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:

News


K. Müllen


M. Jansen


M. Arndt

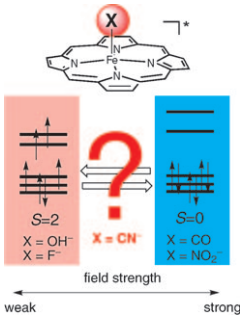
Author Profile

"My first experiment was preparation of proline-derived chiral ligands for asymmetric alkylation. My favorite subjects at school were history and English…." This and more about Keisuke Suzuki can be found on page 2635.

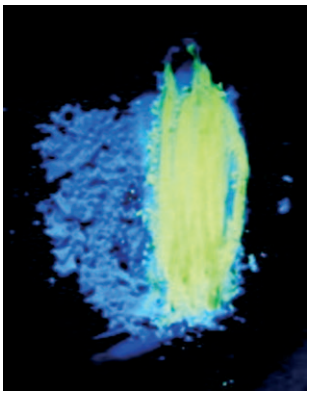
Books

Contents

Highlights

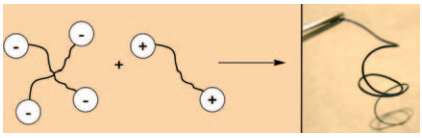


Iron man or weakling? Ligand-field strengths are conveniently expressed by the empirical spectrochemical series. Although cyanide has been deeply entrenched as a strong-field ligand, a couple of recent examples cast doubt toward the position of this ligand, namely the high-spin ($S = 2$) states of $[Cr^{II}(CN)_5]^{3-}$ and $[Fe^{II}(tpp)(CN)]^-$. tpp = *meso*-tetraphenylporphinate.



Back to the grindstone: Certain crystalline complexes of gold, platinum, and vanadium undergo dramatic changes in their luminescence or their color upon grinding. The picture shows the transformation of colorless crystals of $[(F_5C_6Au)_2(\mu\text{-}1,4\text{-}CN_2C_6H_4)]$ powder from a blue-emitting form ($\lambda_{max} = 415$ nm) to a yellow/green-emitting form ($\lambda_{max} = 533$ nm) on grinding with a pestle. The process is reversible.

Charging forward: Ionic interactions presented in a multivalent fashion in small-molecule ionic liquids lead to functional polymer-like materials (see picture) that are consistent with the formation of a supramolecular ionic network. For example, the ionic material formed from a dication consisting of two covalently linked tetraalkyl phosphonium moieties and a porphyrin tetracarboxylate has a viscosity of 10^6 Pa s at 25 °C.



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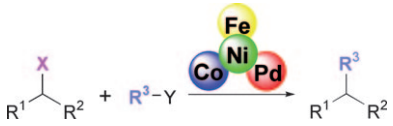
Essays

Through a glass darkly: Several recent autocatalytic reaction models for the origin of homochirality have suggested ways in which one enantiomer of the product might be reconverted into the other by a recycling reaction in a closed system. These models are revealed to violate the principle of microscopic reversibility, a powerful tool for assessing the plausibility of proposed reaction networks even at far-from-equilibrium conditions.

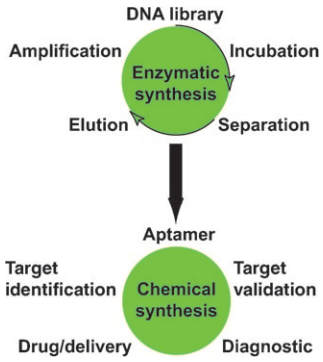
Minireviews

Secondary, but second to none: The use of secondary alkyl halides in transition-metal-catalyzed cross-coupling reactions (see scheme) has advanced significantly over the last five years. Selected examples of these transformations are examined, including mechanistic and stereochemical aspects.

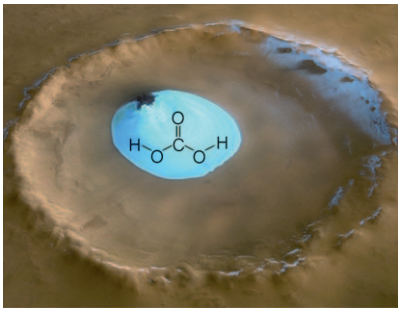


Reviews

Taking a strand: Aptamers are small single-stranded oligonucleotides that fold into a well-defined 3D structure and interact with high affinity and specificity with their target molecules, thereby inhibiting their biological functions. Aptamers can be synthesized by either chemical and/or enzymatic procedures and can thus be considered as both chemical and biological substances. The current status and new developments in this area are described.



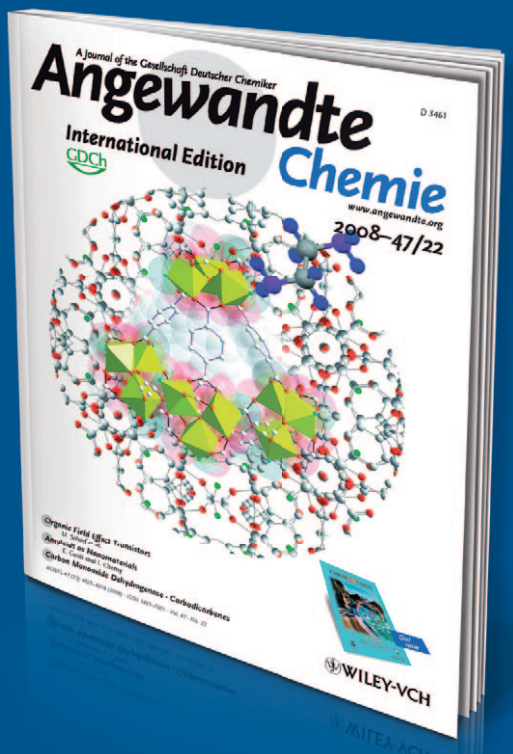
Communications



What's the matter? The laboratory Raman spectra for carbonic acid (H_2CO_3), both for the β-polymorph and its amorphous state, are required to detect carbonic acid on the surface of the pole caps of Mars in 2009, when the Mars Microbeam Raman Spectrometer lands on the planet. The picture shows a martian crater with ice of unknown composition, possibly containing carbonic acid (image adapted from DLR, with permission from ESA, DLR, and FU Berlin – G. Neukum).

Incredibly

ATTRACTIVE



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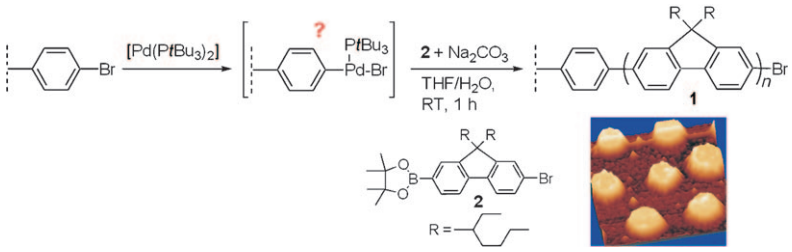
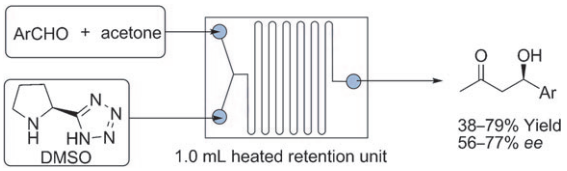


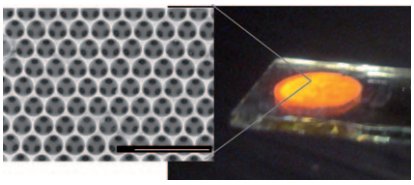
Graft work: The first surface-initiated and site-specific palladium-catalyzed Suzuki polycondensation that allows selective grafting and patterning of semiconducting and emissive poly[9,9-bis(2-ethylhexyl)fluorene] (**1**) at room temperature is developed (see scheme). The pattering is demonstrated by AFM (see image).

Graft Polycondensation



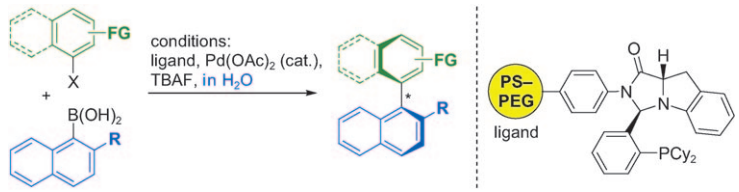
Continuous organocatalysis: Fast aldol and Mannich reactions require less catalyst when conducted in a microreactor. A proline tetrazole derivative (5–10 mol%) catalyzes asymmetric aldol reactions between various aromatic aldehydes and ketones in microreactor at 60°C with reaction times ranging from 10 to 30 min.

Organocatalysis



A promising method for the production of germanium photonic crystals consists of electrodeposition of Ge from $GeCl_4$-containing ionic liquids inside templates of polystyrene colloidal crystals and subsequent removal of the template. This room-temperature method gives rise to the fabrication of a three-dimensional highly ordered macroporous germanium nanostructure (see picture; scale: 2 μm) as a prototype of a photonic crystal.

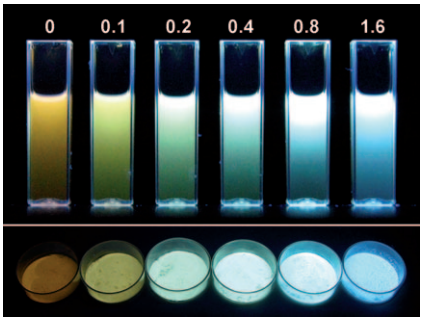
Photonic Crystals



You oughta use water: Broad functional-group (FG) tolerance was observed for the title coupling of aryl halides (X = Cl, Br, I) and aryl boronic acids to give biaryl compounds with up to 94% *ee*. The chiral imidazoindole phosphine–palladium catalyst supported on an amphiphilic polystyrene–poly(ethylene glycol) (PS–PEG) resin could be recycled readily.

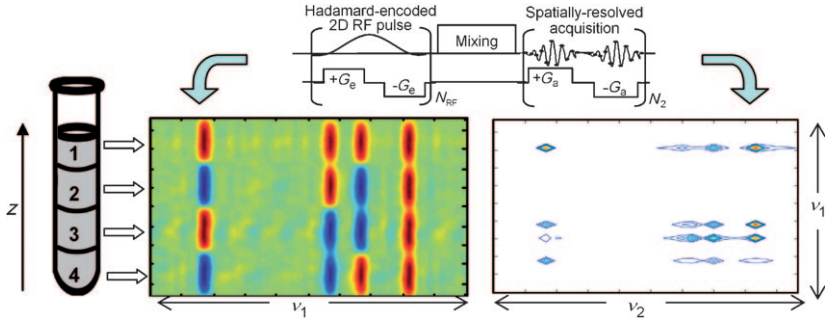
Asymmetric Catalysis

Contents



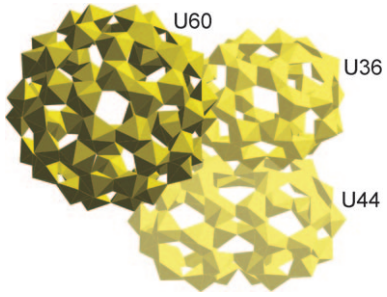
A bright idea: Mg/ZnO nanoparticles that exhibit bright, stable photoluminescence both in colloidal dispersions and in the solid state are formed by doping Mg^{II} ions into ZnO nanoparticles by sonochemical synthesis. The changes in their band gaps and luminescence properties rely on the defect concentrations inside the ZnO nanoparticles; these concentrations are determined by the Mg/Zn molar ratios (see picture).

Nanomaterials



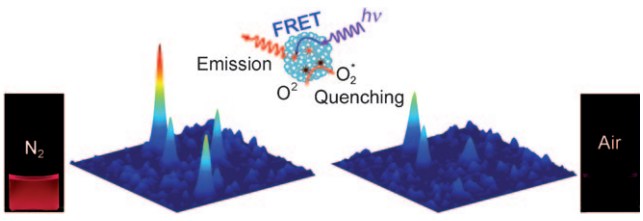
Scan and deliver: By combining imaging-based spectral/spatial 2D radiofrequency manipulations (see scheme, left) with Hadamard-weighting principles, 2D NMR spectra can be retrieved within a single scan (right). This approach can give homo- or heteronuclear correlations with an enhanced sensitivity over conventional ultrafast 2D NMR spectroscopy.

Multidimensional NMR Spectroscopy



C U soon: Clusters containing 60, 44, and 36 uranyl peroxide hydroxide polyhedra (see picture) adopt fullerene topologies of maximum symmetry. The largest of these, denoted U60, is topologically identical to C_{60} with no pentagonal adjacencies and the highest possible symmetry. U44 adopts the topology with maximum symmetry rather than that with the lowest number of pentagonal adjacencies.

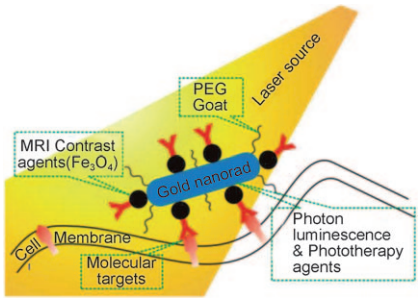
Polyoxometalates



It makes sense: Conjugated polymer nanoparticles doped with a platinum porphyrin dye exhibit bright phosphorescence that is highly sensitive to the concentration of molecular oxygen. The small size, extraordinary brightness, excellent sensitivity, and ratiometric emission, together with the demonstration of single-particle sensing and cellular uptake, indicate the potential of the nanoparticle sensors for quantitative mapping of local molecular oxygen concentration.

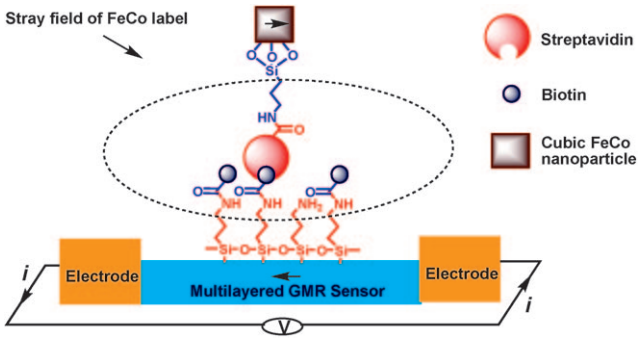
Polymer Dots

Contents



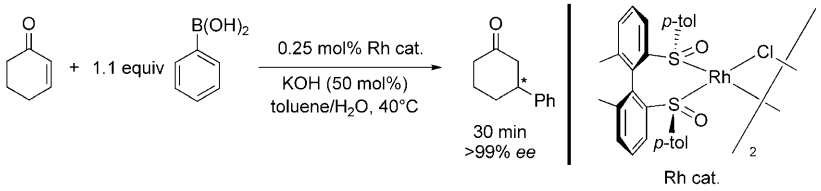
Gold and pearls: Multifunctional nanoparticles, each composed of a single, amine-modified gold nanorod, decorated with multiple "pearls" of Fe_3O_4 nanoparticles capped with carboxy groups, are prepared. Their effectiveness in simultaneous targeting, dual-mode imaging, and photothermal ablation of breast cancer cells is demonstrated.

Multifunctional Nanoparticles



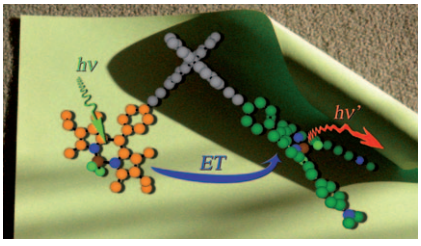
Zeptomole detector: A highly sensitive giant-magnetoresistive chip and FeCo nanoparticles can be used to linearly detect 600–4500 copies of streptavidin. Under unoptimized conditions, this system also detects human IL-6 with a sensitivity 13-times higher than that of standard ELISA techniques.

Biosensors



From zero to hero? Sulfoxides are generally not considered useful ligand entities in asymmetric metal catalysis. However, a chiral disulfoxide as a chelating ligand in the rhodium-catalyzed 1,4-addition of aryl boronic acids to cyclic, α,β-unsaturated ketones and esters gives impressive catalytic results, thus opening the door to future applications of this new chiral ligand class.

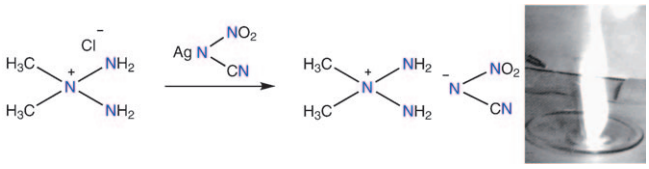
Asymmetric Catalysis



Cutting the corner: An excellent agreement has been obtained between experimental and computed coulombic coupling matrix elements for donor–spacer–acceptor systems, which consist of a boron dipyrromethane donor and acceptor in various stages of protonation. This correlation occurs in spite of reservations about the validity of Förster theory being applied to intramolecular electronic energy transfer (ET) over short (e.g., 20 Å) distances (see picture).

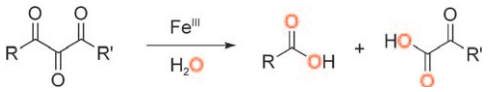
Electronic Energy Transfer

Contents



No flame, no gain: A hypergolic mixture is composed of stable species that readily react/ignite on molecular contact. Both the anion and the cation in an ionic liquid play prominent roles in determining hypergolic properties as well as ignition delay times. With the 2,2-dialkyltriazanium cation, salts with nitrate, chloride, nitrocyanamide, and dicyanamide anions are hypergolic.

Hypergolic Ionic Liquids



Three of a kind: Vicinal tricarbonyl compounds undergo C–C cleavage mediated by ferric ions (see scheme). The observed cleavage of ninhydrin and dehydroascorbic acid has relevance for amino acid detection and the metabolism of vitamin C.

Iron Catalysis

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

Angew. Chem. Int. Ed. **2009**, *48*

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During the preparation of this Communication the authors overlooked references to articles which described the synthesis of interlocked compounds by Glaser coupling and related reactions. These articles should be included in reference [9]. The authors thank Professor Ognjen Š. Miljanić (University of Houston) for his valuable suggestions.

[9] a) S. Saito, E. Takahashi, K. Nakazono, *Org. Lett.* **2006**, *8*, 5133–5136. Glaser coupling and related reactions have been frequently utilized for the synthesis of interlocked compounds, see for example: b) O. Š. Miljanić, W. R. Dichtel, S. I. Khan, S. Mortezaei, J. R. Heath, J. F. Stoddart, *J. Am. Chem. Soc.* **2007**, *129*, 8236–8246; c) O. Š. Miljanić, W. R. Dichtel, S. Mortezaei, J. F. Stoddart, *Org. Lett.* **2006**, *8*, 4835–4838; d) D. G. Hamilton, L. Prodi, N. Feeder, J. K. M. Sanders, *J. Chem. Soc. Perkin Trans. 1* **1999**, 1057–1065; e) D. G. Hamilton, N. Feeder, L. Prodi, S. J. Teat, W. Clegg, J. K. M. Sanders, *J. Am. Chem. Soc.* **1998**, *120*, 1096–1097; f) D. G. Hamilton, J. K. M. Sanders, J. E. Davies, W. Clegg, S. J. Teat, *Chem. Commun.* **1997**, 897–898; g) C. O. Dietrich-Buchecker, C. Hemmert, A. K. Khemiss, J. P. Sauvage, *J. Am. Chem. Soc.* **1990**, *112*, 8002–8008; h) C. O. Dietrich-Buchecker, A. Khemiss, J. P. Sauvage, *J. Chem. Soc. Chem. Commun.* **1986**, 1376–1378; i) A. Godt, *Eur. J. Org. Chem.* **2004**, 1639–1654; j) S. Duda, A. Godt, *Eur. J. Org. Chem.* **2003**, 3412-3420; k) Ö. Ünsal, A. Godt, *Chem. Eur. J.* **1999**, *5*, 1728–1733; l) M. J. Gunter, S. M. Farquhar, *Org. Biomol. Chem.* **2003**, *1*, 3450–3457.

