VIP *The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:*

Author Profile

„In a spare hour I would like to run at sunset or sunrise. The biggest challenge facing scientists is to keep their autonomy and independence and preserve spare time for creativity. …"
This and more about Andreas Kirschning can be found on page 10488.

News

D. Shechtman

Books

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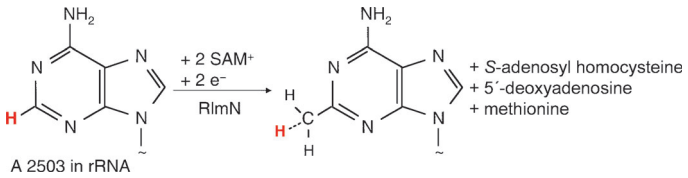
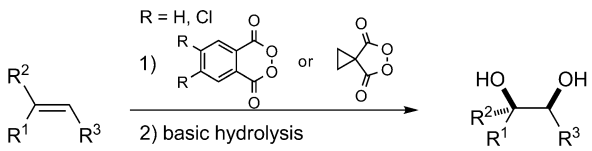
Highlights

Enzymatic C-Methylation



A surprising mechanism: The enzymatic methylation of adenosine at C-2 consumes two molecules of *S*-adenosylmethionine (SAM^+), one in the S_N2 transfer of its methyl group to an active-site cysteine of the methyltransferase, and a second in the formation of a 5′-deoxyadenosine radical (5′-A•) that abstracts a hydrogen atom from the protein-bound methyl group enabling it to attack at C-2 of the adenosine (see scheme).

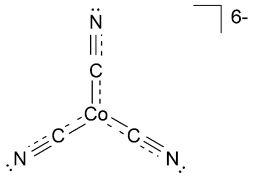
Alkene Dihydroxylation



Dihydroxylation with peroxides: The 1,2-dihydroxy structural motif, which can be generated from a C=C bond, occurs widely in organic compounds. Advances in the *syn* dihydroxylation of alkenes with cyclic acyl peroxides broaden the application of this transformation for a variety of olefins (see scheme). In recent studies the scope, limitations, and a mechanistic pathway have been delineated.

Small Molecules

More than three centuries after its inadvertent preparation in a coordination compound, the noninnocence of cyanide has been established unequivocally by structural and spectroscopic studies of $M_3[Co(CN)_3]$, M = Ba or Sr. The 18-valence-electron ion $[Co(CN)_3]^{6-}$ contains a closed-shell Co^{-I} center and three $CN^{1.67-}$ ligands (see scheme).



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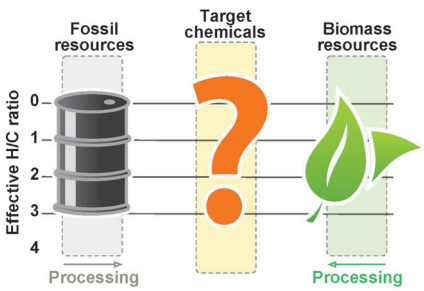
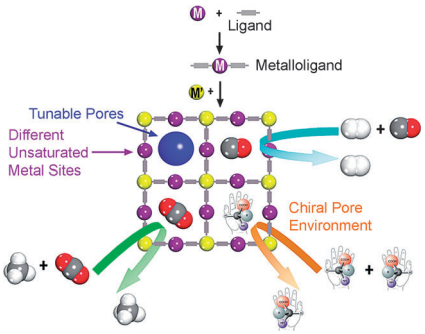
Essays

From petroleum to bioleum: Since biomass is a limited resource, it is necessary to consider its best use. The production of select chemicals from biomass, rather than its use as fuel, could effectively replace the use of petroleum in the chemical industry, but the inherent functionality of biomass must be exploited (see picture).



Renewable Resources

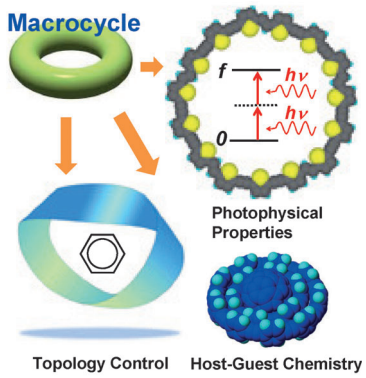
Minireviews



Metal mixer: A novel metalloligand approach allows the rational immobilization of a variety of functional sites in mixed metal–organic frameworks (M′MOFs). This Minireview highlights some important functional M′MOFs with metalloligands for gas storage and separation, enantioselective separation, heterogeneous asymmetric catalysis, sensing, drug delivery, and biomedical imaging.

Metal–Organic Frameworks

Reviews



Going in giant circles: Fully unsaturated macrocycles exhibit unusual optical and magnetic behavior because of their effective cyclic conjugation. In particular, site-specific substitution at interior and exterior sites can afford attractive structures for a wide range of research fields such as organic chemistry, polymer and materials science, and supramolecular chemistry.

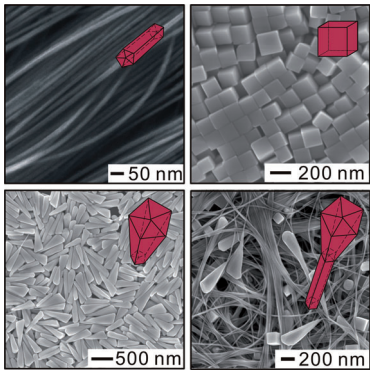
Conjugated Macrocycles

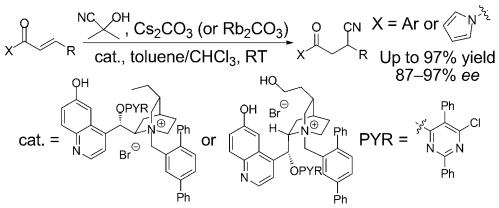
Contents

Communications

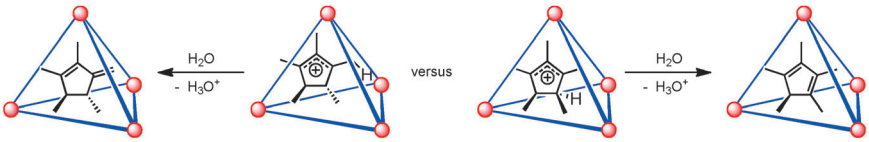
A simple screening method: Phase segregation and domain formation is observed within the protecting monolayer of gold nanoparticles (AuNPs) using ion mobility mass spectrometry (IM-MS), a two-dimensional gas-phase separation technique. Experimental data are compared to a theoretical model. Deviations from this model provide evidence for nanophase separation resulting in anisotropic AuNPs.

Shape up: Copper nanocrystals with different shapes enclosed mainly by {100} facets have been prepared by reducing $CuCl_2$ with glucose. The syntheses were preformed in an aqueous solution at 100 °C with the use of hexadecylamine as a capping agent (see scheme).

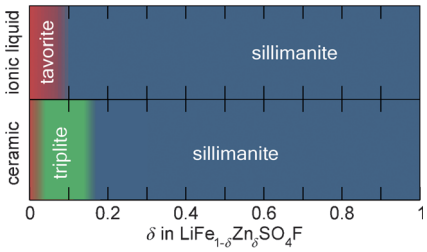




Unprecedented phase-transfer catalysts for the first example of an organocatalytic asymmetric conjugate addition of cyanide with acetone cyanohydrin are reported (see scheme). Utilizing an accessible cupreidinium salt and a cyanation reagent suitable for industrial scale, this reaction holds significant promise for practical asymmetric synthesis. The catalysts were developed as a result of key structural insights gained by X-ray analysis.

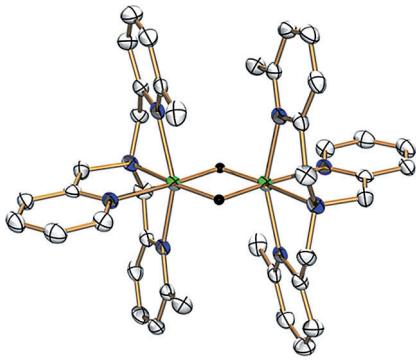


The kinetically controlled, regioselective deprotonation of cyclopentenyl cations is mediated by encapsulation within a metal–ligand assembly. The regiochemistry of the deprotonation step determines which one of two possible products is formed. Moreover, subtle differences in the stereochemistry of the encapsulated cation switch the selectivity of this process (see scheme).



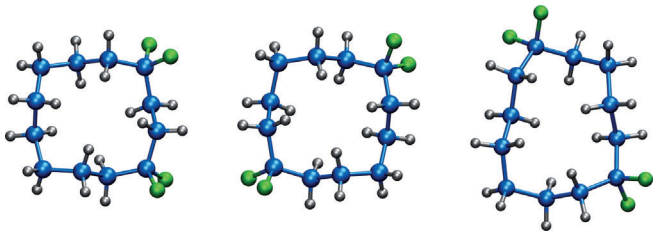
Transition-metal fluorosulfates are currently under intense investigation for their use as anodes in Li-ion batteries. The substitution of Zn into $LiFeSO_4F$ has been found to trigger a transition from the tavorite structure to two separate polymorphs which crystallize in the sillimanite and triplite structures (see picture). These new phases show Fe^{2+}/Fe^{3+} redox potentials of 3.6 and 3.9 V versus Li, respectively.

Solid-State Chemistry



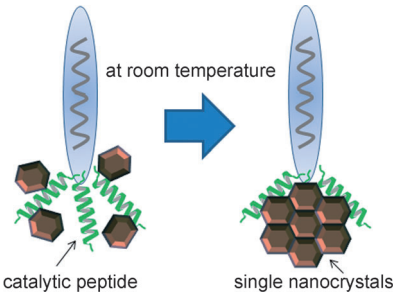
A generous donor: A dinuclear octahedral bis(μ-hydrido)dinickel(II) complex (see picture; C gray, H black, N blue, Ni green) acts as an electron donor to reduce electron acceptors such as methyl viologen. The complex is proposed as a functional model for the dihydride intermediate of an NiRu hydrogenase mimic and, by extension, of [NiFe]hydrogenase itself.

Hydrogenase Mimics



Getting out of the way: In fluorinated cyclododecane structures the CF_2 group locates only at corner positions (see picture). This relaxes 1,4-H,H transannular interactions as a result of C-CF_2-C angle widening. Misplaced CF_2 groups lead to significant ring distortion. It follows that strategic incorporation of CF_2 groups has potential as a design feature to introduce order and polarity into organic hydrocarbon structures.

Organofluorine Chemistry



Screen saver: A simple and convenient route has been developed that allows peptides that catalyze the growth of the target material to be screened directly. This approach has been used to identify a peptide that induces the catalytic growth of single-crystalline ZnO nanocrystals through a nonclassical crystallization process at room temperature (see picture).

Bioinorganic Chemistry

Contents

Nanocrystal Imaging Agents

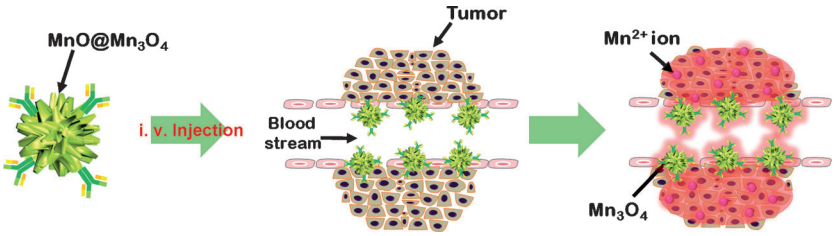
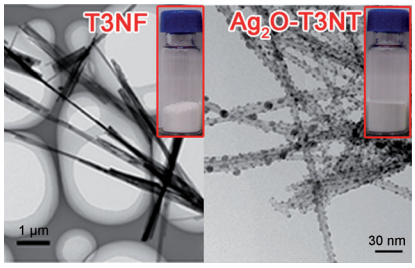


Image enhancement: Core–shell $MnO@Mn_3O_4$ urchin-shaped nanoparticles can be synthesized by means of an anisotropic etching process and used as a pH-activatable T_1 contrast agent for magnetic resonance imaging. The manganese ions released from the MnO phase in the low-pH sites within tumor cells lead to an enhanced T_1 contrast image for the entire tumor mass.

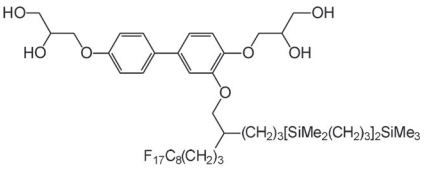
Nanostructures

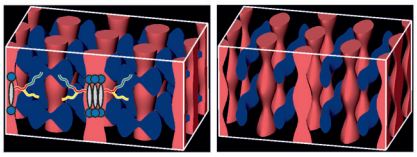


Going down the tubes: The rapid uptake of $^{137}Cs^+$ ions in sodium trititanate nanofibers (T3NF; see picture) and nanotubes (T3NT) triggers a phase transition or deformation of the thin titanate layers. Ag_2O nanocrystals (5–10 nm) were bound to the surface of the nanostructures and efficiently captured I^- anions (ca. 4.5 mmol per gram of sorbent) from aqueous solutions by forming an AgI precipitate on the titanates.

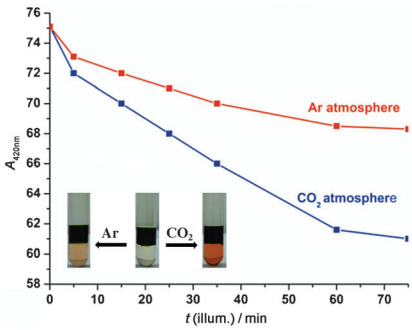
Liquid Crystals

Pleated ribbons and bow ties: Rodlike mesogens (see scheme) with swallow-tail side chains arrange axially in ribbonlike bundles. At high temperatures the ribbons rotate, resulting in a novel 3D hexagonal liquid-crystal phase (see picture, left). At lower temperature, rotation locks in giving a structure of crossed aromatic and fluorinated columns (right). On further cooling the ribbons fuse into aromatic sheets with fluorinated columns intercalated.

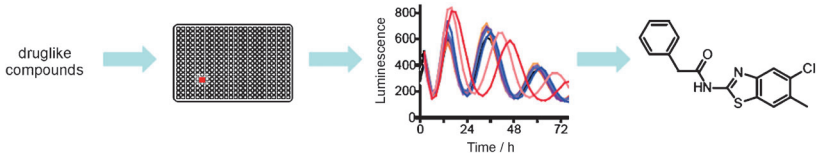




Photosynthesis



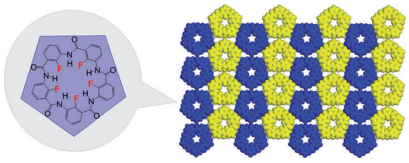
Light to chemical energy: Magnesium tetraphenylporphyrin (MgTPP; **1**), upon treatment with $[Bu_4N]OH$ under a CO_2 atmosphere, formed its bicarbonate adduct, $[Bu_4N][HCO_3MgTPP]$ (**2**). Compound **2** is electrochemically oxidized at a lower potential than that of **1**; under light illumination, it drops to an even lower value, resulting in a more facile electron release (see picture).



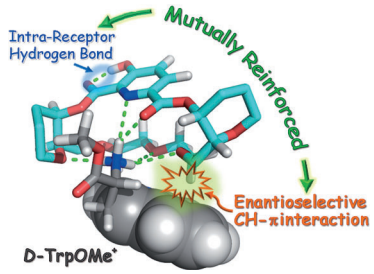
Chemical Biology

Time shift: A high-throughput cell-based screen identified a benzothiazole analogue, LH846, which induces period lengthening of the circadian rhythm. Affinity chromatography coupled with mass spectrometry and genomic analysis identified protein kinase CKIδ as the biological target of LH846 (see picture).

Regular pentagonal adhesive tiles were obtained by designing a cyclic fluoropentamer with an internal CF···HN H-bonded network and "sticky" edges that can glue the molecules together through intermolecular $C_{Ar}H$···O=C H bonds. In the crystal they form the mathematically predicted densest all-pentagon 2D lattice with a packing density of 0.921 (see picture).



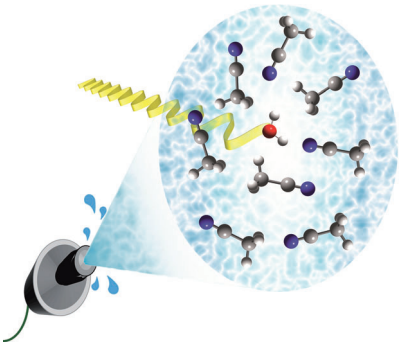
2D Pentagon Packing



Call in the reinforcements: Intra-receptor noncovalent interactions can enantioselectively cooperate with guest binding, thus triggering chiral discrimination. Such cooperativity is described and quantified for a simple synthetic system wherein an intra-receptor hydrogen bond cooperates with a CH–π interaction exclusively formed with the D enantiomer of the guest, thus exemplifying reinforced chiral recognition (see picture).

Molecular Recognition

A liquid microjet was used to obtain oxygen K-edge X-ray absorption and emission spectra of water–acetonitrile mixtures of various compositions. The observed spectral changes are unambiguously related to the increasing number of broken hydrogen bonds with decreasing water concentration, and the hydrogen-bond network of liquid water can thus be addressed on purely experimental grounds without the need for theoretical modeling.



Hydrogen Bonds

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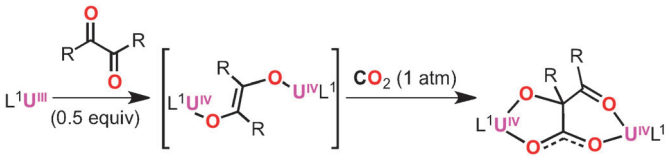
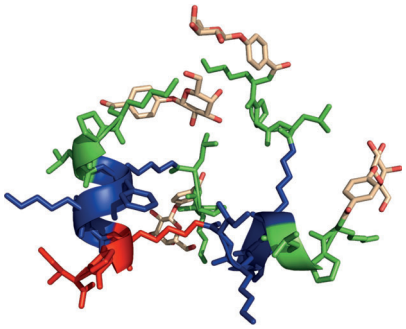
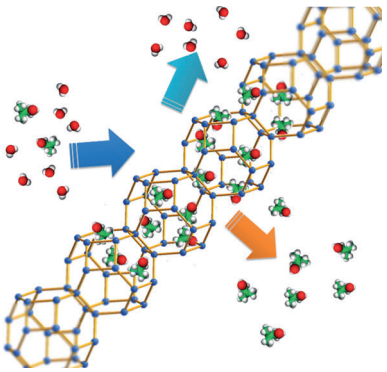


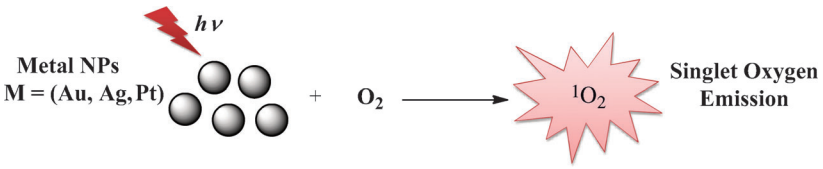
Quick on the uptake: Uranium(III) complexes bearing hexadentate triazacyclononane macrocyclic ligands L^1 engage di- and triketones in both one- and two-electron reduction pathways. The dinuclear enolate generated through one of these pathways reacts with carbon dioxide to generate a new C–C bond (see scheme).



Inhibiting factors: Biofilm inhibition is achieved with a phenylgalactosyl peptide dendrimer (see picture) that binds to the galactose-specific lectin LecA of *P. aeruginosa*. The multivalency of the ligands is critical for biofilm inhibition, although the nature of the linker between the peptide dendrimer and the galactose can provide additional contacts to the lectin and also has an effect on the interaction.

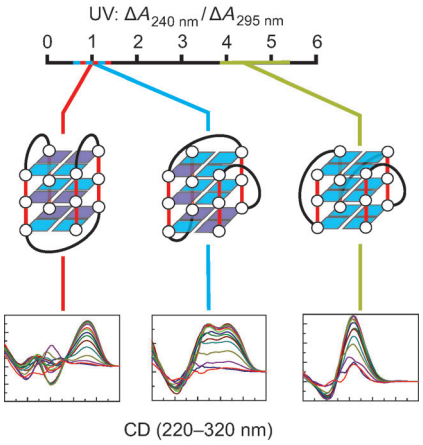
On the road to recovery: The dynamic apertures and superhydrophobic surfaces of the metal–organic framework ZIF-8 result in its extraordinary ability to selectively adsorb alcohols. When incorporated into a polymer matrix, the ZIF-8 nanoparticles provide preferential pathways for the permeation of organic compounds and allow the efficient pervaporative recovery of bio-alcohols from fermentation broths (see picture).



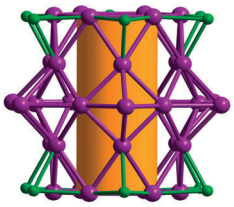


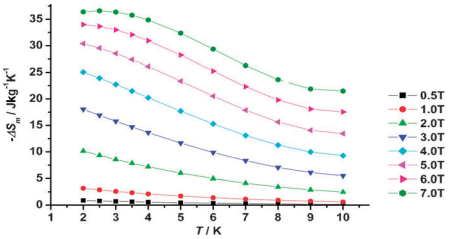
Improving on organic photosensitizers: The photoexcitation of metal nanoparticles results in the formation of singlet oxygen and its phosphorescence emission (see picture). As the nanoparticles are resistant to both photoinduced and enzymatic degradation and also have impressively high extinction coefficients, these findings may have an impact on techniques for the generation of singlet oxygen in biological settings.

Four-fold: Not just the identification, but also the rapid characterization and classification of nucleic acid G-quadruplexes into topology groups is feasible utilizing UV and circular dichroism (CD) spectroscopy (see picture). It is now possible to utilize inexpensive UV spectroscopy to achieve the same level of characterization previously only possible with CD spectroscopy.



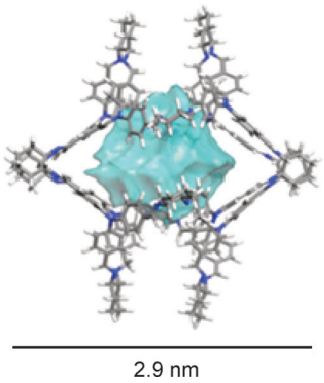
Quadruplex Topologies





A tubelike metal cluster containing 36 Gd and 12 Ni atoms was obtained by anion-templated self-assembly of the metal ions (see picture for arrangement of the 48 metal ions in the cluster core). The huge cryogenic magnetocaloric effects exhibited by this cluster (see plot of magnetic entropy change ΔS_m) can be rationalized in terms of its large metal/ligand mass ratio.

Magnetocaloric Effect



Keep the cage filled: Two large organic cages (see example) with void diameters of 1.2 nm were synthesized through [8+12] imine condensation reactions. The materials become amorphous upon solvent removal and show little permanent porosity. Molecular dynamics simulations give an insight into the mechanism of these processes, suggesting strategies for synthesizing larger shape-persistent organic cages in the future.

Organic cages

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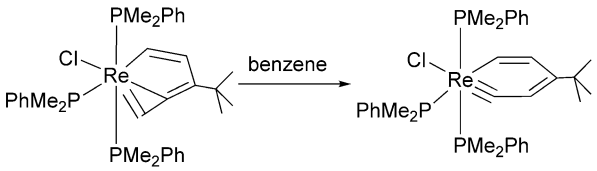
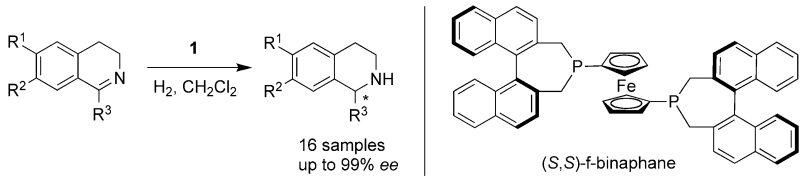


Complex rearrangements: Rhenabenzynes, which are metallaaromatic compounds related to metallabenzenes (see scheme), can be obtained from thermally unstable rhenium–carbyne complexes through rearrangement reactions. The rhenabenzyne complex was characterized by elemental analysis, ^{1}H NMR spectroscopy, and X-ray diffraction analysis. The results show that it is possible to prepare metallabenzynes with different transition metals.

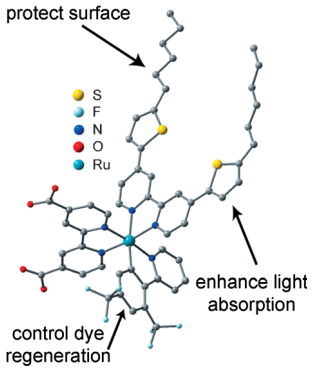
Metallacycles



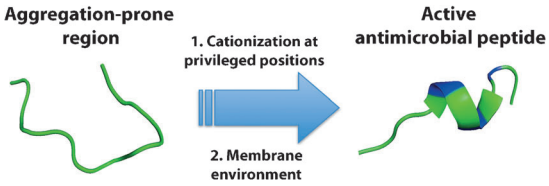
Efficient and enantioselective: Using the iodine-bridged dimeric iridium complex $[\{Ir(H)[(S,S)\text{-}(f)\text{-binaphane}]\}_2(\mu\text{-}I)_3]^+I^-$ (**1**) a wide range of tetrahydroisoquinoline alkaloids, including the substructure of the pharmaceutical drug solifenacin, were obtained with excellent enantioselectivities and high turnover numbers (see scheme).

Asymmetric Catalysis

A trisheteroleptic cyclometalated ruthenium complex (see picture) bearing aliphatic substituents was synthesized, characterized, and evaluated in a dye-sensitized solar cell (DSSC). This thiocyanate-free dye, which has favorable structural elements to exhibit long-term stability, generates a high power output in the DSSC with both iodide-based and Co-based redox shuttles.



Solar Cells

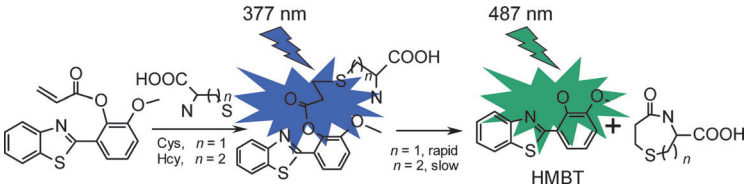


Action stations: Antimicrobial peptides (AMPs) can be derived from amyloid-prone regions by introduction of cationic residues at privileged positions (see picture). The design and testing of 24 de novo amyloid-derived AMPs are described, and the likelihood of evolution of amyloid-prone protein regions, devoid of antimicrobial activity, into potent antimicrobial domains is addressed.

Antimicrobial Peptides

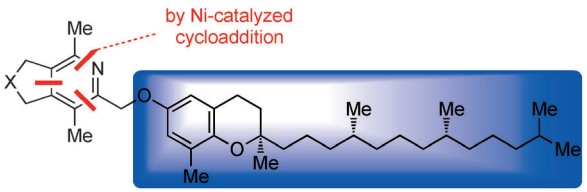
Contents

Fluorescent probes



Similar but different: A benzothiazole derivative can be used to detect cysteine (Cys) and homocysteine (Hcy) simultaneously in neutral media. The method involves thioether formation followed by cyclization to release 2-(2′-hydroxy-3′-methoxyphenyl)benzothiazole (HMBT) and a lactam. The differences in ring-formation kinetics allow spectral or kinetic modes to be used to identify Cys and Hcy.

Heterocycles

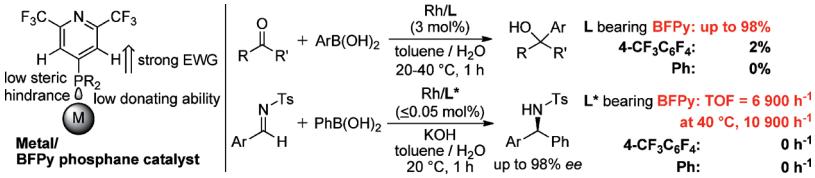


In the nick of time! The catalytic combination of $[Ni(cod)_2]$ (cod = 1,5-cyclooctadiene) and the ligand 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos) was used to access pyridines (see scheme). The reaction proceeds under ambient conditions to provide excellent yields of the products. Comparison of this catalyst with the other state-of-the-art catalysts is also provided.

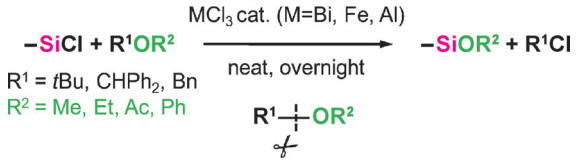
Enzymes

Fishing for a protein: An analogue of the appetite-stimulating hormone ghrelin containing a phosphonofluoridate moiety and a terminal alkyne functions as a probe to capture the protein α_2 macroglobulin (red; see picture). The extraction of the protein is highly selective and a previously undocumented catalytic activity of α_2 macroglobulin as a hydrolase for ghrelin has been identified.

P Ligands

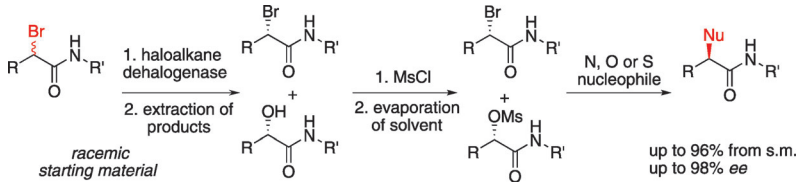


The poor will be rich: BFPy phosphanes (see scheme) mimic the electronic and steric characters of $P(C_6F_5)_3$ and PPh_3, respectively. These novel ligands showed a large ligand acceleration effect on Stille coupling, the Rh-catalyzed 1,2-addition of aryl boronic acid to unactivated ketones and the asymmetric arylation of *N*-tosylimine using phenylboronic acid.



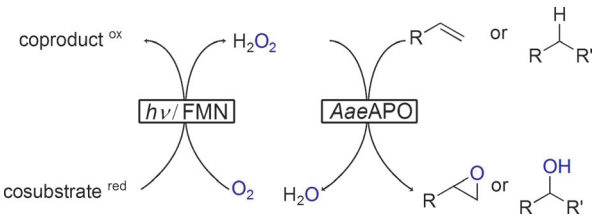
Alcohol-free: A versatile, efficient, and practical synthesis of alkoxysilanes without generation of HCl involves the reaction of chlorosilanes with unsymmetrical ethers in the presence of a Lewis acid (see scheme). The reaction proceeds through selective cleavage of C–O bonds and is superior to conventional processes. Industrially feasible reagents are used and only one by-product results.

Synthetic Methods



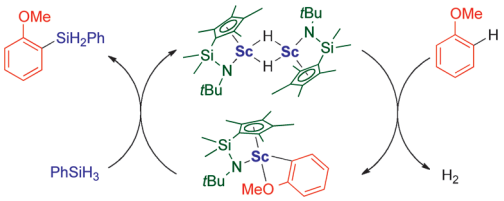
Simple and efficient: The combination of an enzymatic, enantioinverting reaction with simple follow-up processes allows the transformation of readily available racemic compounds into versatile chiral α-substituted amides (see picture; Ms = methanesulfonyl). These important building blocks are prepared in high overall yield and enantiomeric excess; the elimination of intermediate purification steps results in a time- and cost-efficient process.

Enantioconvergent Processes



Turn a light on: Enantiospecific hydroxylation of nonactivated C–H bonds as well as epoxidations of C=C bonds are reported using a novel peroxidase from *Agrocybe aegerita* (*Aae*APO). *Aae*APO represents a more active and more versatile alternative to the current gold standard, chloroperoxidase. H_2O_2 was produced in situ by photocatalytic reduction of O_2 using simple flavin adenine mononucleotide (FMN) catalysts.

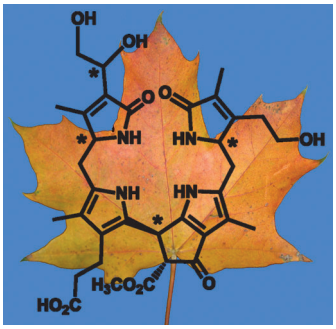
Biocatalysis



Regioselective, hydrogen-acceptor-free C–H bond silylation of anisoles or alkoxy-substituted benzenes with hydrosilanes was achieved by use of a half-sandwich scandium catalyst. The reaction proceeds through *ortho*-C–H activation of an anisole compound by a scandium hydride species followed by the silylation of the resulting scandium 2-anisyl species with a hydrosilane (see scheme).

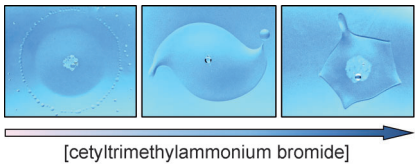
C–H Silylation

Contents



A colorless chlorophyll catabolite was found in senescent leaves of Norway maple, a widespread deciduous tree. This compound is a dioxobilane, a "linear" tetrapyrrole, in which one *meso* carbon of the macrocycle of the hypothetical chlorophyll precursor has been lost. The configuration of this catabolite suggests a path of chlorophyll breakdown in Norway maple that diverges from that found in senescent leaves of other higher plants.

Generation of cohesive motion was observed during the dissolution of mm-sized drops of dicholoromethane into aqueous surfactant solutions. This system shows pulsating drops, multi-armed rotors, and polygonal shapes. The sharp tips of these patterns eject much smaller droplets to form expanding halos or swirling chains. The daughter droplets also undergo cascades of secondary and higher-order splitting events.



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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