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:

*N. Christinat, R. Scopelliti, K. Severin**
Multicomponent Assembly of Boronic Acid Based Macrocycles and Cages

*J. Zhuang, H. Wu, Y. Yang, Y. C. Cao**
Controlling Colloidal Superparticle Growth Through Solvophobic Interactions

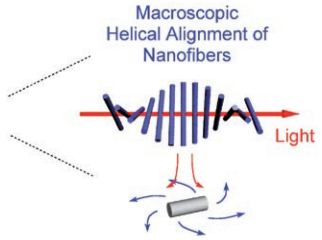
C. Li, L. Qi
Bio-Inspired Fabrication of 3D Ordered Macroporous Single Crystals of Calcite via a Transient Amorphous Phase

*C. Caleman, D. van der Spoel**
Picosecond Melting of Ice by an Infrared Laser Pulse: A Simulation Study

Books

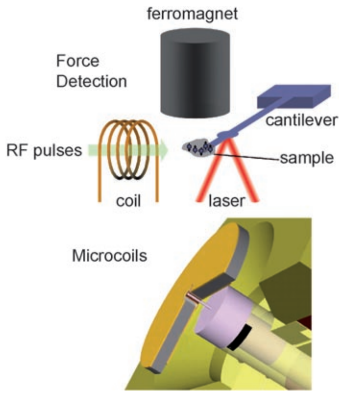
Highlights

Macroscopic Chirality



Turn, turn, turn: Achiral supramolecular assemblies are able to align by convective flows or by a vortex flow generated by mechanical stirring in dilute solutions (see picture). The linear dichroism and the linear birefringence created by the alignment result in strong circular dichroism signals.

NMR Spectroscopy

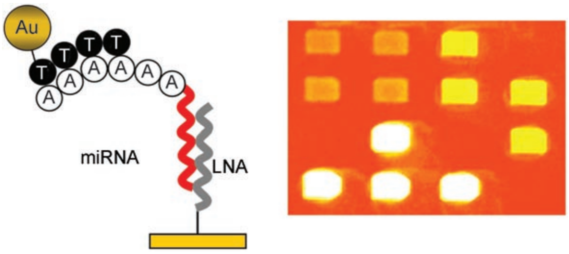


Impressively sensitive: To meet the challenges of miniaturization and limited sample quantity, new approaches for substantially increasing the sensitivity of NMR spectroscopy for gases, liquids, and solids have been developed (for two examples, see picture). These and future developments will assure that NMR spectroscopy remains a major tool for chemistry and other fields for years to come.

Contents

Minireviews

Bioanalytical Methods

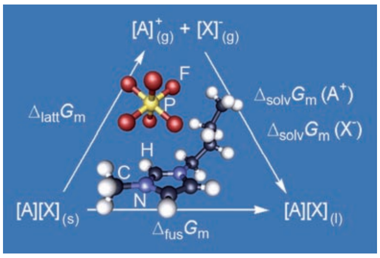


Good things come in small packages: MicroRNA molecules (miRNAs) have recently been discovered to be important regulators of gene expression, and aberrant miRNA expression patterns are increasingly being linked to a variety of diseases, including cancer. Owing to the special features of miRNAs, the development of quantitative multiplex methods for miRNA profiling is a highly challenging task for bioorganic and analytical chemists. LNA = locked nucleic acid.

Reviews

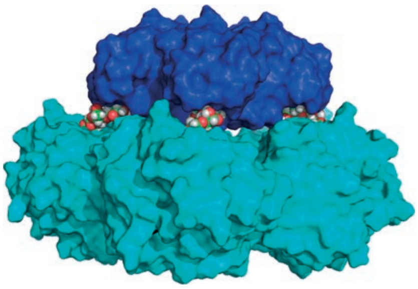
Ionic Liquids

IL-informed? What is actually known about ionic liquids (ILs)? The Review addresses this question from the physicochemical stand point and the molecular basis for the properties of ILs is discussed. The picture shows a cycle for calculating the molar Gibbs energy of fusion, $\Delta_{\text{fus}}G_{\text{m}}$, of an IL from the lattice Gibbs energy, $\Delta_{\text{latt}}G_{\text{m}}$, and the Gibbs energy of solvation, $\Delta_{\text{solv}}G_{\text{m}}$.



Communications

Inhibitors



A compact heterobifunctional ligand devoid of a linker between binding functionalities induces a supramolecular assembly between two pentameric proteins, Shiga toxin (blue) and serum amyloid P component, a human serum protein (turquoise). The use of an endogenous protein as a template brings about a 10000-fold enhancement of ligand activity.

For the USA and Canada:
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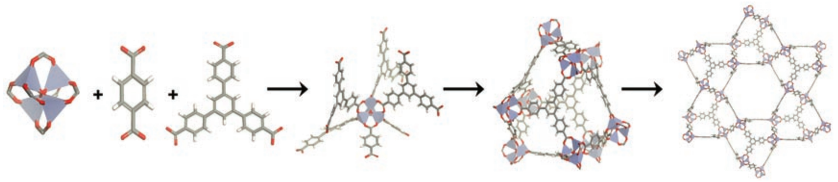
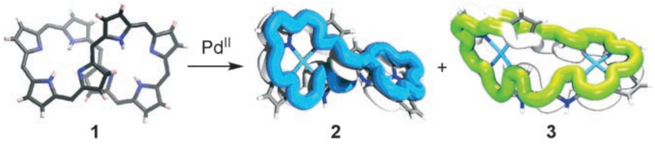
Coordination Polymers



Mixing it up: UMCM-1 (University of Michigan Crystalline Material-1), a mesoporous material with unprecedented levels of microporosity, arises from the coordination copolymerization of a dicarboxylate and a tricarboxylate linker mediated by zinc (see picture; blue tetrahedra Zn_4O clusters, C gray, H white, O red). Exceptionally high surface area derives from the microporous cages lining the 1D mesoporous channels.

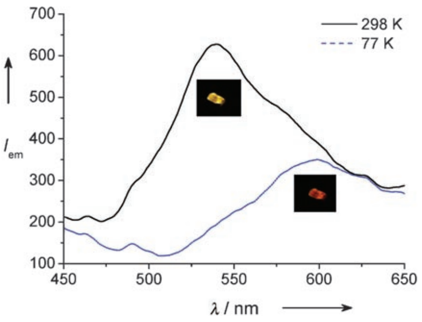
Aromaticity

VIP



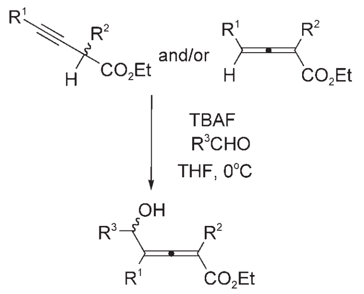
Round the twist: Metalation of [36]octaphyrin **1** provided the Möbius aromatic Pd_2 complex **3** as well as the Hückel antiaromatic Pd_2 complex **2**. This method can be applied to other expanded porphyrins and Group 10 metal ions. The aromatic/antiaromatic character was supported by NMR spectrscopy, NICS calculation, and two-photon absorption measurements.

Coordination Polymers

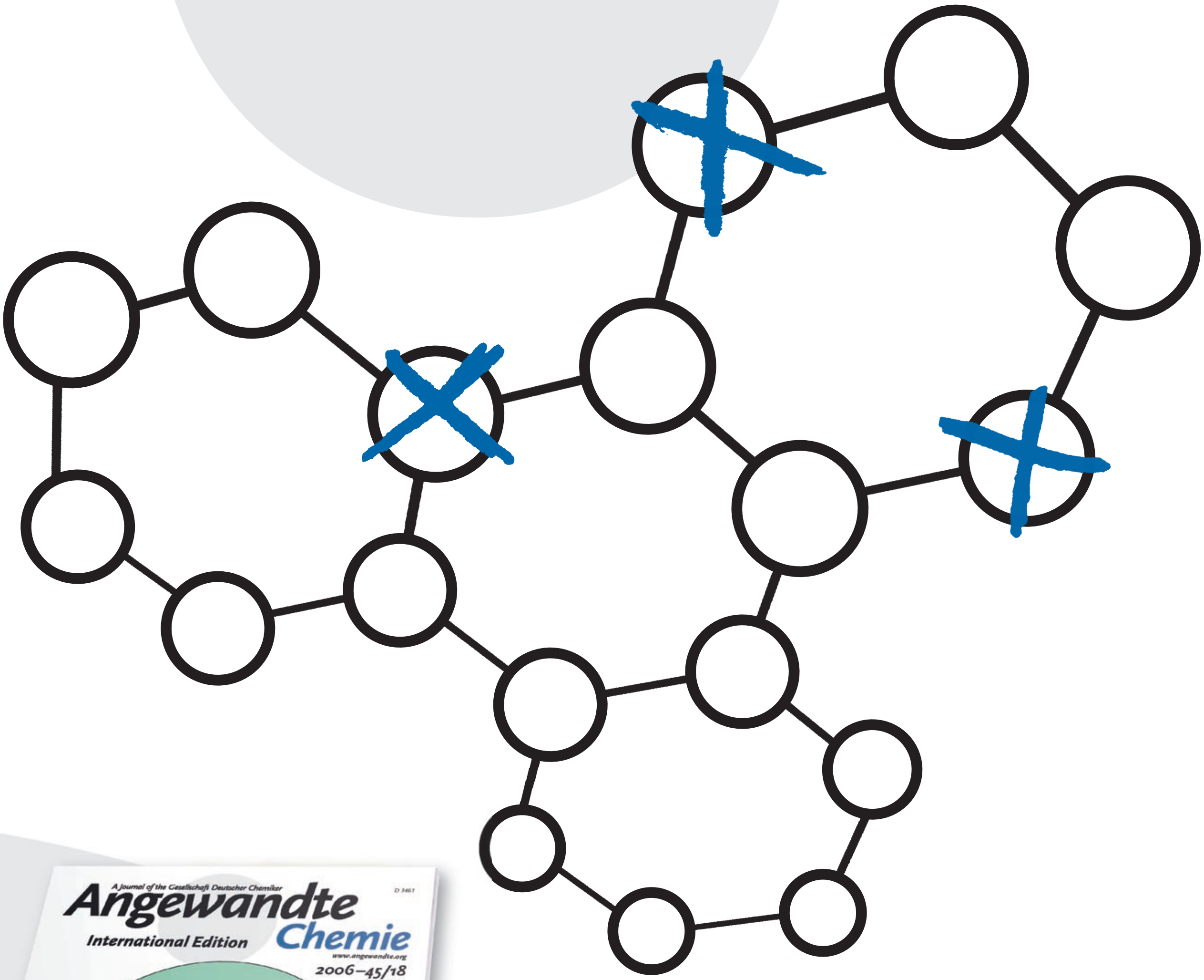


Temperature-dependent Cu⋯Cu distances lead to the luminescence thermochromism of copper(I) coordination polymers with cubane-like Cu_4X_4 cluster nodes (X = halogen) according to a study on three copper(I) coordination polymers with a bis-thioether ligand (**L**). The picture shows solid-state luminescence spectra and photographs of the two-dimensional network polymer $[Cu_4I_4\mathbf{L}_2]_n$ at 298 and 77 K.

Aldol Reactions

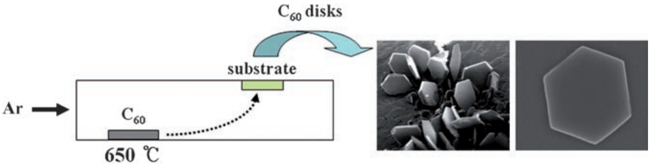


Retroaldol regains control: A countercation may exert an important effect in promoting thermodynamic control in the TBAF-mediated aldol reaction of propargyl or allenyl esters (or a mixture of both) to produce, under mild conditions, carbinol allenoates exclusively (see scheme; TBAF = tetra-*n*-butylammonium fluoride).



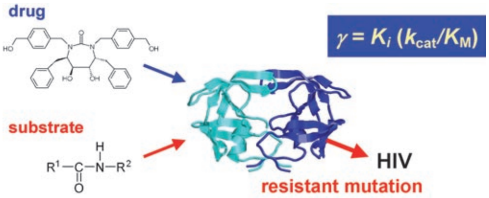
O
Pt
Co

C_{60} Structures



New jobs for disk jockeys: Single-crystalline C_{60} disks were selectively synthesized on an HOPG substrate by a vapor–solid process with C_{60} powder as the precursor. The photoluminescence intensity of the disks is much greater than that of thin films and powders. In photoconductivity measurements with a single disk the current was increased by about tenfold. These properties point to intriguing applications.

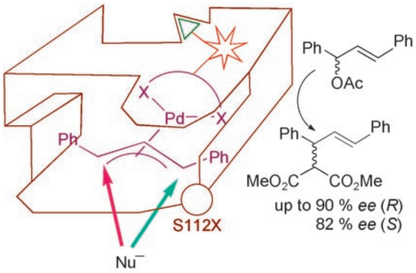
Drug Resistance



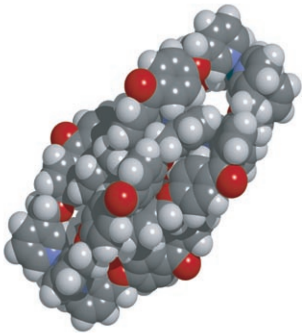
Pièces de résistance: The human immunodeficiency virus (HIV) can acquire drug resistance by mutating the key enzyme HIV protease that is being used as a drug target. A strategy has been developed to predict drug resistance that focuses on the fact that the virus must retain reasonable efficiency for its catalytic reaction while reducing its affinity to the given drug (γ_M: vitality values for the mutant protein M, K_i: inhibition constant).

Asymmetric Catalysis

Palladium in the active site: The incorporation of a biotinylated palladium diphosphine within streptavidin yielded an artificial metalloenzyme for the title reaction (see scheme). Chemogenetic optimization of the catalyst by the introduction of a spacer (red star) between biotin (green triangle) and palladium and saturation mutagenesis at position S112X afforded both *R*- and *S*-selective artificial asymmetric allylic alkylases.

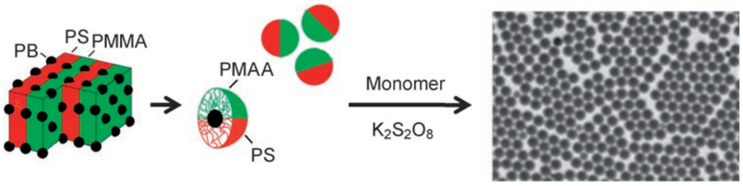


Supramolecular Chemistry



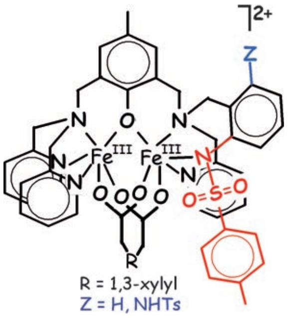
Making up a foursome: Self-assembly of 4,4′-(3-pyridinemethoxy)benzophenone (L) and $Pd(NO_3)_2$ resulted in the quantitative formation of a quadruply stranded metallohelicate $[Pd_2(L)_4]$, which undergoes spontaneous dimerization to an unprecedented chiral interlocked metallohelicate $[Pd_2(L)_4]_2$ (see X-ray structure; C black, H white, N blue, O red).

Emulsion Polymerization



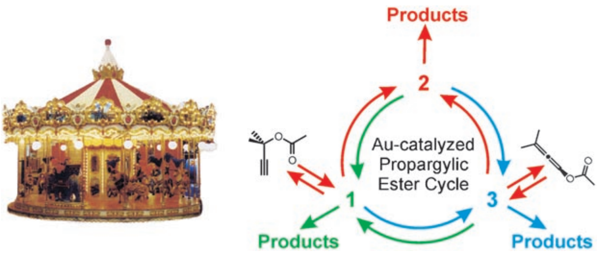
Two-faced particles: The emulsion polymerization of monomers in the presence of Janus particles, which combine the Pickering effect with amphiphilicity, leads to well-defined and stable latex dispersions (see picture). Only a few Janus beads are necessary on a latex particle surface to sufficiently stabilize the dispersion against coagulation. PB = polybutadiene, PS = polystyrene, PMMA = poly(methyl methacrylate), PMAA = poly(methacrylic acid).

Iron-Mediated Amination



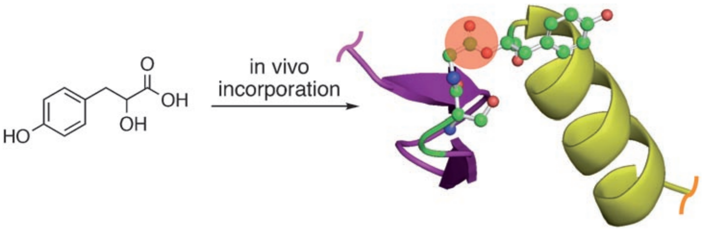
Stop-frame amination: A very efficient amine transfer reaction is mediated by a biomimetic diiron complex, giving both single and double insertions of a tosylamine group into a pendant benzyl group of the ligand (see structure). The mono-insertion product has been shown by X-ray crystallography and other physical methods to be a tosylanilinato diiron(III) complex.

Reaction Mechanisms



Round and round it goes: Propargylic esters are versatile substrates for Au-based catalysts. However, under typical conditions the starting Au-coordinated propargylic ester **1** is in rapid equilibrium with the gold vinylic carbenoid species **2** and with gold allene species **3**. A number of factors dictate which intermediate is lower in energy and which type of products form.

Protein Modifications

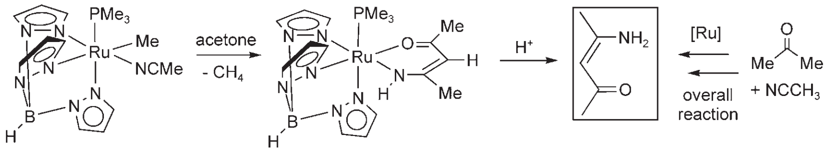


Playing tag: The α-hydroxy acid *p*-hydroxy-L-phenyllactic acid has been genetically incorporated into proteins in *E. coli* in response to an amber nonsense codon. The site-specific introduction of backbone ester mutations was used for the site-specific hydrolysis of an affinity tag, as well as for determination of the energetic contributions of backbone hydrogen bonds to protein stability.

C–H Activation

N. A. Foley, T. B. Gunnoe,* T. R. Cundari,*
P. D. Boyle, J. L. Petersen ——— **726 – 730**

Activation of sp^3 Carbon–Hydrogen Bonds by a Ruthenium(II) Complex and Subsequent Metal-Mediated C–C and C–N Bond Formation

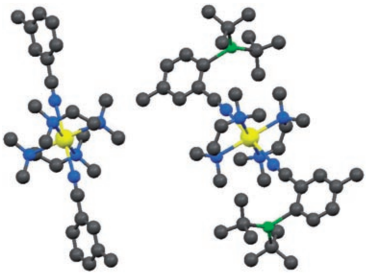


Better H than N: The Ru^{II} fragment {TpRu(PMe$_3$)Me} cleanly activates the sp^3 C–H bonds of functionalized substrates in preference to reactivity with the heterofunctional groups. C–H activation of acetonitrile, acetone, and nitromethane releases CH$_4$ with subsequent intramolecular C–C or C–N bond-forming reactions. For example, acetone and acetonitrile are converted into free enamine (see scheme).

Zincation

W. Clegg, S. H. Dale, E. Hevia, L. M. Hogg, G. W. Honeyman, R. E. Mulvey,*
C. T. O'Hara, L. Russo ——— **731 – 734**

Structurally Defined Reactions of Sodium TMP–Zincate with Nitrile Compounds: Synthesis of a Salt-Like Sodium Sodiumdizincate and Other Unexpected Ion-Pair Products

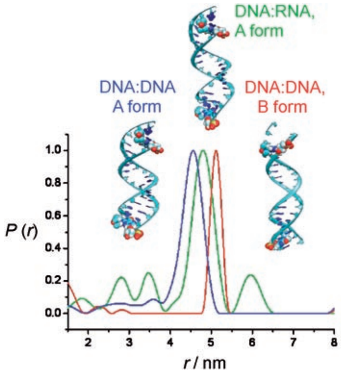


Zany zincation: Seemingly simple zincation reactions of aromatic or aliphatic nitriles are in reality highly complicated affairs involving separated ion pairs (see X-ray structure; yellow Na, blue N, green Zn; left cation, right anion) or joined ion pairs. The results also show that the free zincate anions can engage in complicated dismutation processes.

DNA Structures

G. Sicoli, G. Mathis, O. Delalande,
Y. Boulard, D. Gasparutto,
S. Gambarelli* ——— **735 – 737**

Double Electron–Electron Resonance (DEER): A Convenient Method To Probe DNA Conformational Changes

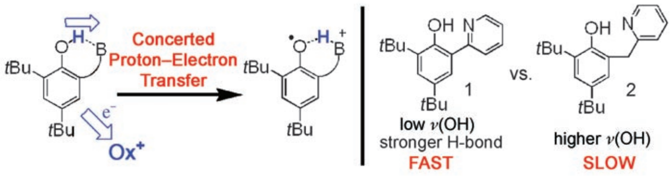


Oh DEER! The DEER technique is capable of detecting even slight conformational changes in site-directed spin-labeled DNA structures, which are extremely difficult to measure by more classical methods. The B–A transition (see picture) in DNA duplexes is induced by trifluoroethanol. DEER can be applied to the study of modifications of DNA induced by various agents.

Concerted Proton–Electron Transfer

T. F. Markle, J. M. Mayer* ——— **738 – 740**

Concerted Proton–Electron Transfer in Pyridylphenols: The Importance of the Hydrogen Bond

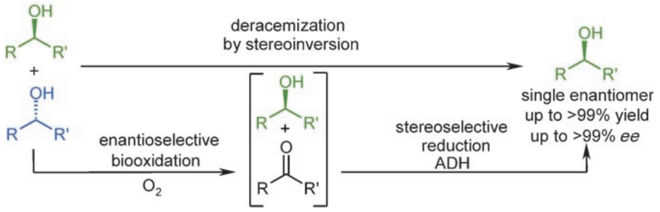


Slowed down by a break up: One-electron oxidation of intramolecularly hydrogen-bonded phenol–pyridine compounds **1** and **2** involves proton transfer coupled with electron transfer (see scheme; B = base). At the same driving force, **2** reacts substantially slower than **1**. The methylene group between the phenol and pyridine groups in **2** breaks the conjugation between the rings, which has a marked effect on the hydrogen bond and is likely the origin of the difference in rate constants.

Biocatalytic Deracemization

C. V. Voss, C. C. Gruber,
W. Kroutil* ________________ **741 – 745**

Deracemization of Secondary Alcohols through a Concurrent Tandem Biocatalytic Oxidation and Reduction

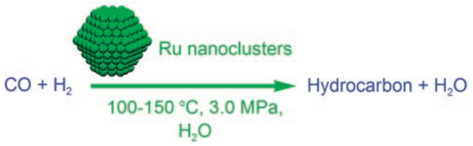


Breaking the mirror: A purified alcohol dehydrogenase (ADH) for stereoselective reduction and whole cells of a microorganism for enantioselective oxidation operated concurrently to effect the stereoinversion of one enantiomer of a racemic secondary alcohol and provide the optically pure alcohol in > 99 % yield (see scheme). R,R′ = alkyl.

Heterogeneous Catalysis

C.-X. Xiao, Z.-P. Cai, T. Wang, Y. Kou,*
N. Yan* ________________ **746 – 749**

Aqueous-Phase Fischer–Tropsch Synthesis with a Ruthenium Nanocluster Catalyst

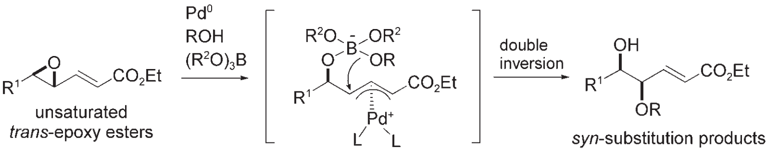


No need for support: An aqueous-phase Fischer–Tropsch synthesis with a high turnover frequency of 12.9 h^{-1} has been realized over a ruthenium nanocluster catalyst (with particle diameter of 2.0 nm) at 150 °C. This catalyst, in the absence of any support, achieves an activity that exceeds those of conventional supported catalysts.

Homogeneous Catalysis

X.-Q. Yu, F. Yoshimura, F. Ito, M. Sasaki,
A. Hirai, K. Tanino,
M. Miyashita* ________________ **750 – 754**

Palladium-Catalyzed Stereospecific Substitution of α,β-Unsaturated γ,δ-Epoxy Esters by Alcohols with Double Inversion of Configuration: Synthesis of 4-Alkoxy-5-hydroxy-2-pentenoates

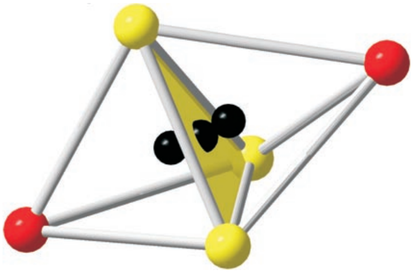


Accessing the inaccessible: Highly functionalized compounds that were previously inaccessible can be readily prepared in a highly stereoselective manner, in high yields, and even in chiral forms by the palladium-catalyzed substitution of α,β-unsaturated γ,δ-epoxy esters with various alcohols (see scheme). The products formed can serve as versatile synthetic intermediates for further transformations.

Lithium Ion Conductors

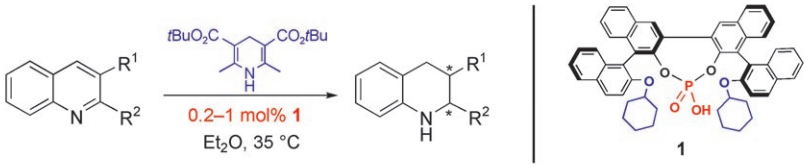
H.-J. Deiseroth,* S.-T. Kong, H. Eckert,
J. Vannahme, C. Reiner, T. Zaiß,
M. Schlosser ________________ **755 – 758**

Li_6PS_5X: A Class of Crystalline Li-Rich Solids With an Unusually High Li$^+$ Mobility



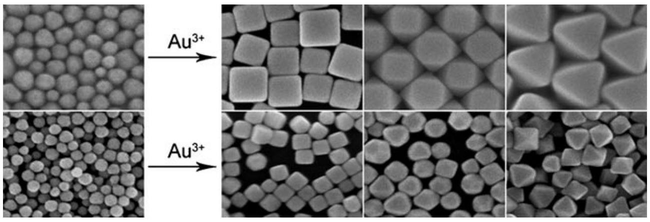
Mobile metal ions: Halide-substituted lithium argyrodites form a new class of Li-rich solids with an unusually high Li mobility. Single-crystal X-ray studies (see picture; Li black, S yellow, I red) at room temperature and MAS-NMR measurements in a wide temperature range provide insights into the Li$^+$ ion dynamics.

Asymmetric Catalysis



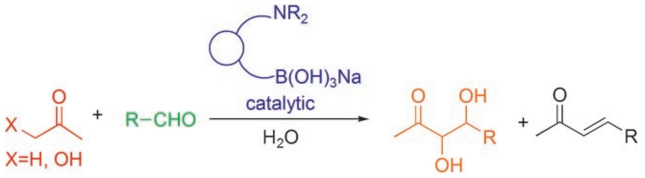
Building a better scaffold: Low loadings (0.2–1 mol%) of new double axially chiral phosphoric acid catalysts **1** based on bisbinol scaffold were used for asymmetric transfer hydrogenation. 2-Aryl- and 2-alkyl-substituted quinolines gave tetrahydroquinolines in excellent yields and with up to 98% *ee* and 2,3-disubstituted tetrahydroquinolines were prepared in high diastereo- and enantioselectivities (up to >20:1 and 92% *ee*).

Gold Nanocrystals



Shapeshifters: The shape and size of gold nanocrystals were controlled simultaneously through directed surface overgrowth from polyhedral and spherical seeds of different sizes. The resulting cubes, cuboctahedra, and octahedra (shown as SEM images for growth from spherical seeds of two sizes) exhibited characteristic optical properties in the visible range, which were analyzed by discrete dipole approximation calculations.

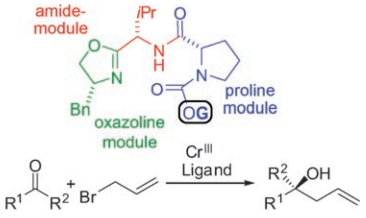
Aqueous Catalysis



Cooperation is key: *N*-Butyl-1-benzimidazole-2-phenylboronic acid hydroxide complex catalyzes the aldol condensation and aldol addition between hydroxyacetone or acetone, and different aldehydes in water. The catalytic activity results from cooperative interactions between the boronate complex and the imidazole function. Aldol condensation gives the unsaturated methyl ketones of acetone, whereas aldol addition predominates with hydroxyacetone.

Enantioselectivity

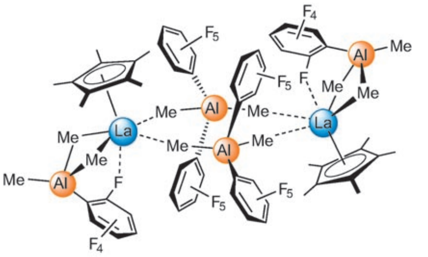
Is bigger better? By systematically evaluating the size of the substituent G in a modular ligand (see picture), a linear free energy relationship was observed relating the product enantiomeric ratio to steric parameters developed by Charton. The reaction studied was the addition of allyl bromide to three different carbonyl substrates.



Polymerization

M. Zimmermann, K. W. Törnroos,
R. Anwander* ______ 775 – 778

Cationic Rare-Earth-Metal Half-Sandwich Complexes for the Living *trans*-1,4-Isoprene Polymerization

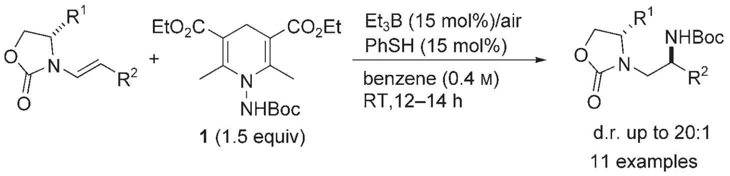


Rare, but well done! Fluorinated borates $[Ph_3C][B(C_6F_5)_4]$ and $[PhNMe_2H][B(C_6F_5)_4]$ and the borane reagent $B(C_6F_5)_3$ activate rare-earth-metal bis(tetramethylaluminate) complexes in a distinct and efficient manner (an activated catalyst is shown in the picture) for the fabrication of synthetic gutta-percha (99.5 % *trans*-1,4-polyisoprene, $M_n = 0.8–4.4 \times 10^5$ g mol^{-1}, $M_n/M_w = 1.18$).

Synthetic Methods

J. Guin, R. Fröhlich, A. Studer* 779 – 782

Thiol-Catalyzed Stereoselective Transfer Hydroamination of Olefins with N-Aminated Dihydropyridines

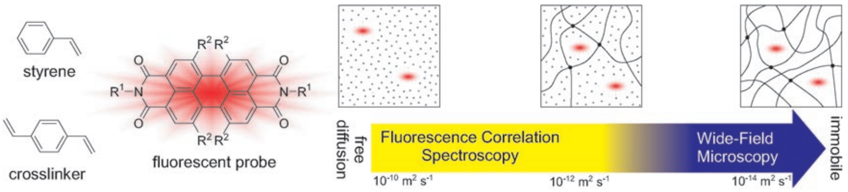


Hantzsch dihydropyridines are popular reducing reagents in organocatalysis. The N-aminated Hantzsch dihydropyridine **1** has now been used as a novel efficient precursor for Boc-protected carbamoyl radicals. The readily prepared reagent was employed for the radical-transfer hydroamination of various olefins. Stereoselective hydroamination of chiral enecarbamates afforded vicinal diamines in good stereoselectivities. Boc = *tert*-butyloxycarbonyl.

Polymerization

D. Wöll, H. Uji-i, T. Schnitzler, J.-I. Hotta,
P. Dedecker, A. Herrmann,
F. C. De Schryver, K. Müllen,
J. Hofkens* ______ 783 – 787

Radical Polymerization Tracked by Single Molecule Spectroscopy

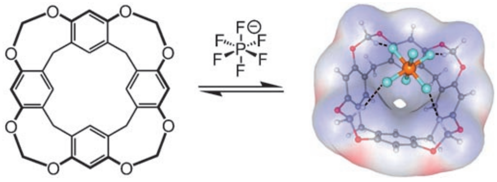


Polymerization—a single molecule view: Molecular motion of free and incorporated single perylene diimide derivatives during radical polymerization of styrene and styrene networks, studied by a combination of fluorescence correlation spectroscopy and wide-field microscopy, can be observed over the entire conversion range from free diffusion to immobilization of the dyes. In particular, the presence of evolving heterogeneities could be visualized.

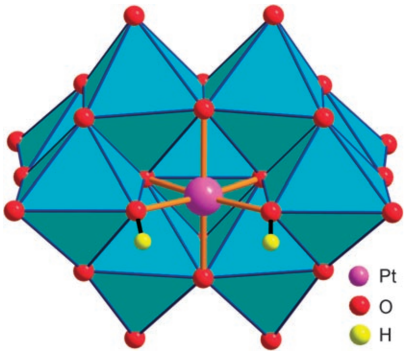
Weak Interactions

S. S. Zhu, H. Staats, K. Brandhorst,
J. Grunenberg, F. Gruppi, E. Dalcanale,
A. Lützen, K. Rissanen,
C. A. Schalley* ______ 788 – 792

Anion Binding to Resorcinarene-Based Cavitands: The Importance of C–H···Anion Interactions



Anions rather than cations: While resorcinarenes bind cations through cation–π interactions, methylene-bridged cavitands surprisingly bind anions through C–H···anion interactions with the acetal protons at the wider rim (see model of the complex in the scheme). Mass spectrometry, in agreement with theory, provides evidence for anion binding on the concave side of the cavitand bowl.



A new mate for vanadate: The platinum(IV)-containing polyoxovanadate $[H_2Pt^{IV}V_9O_{28}]^{5-}$ (**1**) has been synthesized and structurally characterized (see polyhedral representation). The characterization of polyanion **1** in solution by ^{195}Pt NMR spectroscopy is unprecedented in POM chemistry. The facile synthetic procedure with the Pt^{IV} precursor $H_2Pt(OH)_6$ appears to be a convenient and general methodology for making a large variety of Pt^{IV}-containing polyoxometalates.

Pt-Containing Polyoxometalates

Supporting information is available on the WWW (see article for access details).

A video clip is available as Supporting Information on the WWW (see article for access details).

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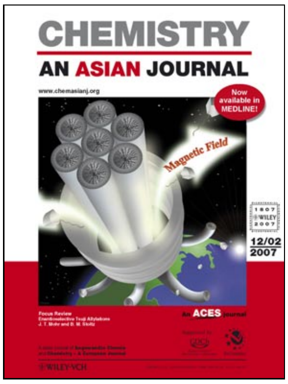


Corrigenda

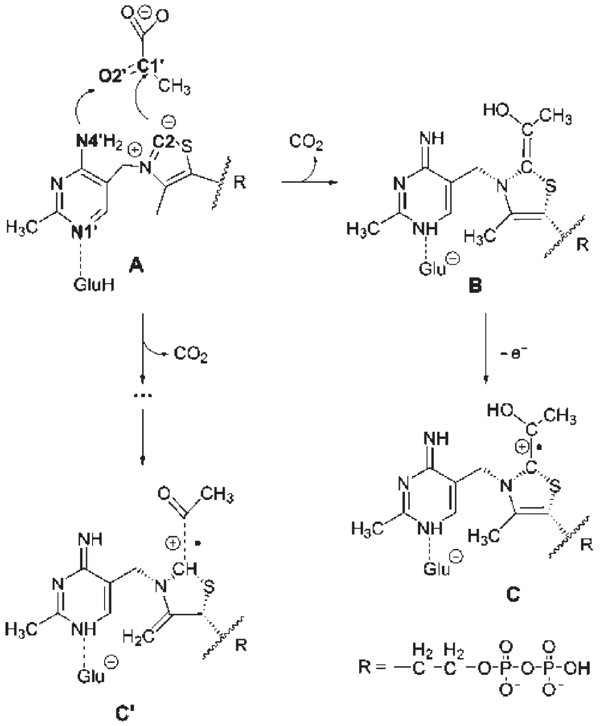
The Enamine Intermediate May Not Be Universal to Thiamine Catalysis

P. Amara,* I. Fdez. Galván,
J. C. Fontecilla-Camps,*
M. J. Field ______________ **9019–9022**

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

DOI 10.1002/anie.200702993

In Scheme 1 of this Communication, a CO_2 product molecule is missing in the top reaction (**A** → **B**). The correct scheme is shown here.



Scheme 1. Decarboxylation of pyruvate by ThDP in the "V" conformation starting from the ylide in the presence of pyruvate (state **A**). Upper scheme: Formation of the HE-ThDP (or enamine) intermediate (state **B**) followed by one-electron oxidation to the HE-ThDP π radical (state **C**).[1,5,26] Lower scheme: Formation of a σ/n-type cation radical (state **C**′) by one-electron oxidation with no enamine intermediate.[11] Atoms mentioned in the manuscript are shown in bold type.

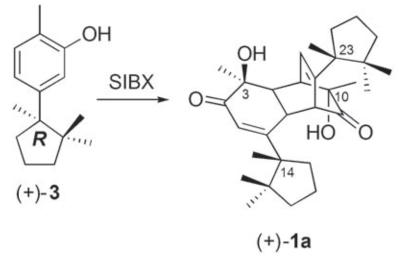
Total Synthesis of (+)-Aquaticol by Biomimetic Phenol Dearomatization: Double Diastereofacial Differentiation in the Diels–Alder Dimerization of Orthoquinols with a C_2-Symmetric Transition State

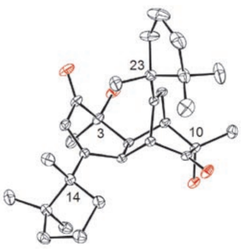
J. Gagnepain, F. Castet,
S. Quideau* ______________ **1533–1535**

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

DOI 10.1002/anie.200604610

The absolute configuration of (+)-aquaticol (**1a**) described in this Communication should be revised to 3*S*,10*S*,14*R*,23*R* as shown on the structure below and its accompanying ORTEP diagram (monoclinic, $P2_1$, Flack factor = −0.2(2), CCDC—295794). (+)-Aquaticol was derived from SIBX-mediated oxidation of (+)-(*R*)-hydroxycuparene (**3**). We thank Professor John Porco and Suwei Dong (Boston University) for pointing out this issue.





Corrigendum

Gulliver T. Dalton, Australian National University, Canberra, ACT 0200 (Australia), was inadvertently omitted from the author list of this Communication. The authors apologize for this oversight.

Electrochemical Switching of the Cubic Nonlinear Optical Properties of an Aryldiethynyl-Linked Heterobimetallic Complex between Three Distinct States

M. Samoc,* N. Gauthier, M. P. Cifuentes,
F. Paul,* C. Lapinte,
M. G. Humphrey* ________ **7376–7379**

Angew. Chem. Int. Ed. **2006**, *45*

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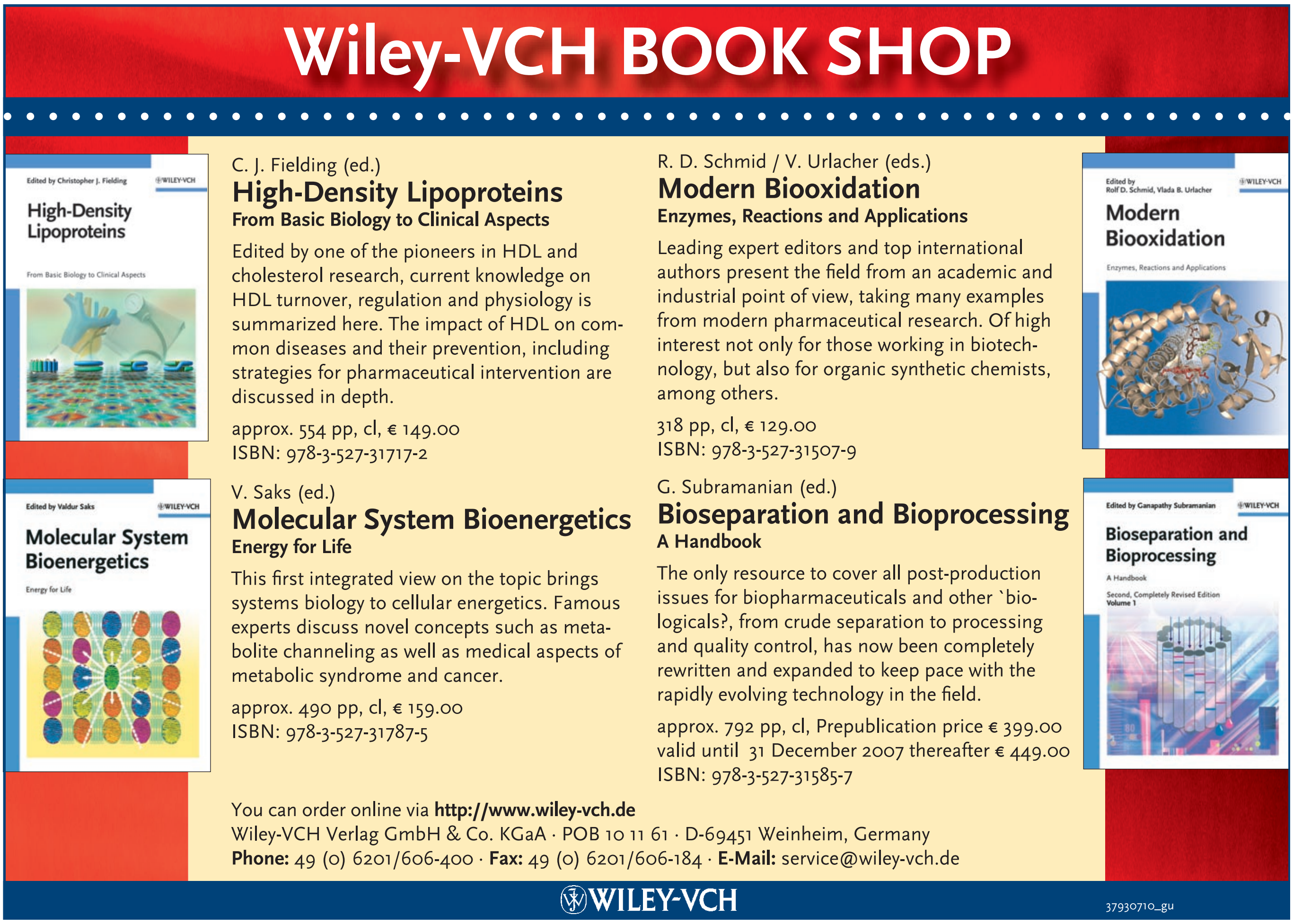
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