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

"Three qualities that make a good scientist are curiosity, creativity, and a very critical mind. My favorite subjects at school were art and natural sciences …"
This and more about Bernhard Kräutler can be found on page 7620.

News

C. Cummins

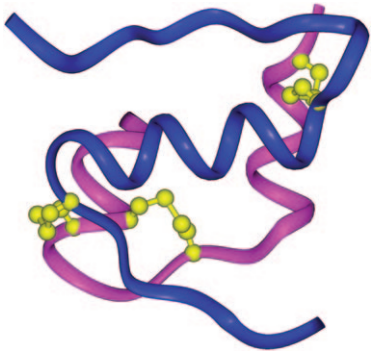
K. Suzuki

E. N. Jacobsen

Books

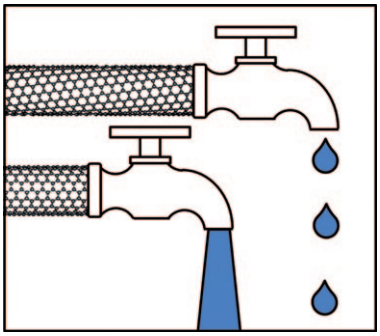
Contents

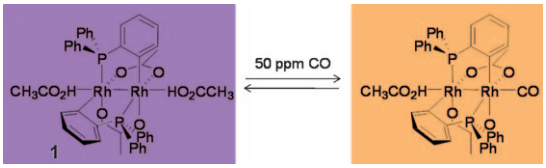
Highlights



Coupled chains: A fully synthetic single-chain branched depsipeptide precursor lacking a proinsulin-like tethering of the A and B chains leads, by oxidative folding to the insulin characteristic cystine topology and by subsequent saponification of the ester bond, to the target two-chain insulin molecule with high efficiency (see picture; violet/blue A/B chain, yellow cystine units).

Go with the flow: The transport of salt ions and single-stranded DNA through individual single-walled carbon nanotubes marks the advent of a new type of solid-state nanopore. Surprisingly, the transport process shows a marked dependence on the electronic properties of the nanotubes: two nanotube "pipes" with the same diameter but different chiralities could exhibit orders of magnitude differences in ionic conductivity.





Toxic CO concentrations can be detected by a very clear induced color change of the dirhodium complex **1** (see scheme) upon binding of CO, as reported by Esteban et al. Other atmospheric compounds such as H_2O, CO_2, O_2, CH_4, SO_2, NO_x, and volatile organic compounds do not interfere with the CO sensing.

For the USA and Canada:
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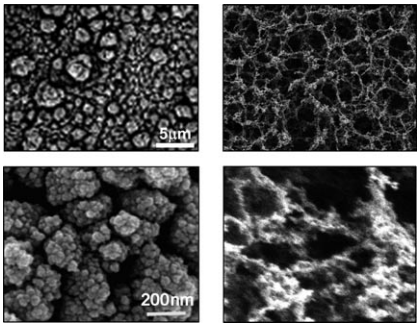
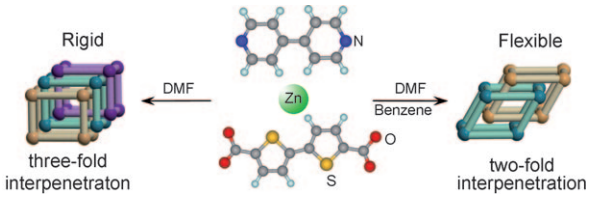
Reviews

Sense and sensitivity: Dry processes allow the rapid and scalable synthesis of nanostructured metal oxide films for use as semiconductor-based gas sensors. Dense, particulate, or porous films, with thicknesses in the nm–μm range can be prepared by the appropriate synthesis and deposition method. A wide variety of oxides with controlled properties (see pictures) are obtained, allowing miniature sensing devices with improved sensitivity and stability to be developed.



Semiconductor Sensors

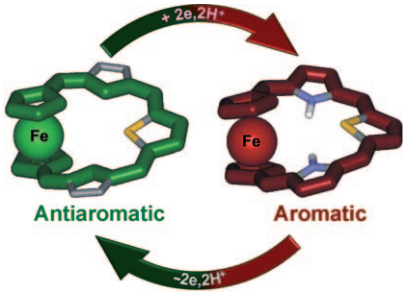
Communications



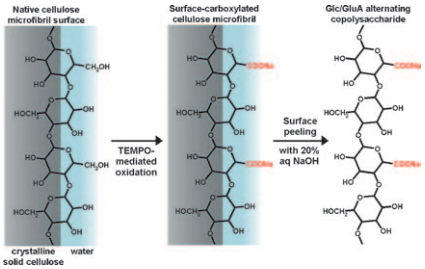
Transforming jungle gyms: Structural flexibility and sorption behavior can be tuned by controlling the degree of interpenetration of 3D porous coordination polymers (PCPs). The architectural connectivity of PCPs, even those that are composed of the same chemical components, has a significant impact on the structural flexibility and sorption behavior, which was confirmed by coincident XRPD/adsorption measurements.

Coordination Polymers

Setting the 'cene: The structural features of ferrocenophanes and porphyrinoids are combined in ferrocene–porphyrin hybrids. Ferrocenothiaporphyrin (see picture, green) and dihydroferrocenothiaporphyrin (red) are macrocyclic antiaromatic and aromatic systems, respectively. These two systems provide evidence for direct transmission of π-electron conjugation across a d-electron metallocene.



Porphyrinoids

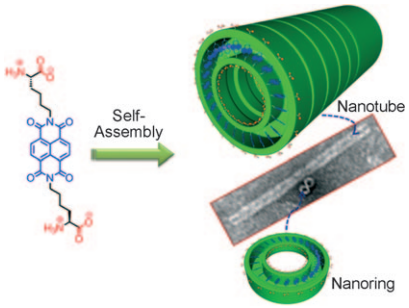


Two native celluloses with different nanofibril widths and crystallinity were subjected to TEMPO-mediated oxidation. Constant-time heteronuclear multiple-bond correlation analysis of the water-soluble products and subsequent surface peeling revealed that more than 90% of the products were (1→4)-β-linked glucose/glucuronic acid (Glc/GluA) alternating copolysaccharides (see scheme; TEMPO = 2,2,6,6-tetramethylpiperidin-1-yloxyl).

Alternating Copolysaccharides

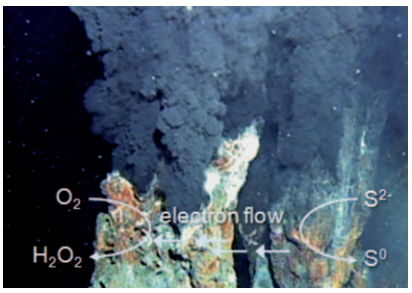
Contents

Mmm—stacks of donuts! A one-dimensional n-type nanotube was formed by stacking rings formed from the bolaamphiphilic self-assembly of 1,4,5,8-naphthalenetetracarboxylic acid diimide (NDI) with L-lysine headgroups (see picture). Solid-state NMR studies demonstrate the exceptional conformational homogeneity of the constituent molecules that make up the nanotubes.



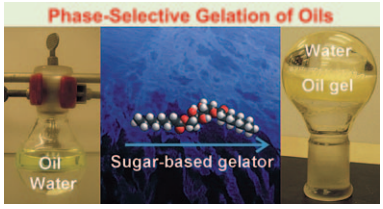
Nanotube Self-Assembly

Some like it hot: Metal-like electrical conduction and electrocatalytic function of a black smoker chimney point to a possible new form of energy transfer from hot, reductive hydrothermal fluid to cold, oxygenated seawater by electrical current generation in the sulfide chimney wall.



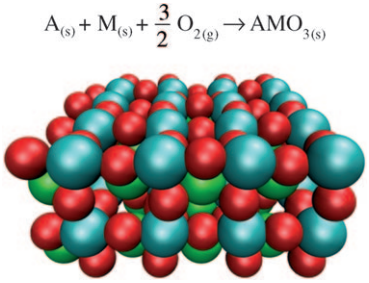
Marine Chemistry

Mopping up: Phase-selective gelators were synthesized from sugar alcohols using biocatalysis. The gelators exhibited an unprecedented ability to phase-selectively gel only organic liquids including crude-oil fractions in the presence of water at room temperature. Oil can be recovered from the gelled phase by heating and distillation. Thus this class of materials may be useful in recovering oil from spills.



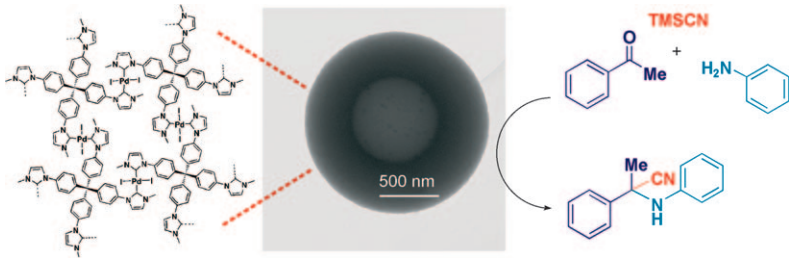
Molecular Gelators

Trends in formation energies ΔG^{form}_{exptl} of 41 perovskites AMO_3 at 298 K are reproduced by ΔG^{form}_{DFT} from DFT calculations with the RPBE-GGA functional (see picture; A green, M blue, O red). Moreover, the calculations rationalize systematic trends in their properties, reveal a direct connection between composition and stability in perovskites, and open up a path to ab initio constructions of complete phase diagrams.



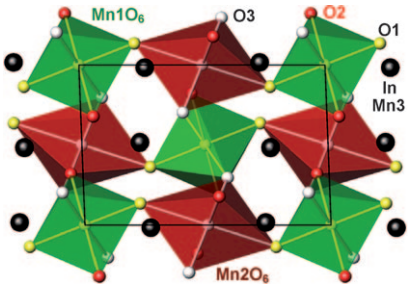
Perovskite Phases

Contents



Organometallic Hollow Spheres

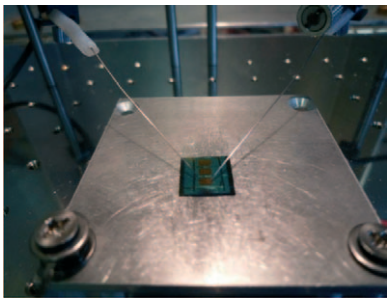
Hollow-sphere catalysts were prepared by means of 3D network formation between a tetraimidazolium building block and palladium acetate. The bis(N-heterocyclic carbene)–palladium species that were concomitantly formed during growth of the hollow spheres showed excellent activity as heterogeneous catalysts in one-pot three-component Strecker reactions of ketones (see picture; TMS = trimethylsilyl).



Perovskites

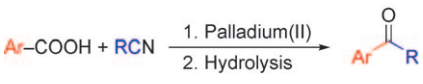
More Mn: New perovskite oxides $(In_{1-y}Mn_y)MnO_3$ ($1/9 \le y \le 1/3$, see picture) were prepared by using a high-pressure technique. The A site is doped with Mn^{2+} ions, and $(In_{1-y}Mn_y)MnO_3$ is similar to $(Lu_{1-y}Ca_y)MnO_3$. The B-site-ordered structure is realized through the ordering of Mn^{3+} and Mn^{4+} ions. Materials with $y \le 0.25$ demonstrate spin-glass-like properties, while $(In_{2/3}Mn_{1/3})MnO_3$ shows magnetic properties typical for canted antiferromagnets.

Extended π system: A nickel(0)-mediated reaction afforded dinaphthopentalene derivatives, whose electronic and electrochemical properties depend on the fusion patterns. Very high hole mobility was observed for an amorphous material, and the compounds are applicable to organic heterojunction photovoltaic cells (see picture).



Molecular Electronics

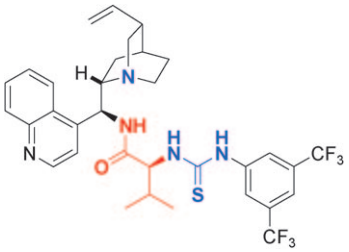
An efficient, sustainable method for the preparation of aryl ketones from *ortho*-substituted benzoic acids proceeds through their decarboxylation to generate an aryl–palladium species, followed by addition to a nitrile and hydrolysis of the intermediate ketimine.



Coupling Reactions

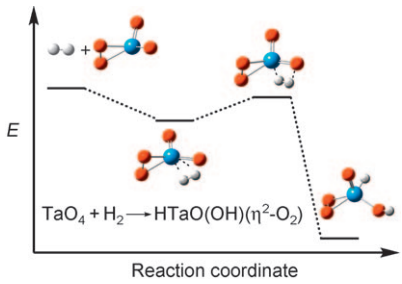
Contents

Multifunctional catalysts in operation: A novel class of trifunctional thiourea catalysts containing natural amino acid residues have been prepared (see scheme), and found to be very effective towards the asymmetric addition of 3-alkyl-oxindoles to 1,1-bis(benzenesulfonyl)ethylene. This synthetic protocol has led to the enantioselective synthesis of 3-alkyl-3-aryl-disubstituted oxindoles and indolines with an all-carbon quaternary stereogenic center.



Asymmetric Catalysis

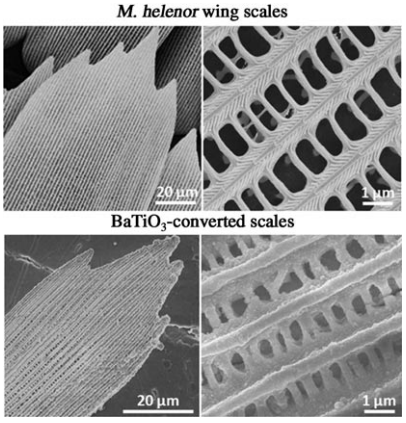
Get active: Neutral TaO_4 d^0 complex is able to cleave dihydrogen heterolytically and spontaneously to form [HTaO(OH)-(η^2-O_2)] in solid argon at cryogenic temperatures. Theoretical calculations predict that the hydrogen atoms in [HTaO(OH)-(η^2-O_2)] can easily be transferred to organic compounds. Thus, TaO_4 can serve as a model catalyst for hydrogenation reactions.



Small-Molecule Activation

Getting up to speed: Both LiCl and the YCl_3/MeLi catalyst system have an acceleration effect upon the substitution of silanes using Grignard reagents (see scheme). The method provides access to benzyl-, allyl-, and arylsilanes in good yields from the starting silanes.

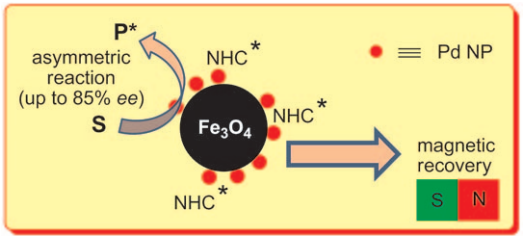
Synthetic Methods



Chitinous wing scales of *Morpho helenor* butterflies were converted into $BaTiO_3$ replicas through the use of a layer-by-layer surface sol-gel process, organic pyrolysis, and a microwave hydrothermal reaction (see picture). This general structure-preserving process may be used to convert microscale nanostructured bioorganic or synthetic organic templates into a variety of functional multicomponent oxides.

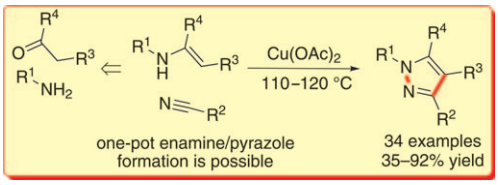
Bioorganic Replication

Contents



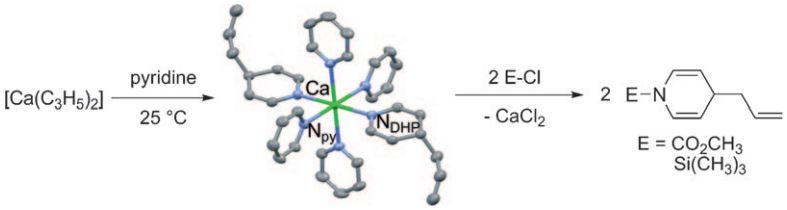
Superficial success: A chiral N-heterocyclic carbene (NHC*) is used to modify Fe_3O_4/Pd nanoparticles, which then catalyze asymmetric α-arylations. This successful synthesis of a heterogeneous catalyst and its appliation in asymmetric catalysis is in stark contrast to the simple immobilization of an established chiral homogeneous catalyst.

Nanocatalysis



Golden section: A novel synthetic strategy for the synthesis of tetrasubstituted pyrazoles is provided. In an efficient C–C/N–N bond-formation cascade, enamines and nitriles are oxidatively coupled to deliver pyrazoles in good yields (see scheme). The ready availability of the starting materials, the high level of practicability of the reaction and work up, and the avoidance of hydrazine starting materials make the method attractive.

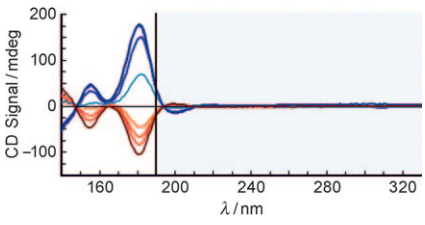
Heterocycles



The remarkable balance between nucleophilicity and basicity that is found for bis(allyl)calcium has not been previously reported for organolithium and organomagnesium reagents. Pyridine undergoes regioselective 1,4-insertion into the calcium allyl bond of bis(allyl)calcium. The resulting calcium 4-allyl-1,4-dihydropyridyl compound can be readily converted into the N-protected 1,4-dihydropyridine derivatives.

Organocalcium Chemistry

Extending CD spectroscopy: Strong circular dichroic (CD) transitions in amino acids were observed when CD spectroscopy was extended to the vacuum-ultraviolet spectral range between 140 and 190 nm (see picture). Here, proteinogenic amino acids show the same CD magnitude and the same sign, and circularly polarized light is thus capable of inducing enantiomeric excesses of the same handedness. Interestingly, typical "meteoritic" amino acids have different CD properties.



Homochirality

Contents

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

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