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:

*K. W. Eberhardt, C. L. Degen, A. Hunkeler, B. H. Meier**
One- and Two-Dimensional NMR Spectroscopy with a Magnetic-Resonance Force Microscope

*S. Wan, J. Guo, J. Kim, H. Ihee, D. Jiang**
A Belt-Shaped, Blue-Luminescent and Semiconducting Covalent Organic Framework

*R. E. Jilek, M. Jang, E. D. Smolensky, J. D. Britton, J. E. Ellis**
Structurally Distinct Homoleptic Anthracene Complexes $[M(C_{14}H_{10})_3]^{2-}$, M=Ti, Zr, Hf: Tris(arene) Complexes for a Triad of Transition Metals

M. Inoue, N. Lee, K. Miyazaki, T. Usuki, S. Matsuoka, M. Hirama**
Critical Importance of the Nine-Membered F Ring of Ciguatoxin for Potent Bioactivity: Total Synthesis and Biological Evaluation of F-Ring-Modified Analogues

*J. Steill, J. Zhao, C.-K. Siu, Y. Ke, U. H. Verkerk, J. Oomens, R. C. Dunbar, A. C. Hopkinson, K. M. Siu**
Structure of the Observable Histidine Radical Cation in the Gas Phase: a Captodative α Radical Ion

*Z. Deng, I. Bald, E. Illenberger, M. A. Huels**
Bond- and Energy-Selective Carbon Abstraction from D-Ribose by Hyperthermal Nitrogen Ions

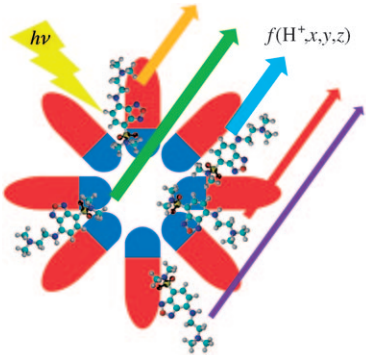
News

Books

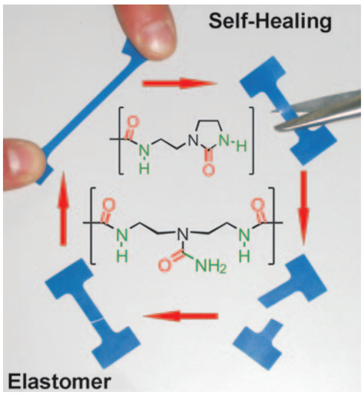
Highlights

Molecular Sensors

A remarkably high spacial resolution can be achieved by using multiplexing fluorescent sensors in micellar systems to determine position-dependent proton concentrations which are difficult to determine by other techniques. Such systems coupled with logic elements mimic complex biological systems and can be used as molecular sensing computers. The picture shows a micelle with position-selective sensors, which give information about the chemical environment by their fluorescence.

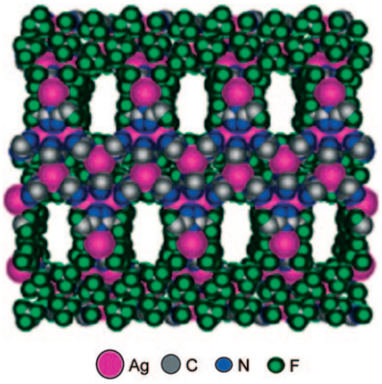


Polymeric Materials



“Heal thyself!”: A thermoplastic rubber material has recently been developed that can completely mend itself when the fracture interfaces are rejoined and left to heal for a moderate time. This “smart” rubber is easy to synthesize and displays excellent mechanical properties.

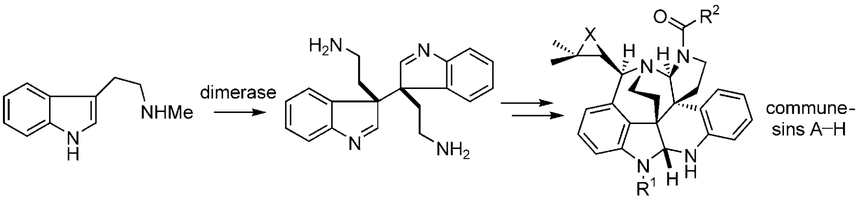
Metal–Organic Frameworks



Two significant advances in the development of metal–organic frameworks (MOFs) are perfluoro MOFs (see structure) with an outstanding volumetric gas uptake and hysteretic sorption of dihydrogen. The modular synthesis of functional MOFs involves a two-component framework, in which one component is an integral component of the framework and the other can be exchanged after formation of the matrix.

Minireviews

Bioinspired Synthesis



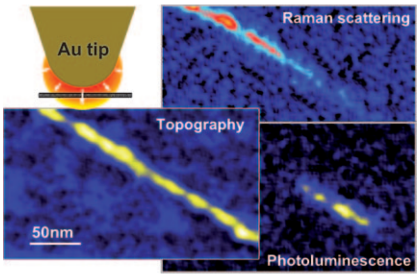
Inspired by the crafts of nature: Research on the communesins/nomofungin and perophoramidine provides an impressive example of how biosynthetic considerations (see scheme) can lead to the correction of structural misassignments and inspire synthetic chemists. After intensive studies, which culminated in a total synthesis of perophoramidine by the research group of Funk in 2004, Qin and co-workers completed the first total synthesis of a communesin in 2007.

For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Wiley-VCH, 111 River Street, Hoboken, NJ 07030. Annual subscription price for institutions: US$ 7225/6568 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Reviews

Optics on the Nanoscale

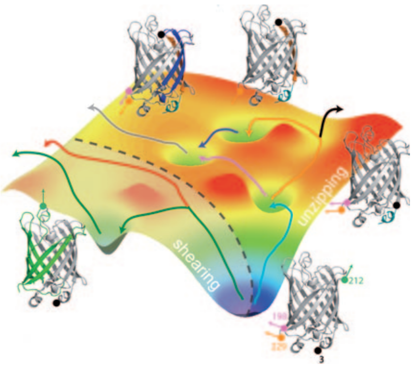
Taking a closer look: Tip-enhanced near-field optical microscopy (TENOM) has developed into a powerful and versatile tool for surface analysis and provides detailed spectroscopic information through the observation of Raman scattering and photoluminescence. By combining nanometer-scale spatial resolution and ultrahigh detection sensitivity, the technique has been shown to be ideally suited to the study of single nanoobjects and trace amounts of different materials.



Communications

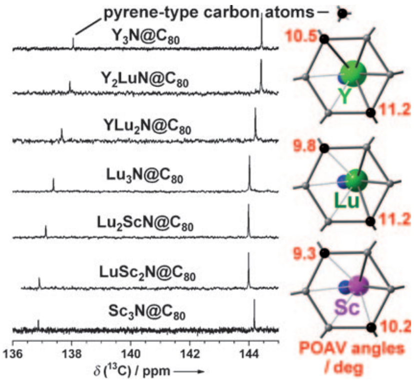
Protein Folding

The directed application of force to different points on the surface of the green fluorescent protein (GFP) makes it possible to shift between two different pathways with distinct unfolding intermediates. One pathway resembles a "folding-like" pathway, whereas the other may play a role during processes such as import through a pore. The picture shows the energy landscape of GFP with intermediates and pathways.



Fullerenes

Effect of the endohedral species: With the successful isolation of $LuY_2N@C_{80}$ and $Lu_2YN@C_{80}$—the first mixed metal clusterfullerenes not to involve Sc, the effect of the encaged cluster size on the structure of the carbon cage is addressed: the increase in cluster size is found to result in an increase of the pyramidalization of pyrene-type carbon atoms and the upfield shift of corresponding ^{13}C NMR signals.

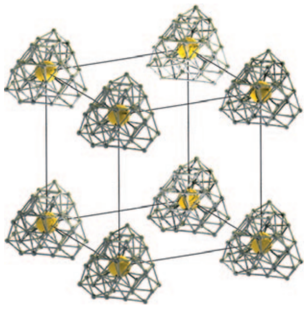



A Journal of the Gesellschaft Deutscher Chemiker
Angewandte
International Edition
GDCh
Chemie
D 3461
www.angewandte.org
2008–47/4
WILEY-VCH

Silicon-Doped Aluminum Clusters

M. Huber, A. Schnepf, C. E. Anson, H. Schnöckel* ______ **8201 – 8206**

$Si@Al_{56}[N(2,6\text{-}iPr_2C_6H_3)SiMe_3]_{12}$: The Largest Neutral Metalloid Aluminum Cluster, a Molecular Model for a Silicon-Poor Aluminum–Silicon Alloy?

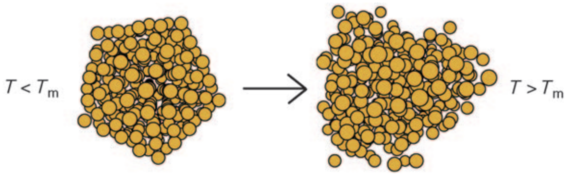


Silicon filling: Silicon-doped Al_{44} superatoms form a cubic-primitive crystal lattice (see picture; ● Al, ● Si) in the cluster $Si@Al_{56}[N(dipp)SiMe_3]_{12}$, which is prepared from a metastable AlCl solution and the silicon-containing ligand $N(dipp)SiMe_3$ (dipp = 2,6-$iPr_2C_6H_3$). The central silicon atom has a strong influence on the structure and the bonding situation in the cluster.

Noble Gas Clusters

E. Pahl, F. Calvo, L. Koči, P. Schwerdtfeger* ______ **8207 – 8210**

Accurate Melting Temperatures for Neon and Argon from Ab Initio Monte Carlo Simulations

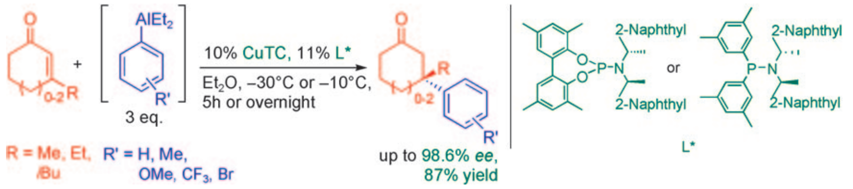


Monte Carlo simulations using first-principles many-body interaction potentials for clusters containing "magic numbers" of neon and argon atoms (Ne_N, Ar_N, $N = 13, 55, 147, 309, 923$) can provide melting temperatures T_m, which when extrapolated to the bulk are in excellent agreement with experimental findings.

Asymmetric Catalysis

C. Hawner, K. Li, V. Cirriez, A. Alexakis* ______ **8211 – 8214**

Copper-Catalyzed Asymmetric Conjugate Addition of Aryl Aluminum Reagents to Trisubstituted Enones: Construction of Aryl-Substituted Quaternary Centers



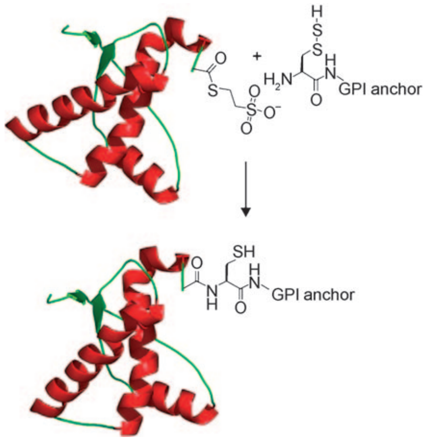
Al be back: Novel aryl and alkenyl aluminum reagents are generated through a halogen/Li exchange–Li/Al transmetalation sequence. These aryl alanes are used in the copper-catalyzed asymmetric conjugate addition reaction to a variety of cyclic enones giving chiral aryl-substituted quaternary centers (see scheme). Both, electron-donating and electron-withdrawing groups give full conversion and very good *ee* values.

Synthetic Prion Protein

C. F. W. Becker,* X. Liu, D. Olschewski, R. Castelli, R. Seidel, P. H. Seeberger* ———— **8215 – 8219**

Semisynthesis of a Glycosylphosphatidylinositol-Anchored Prion Protein

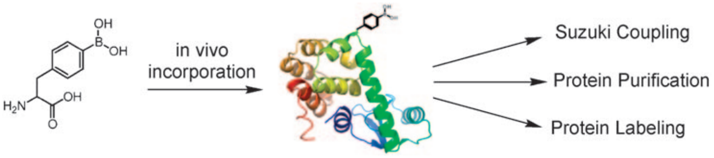
Pinning down the role of the anchor: The chemical synthesis of a cysteine-modified glycosylphosphatidylinositol (GPI) anchor provides access to homogeneous GPI-anchored prion protein through expressed protein ligation (see scheme). By this method, it should be possible to investigate the influence of the complex post-translational GPI modification on protein structure and function.



Expanded Genetic Code

E. Brustad, M. L. Bushey, J. W. Lee, D. Groff, W. Liu, P. G. Schultz* ———— **8220 – 8223**

A Genetically Encoded Boronate-Containing Amino Acid

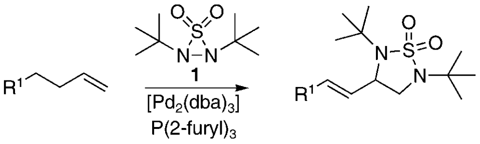


A biological boronate: An orthogonal tRNA/aminoacyl-tRNA synthetase pair has been evolved for the genetic incorporation of a boronic acid into proteins. This amino acid has been used to purify proteins in a one-step scarless purification procedure as well as for the site-specific labeling of proteins using various boronic acid chemistries.

Palladium Catalysis

B. Wang, H. Du, Y. Shi* ———— **8224 – 8227**

A Palladium-Catalyzed Dehydrogenative Diamination of Terminal Olefins



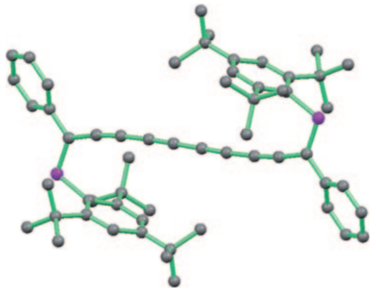
A dynamic diamination: The title transformation has been developed with diaziridine **1** as the nitrogen source (see scheme; dba = *trans,trans*-dibenzylideneacetone). The reaction proceeds through an allylic amination and subsequent cyclization, and a variety of terminal olefins can be effectively diaminated with high regioselectivity.

Phosphaorganic Chemistry

B. Schäfer, E. Öberg, M. Kritikos, S. Ott* ———— **8228 – 8231**

Incorporating Phosphaalkenes into Oligoacetylenes

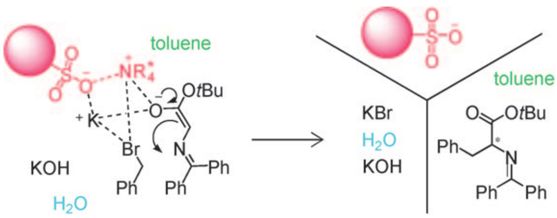
Mind the gap! Replacing the two terminal carbon atoms of a tetrayne-linked bisalkene by two phosphorus centers leads to a decrease of the HOMO–LUMO gap by 0.5 eV. The acetylenic phosphaalkenes are accessible from an ambivalent carbene-type C_5 intermediate and are shown to be viable building blocks for the construction of elaborate phosphorus- and carbon-rich molecules (see picture; C gray, P purple).



Polymeric Catalysts

Y. Arakawa, N. Haraguchi,
S. Itsuno* ——— **8232 – 8235**

An Immobilization Method of Chiral Quaternary Ammonium Salts onto Polymer Supports



Direct support: The title compounds have been used as polymeric organocatalysts (see structure) in the asymmetric alkylation of a glycine derivative to give the corresponding phenylalanine with high enantioselectivity. The polymeric catalyst can be reused without loss of its catalytic activity.

Spin Crossover

J. Larionova,* L. Salmon, Y. Guari,
A. Tokarev, K. Molvinger, G. Molnár,
A. Bousseksou* ——— **8236 – 8240**

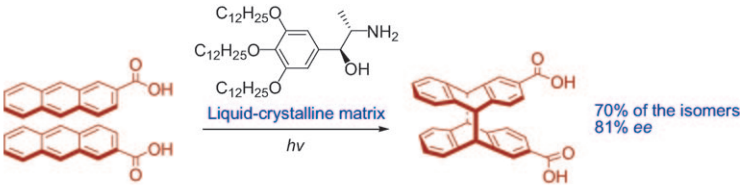
Towards the Ultimate Size Limit of the Memory Effect in Spin-Crossover Solids

Take it to the limit: Monodisperse nanoparticles of the 3D coordination polymer [Fe(pyrazine){Ni(CN)$_4$}] have been obtained in biopolymer chitosan beads matrix (see picture). These ultra-small nanoparticles (ca. 4 nm) exhibit spin crossover phenomenon with hysteresis.

Chiral Reaction Media

Y. Ishida,* Y. Kai, S.-y. Kato, A. Misawa,
S. Amano, Y. Matsuoka,
K. Saigo* ——— **8241 – 8245**

Two-Component Liquid Crystals as Chiral Reaction Media: Highly Enantioselective Photodimerization of an Anthracene Derivative Driven by the Ordered Microenvironment

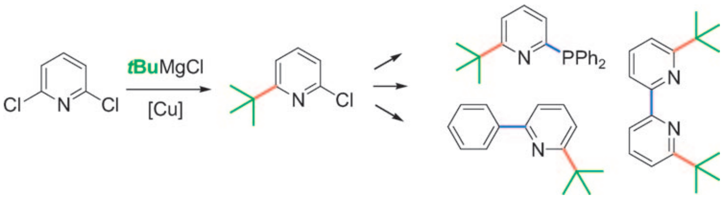


Tailored to the reaction: Within a liquid-crystalline matrix provided by a chiral amphiphilic amino alcohol, the photodimerization of an anthracenecarboxylic acid proceeds with high probability and with excellent regio-, diastereo-, and enantioselectivities (up to 81 % *ee*).

Homogeneous Catalysis

L. Hintermann,* L. Xiao,
A. Labonne ——— **8246 – 8250**

A General and Selective Copper-Catalyzed Cross-Coupling of Tertiary Grignard Reagents with Azacyclic Electrophiles



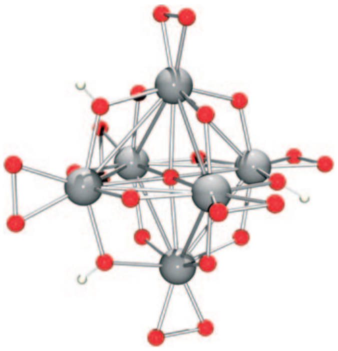
Bulky heterocycles: A highly selective catalytic cross-coupling reaction of tertiary Grignard reagents with chloroazacycles provides a shortcut to heterocyclic building blocks for applications in pharmaceutical chemistry and supramolecular chemistry, or as ligand precursors in transition-metal catalysis (see scheme).

Contents

Polyoxometalates

C. A. Ohlin, E. M. Villa, J. C. Fettinger, W. H. Casey* ______ **8251 – 8254**

Distinctly Different Reactivities of Two Similar Polyoxoniobates with Hydrogen Peroxide

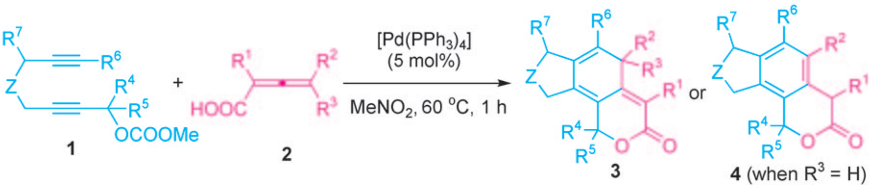


Peroxoniobate species are found whenever niobium oxides are employed as photocatalysts or used to sequester radionuclides. The reactions of $[Nb_6O_{19}]^{8-}$ and $[Nb_{10}O_{28}]^{6-}$ with hydrogen peroxide each behave differently, and the first example of a peroxopolyoxoniobate species, $[N(CH_3)_4]_5[H_3Nb_6O_{13}(O^{(I)}_2)_6]\cdot 9.5\,H_2O$, was structurally characterized (see picture; Nb gray, O red, H white).

Cyclization Reactions

X. Lian, S. Ma* ______ **8255 – 8258**

An Efficient Approach to Substituted 1,5,7,8,9-Pentahydrocyclopenta[*h*]-2-Benzopyran-3-one Derivatives by a Palladium-Catalyzed Tandem Reaction of 2,7-Alkadiynylic Carbonates with 2,3-Allenoic Acids

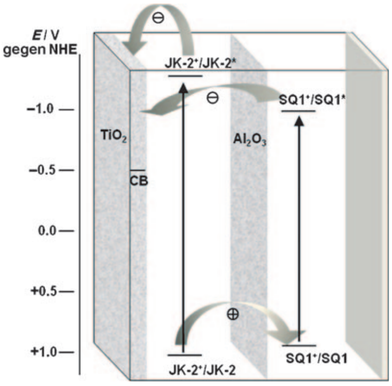


An unexpected palladium(0)-catalyzed cyclization of **1** with **2** leads to derivatives **3** or **4**. This reaction allows for broad substrate diversity and proceeds through a proposed sequential process involving regioselective intramolecular carbopalladation.

Dye-Sensitized Solar Cells

H. Choi, S. Kim, S. O. Kang, J. Ko,* M.-S. Kang, J. N. Clifford, A. Forneli, E. Palomares,* M. K. Nazeeruddin,* M. Grätzel ______ **8259 – 8263**

Stepwise Cosensitization of Nanocrystalline TiO_2 Films Utilizing Al_2O_3 Layers in Dye-Sensitized Solar Cells



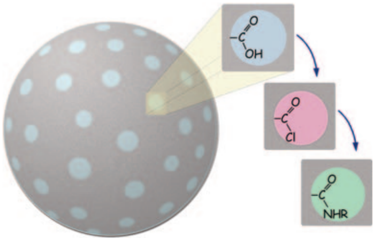
Doubly sensitized: Stepwise cosensitization is carried out on Al_2O_3-coated nanocrystalline TiO_2 layers using two organic dyes (JK-2 and SQ1) having complementary spectral absorption bands in the visible region. The Al_2O_3 coating results in the retardation of the interfacial charge recombination dynamics at the oxide/sensitizer interface and improves the overall performance of the dye-sensitized solar cells. CB = conduction band.

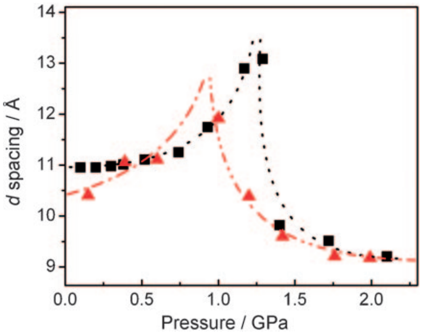
Functionalized Nanopores

S. A. Dergunov, E. Pinkhassik* ______ **8264 – 8267**

Functionalization of Imprinted Nanopores in Nanometer-Thin Organic Materials

Taking on new functions: By using liposomes as temporary self-assembled scaffolds, nanocapsules with uniformly sized nanopores are formed. The as-formed nanopores have a single carboxy functional group, which can be converted into an acyl chloride group and then into an amide group (see picture).





Expansion under compression: The unit-cell volume of graphite oxide pressurized in water media, continuously increases reaching a sharp maximum at ca. 1.3–1.5 GPa (see picture, squares). Expansion of the lattice to a maximum of about 28–30 % is because of gradual pressure-induced water insertion into the interlayer space of graphite oxide. The effect is reversible (triangles), resulting in a unique "breathing" of the structure upon pressure variation.

Graphite Oxide

A. V. Talyzin,* V. L. Solozhenko,
O. O. Kurakevych, T. Szabó, I. Dékány,
A. Kurnosov, V. Dmitriev ____ **8268 – 8271**

Colossal Pressure-Induced Lattice Expansion of Graphite Oxide in the Presence of Water

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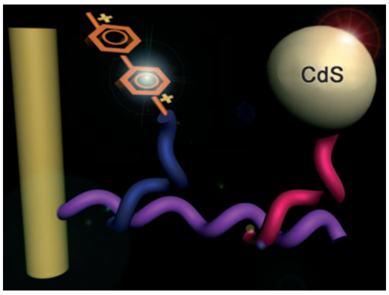

A change of direction: The intensity and direction of photocurrents in photosensitizer–electron acceptor dyads anchored to electrodes is controlled by the orientation and composition of the subunits. DNA templates attached to electrode surfaces act as scaffolds for the assembly of the dyads, which comprise either CdS nanoparticles or ruthenium(II) polypyridyl complexes in conjunction with viologen units that act as relays (see picture).

Photosystems

R. Tel-Vered, O. Yehezkeli, H. B. Yildiz,
O. I. Wilner, I. Willner* ____ **8272 – 8276**

Photoelectrochemistry with Ordered CdS Nanoparticle/Relay or Photosensitizer/Relay Dyads on DNA Scaffolds

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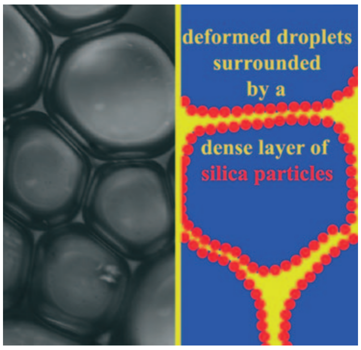

Small but mighty: Oleic acid functionalized silica particles possess adequate hydrophobicity to stabilize water/oil Pickering high internal phase emulsions. The particles adsorb irreversibly at the aqueous/organic interface and prevent droplet coalescence and phase inversion. Polymerization of the emulsions produced highly porous polymer foams.

Emulsions

V. O. Ikem, A. Menner,
A. Bismarck* ____ **8277 – 8279**

High Internal Phase Emulsions Stabilized Solely by Functionalized Silica Particles

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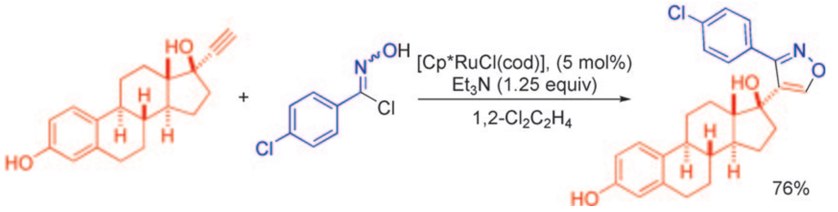
In one ear ... : The outer shape and inner architecture of individual particles of a complex calcite–gelatine composite resemble the known characteristics of biogenic otoconia ("ear dust"; see picture). The relationships between the morphology of artificial and biogenic specimens are discussed.

Biomimetic Composites

Y.-X. Huang, J. Buder, R. Cardoso-Gil,
Yu. Prots, W. Carrillo-Cabrera, P. Simon,
R. Kniep* ____ **8280 – 8284**

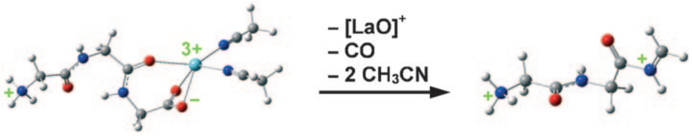
Shape Development and Structure of a Complex (Otoconia-Like?) Calcite–Gelatine Composite

Ruthenium Catalysis



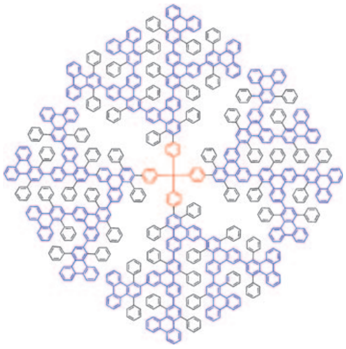
3,4-Disubstituted and 3,4,5-trisubstituted isoxazoles have been formed from alkynes and nitrile oxides in a ruthenium(II)-catalyzed process (see scheme; cod = cycloocta-l,5-diene, Cp* = C_5Me_5). These reactions are experimentally simple, proceed at room temperature, and produce isoxazoles with excellent regioselectivity in high yield.

Protonated Ions



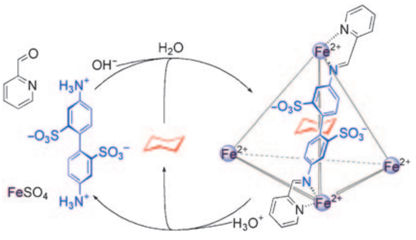
Stay positive! Dissociation of a lanthanum complex of triglycine generates a novel diprotonated iminium ion (see picture; gray C, white H, light blue La, dark blue N, red O), which undergoes rich fragmentations. This class of peptide fragment ions provides a system to model multiple charge effects and is potentially useful in peptide sequencing.

Dendrimers

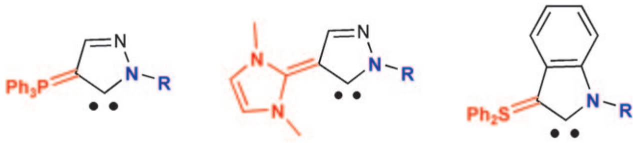


Into the blue: A unique family of polytriphenylene dendrimers (see picture) that emit blue light with high photoluminescence quantum yield were synthesized. The triphenylene units are twisted out-of-plane, and the highly stiff dendritic backbones prevent intermolecular fluorescence quenching.

Host–Guest Systems

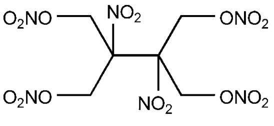


In irons bound: Linear diamine and formylpyridine subcomponents form a tetrahedral cage with iron(II) in water (see scheme). This cage traps hydrophobic guests with high specificity within a rigid cavity, isolating them from the aqueous environment. The cage may be broken, releasing the guest, upon the addition of a triamine. It may also be unlocked by adding acid, allowing the guest to be reversibly released until base is added, relocking it within.



Being neighborly: The concept of placing two reactive intermediates next to each other to gain stability is borne out in amino(ylide)carbenes (AYCs). Different kinds of ylides stabilize an adjacent singlet carbene by donation of electron density from the ylidic carbon atom into the empty p orbital to give AYCs of various structural formats (see picture) that are distinguished by their exceptionally strong σ-donor qualities.

Carbenes

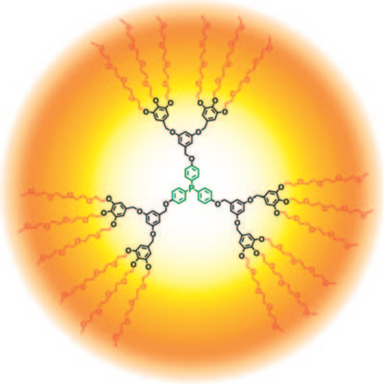


1

Going out with a bang! A high-energy-density nitrate ester **1** with unique properties was synthesized in good yield in a three-step process. Destructive stimuli studies and explosive performance calculations show that **1** has similar performance properties to those of well-characterized explosives. **1** has a density of 1.917 g cm^{-3} and a melting point of 85–86 °C, which may lead to high-performance melt-castable applications.

Energetic Materials

Peripheral vision: A second generation dendritic phosphane, with tetraethylene glycol (TEG) moieties at the periphery, has been designed and prepared (see structure). It is particularly effective as a ligand for the title transformation when using aryl chloride substrates. To realize high catalytic activity, the TEG groups must be connected to the phosphane framework.



Dendritic Catalysts

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).

Service

Corrigendum

Which Oxidant is Really Responsible for Sulfur Oxidation by Cytochrome P450?

C. Li, L. Zhang, C. Zhang, H. Hirao,
W. Wu,* S. Shaik* ________ **8168–8170**

Angew. Chem. Int. Ed. **2007**, *46*

DOI 10.1002/anie.200702867

A correction of the imaginary frequency is necessary for $^{2}\mathbf{TS}_{\mathbf{SO}}$ in Figure 1 of this paper. The old $^{2}\mathbf{TS}_{\mathbf{SO}}$ shown there (located with the option opt = loose in Gaussian 03) and the new one (reoptimized with the default convergence criterion; see also the Supporting Information) are both given below, along with their frequencies and relative energies (B3LYP/LACVP** level). The large imaginary frequency in the old structure was caused by the use of a loose geometry optimization criterion. The relative energies are almost identical, and mechanistic conclusions are not affected.