\text{-NTer})]_2$, which can be referred to as a high-temperature stable biradicaloid, is formed, when a bulky substituent, such as the terphenyl group, prevents dimerization. Addition reactions of elemental sulfur and selenium (see scheme) as well as the double bond of CS_2 demonstrate that $[As(\mu\text{-NTer})]_2$ has radical-type behavior.

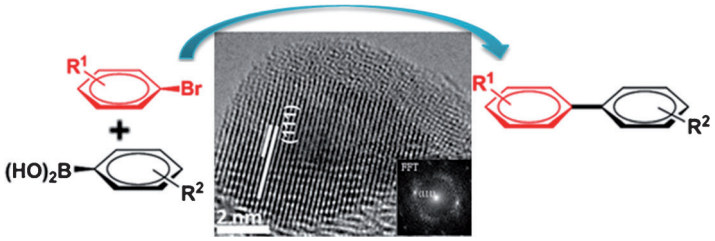
Biradicaloids

Heterogeneous Catalysis



Thanks to nitrogen introduced into the layered carbon framework of graphite, the chemical reactivity of the carbon atoms was increased. N-doped graphitic catalysts generate reactive oxygen species and display excellent activity for hydrocarbon activation even at room temperature.

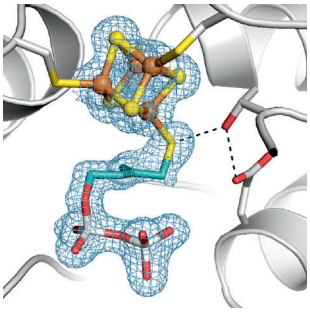
Surface Catalysis



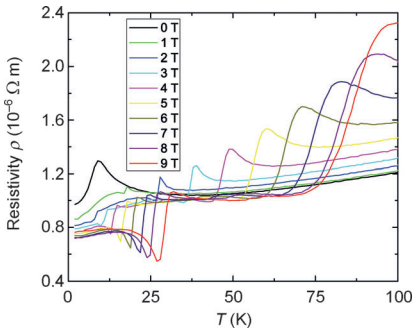
More than scratching the surface: The mechanism by which supported Pd nanoparticles (PdNPs) catalyze cross-coupling reactions is the subject of debate. The changes in supported PdNPs during coupling reactions are studied by exploiting modified carbon nanotubes (CNTs) as support materials. After catalysis, CNTs with scratched walls and PdNPs with surface crystalline distortions were discovered, offering insights into the catalytic mechanism.

Biosynthesis

The iron–sulfur protein IspH catalyzes a key step in isoprenoid biosynthesis in bacteria and malaria parasites. Crystal structures of IspH complexed with three substrate analogues reveal their mode of binding and suggest new routes to inhibitor design.



Magnetic Zintl Phases



Watch the signs! The new Zintl phase $Eu_{5+x}Mg_{18-x}Si_{13}$ ($x = 2.2$) displays a negative as well as a positive magnetoresistive effect depending on the temperature. The maximal value of the magnetoresistivity of 92% occurs at 100 K and 9 T (see plot).

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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