



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:

Q. Wang, M. Zhang, C. Chen, W. Ma, J. Zhao*

**Photocatalytic Aerobic Oxidation of Alcohols on TiO₂:
The Acceleration Effect of Brønsted Acids**

Y. Fu, Q. Dai, W. Zhang, J. Ren, T. Pan,* C. He*

**AlkB Domain of Mammalian ABH8 Catalyzes Hydroxylation of
5-Methoxycarbonylmethyluridine at the Wobble Position of tRNA**

M. Roth, P. Kindervater, H.-P. Raich, J. Bargon, H. W. Spiess,*
K. Münnemann*

**Continuous ¹H and ¹³C Signal Enhancement in NMR
Spectroscopy and MRI Using Parahydrogen and Hollow Fiber
Membranes**

H. Zheng, J. Gao*

**Highly Specific Heterodimerization Mediated by Quadrupole
Interactions**

S. P. Annen, V. Bambagioni, M. Bevilacqua, J. Filippi,
A. Marchionni, W. Oberhauser, H. Schönberg, F. Vizza,*
C. Bianchini,* H. Grützmacher*

**A Biologically Inspired Organometallic Fuel Cell (OMFC) that
Converts Renewable Alcohols into Energy and Chemicals**

M. Willis, M. Götz, A. K. Kandalam, G. F. Ganteför,* P. Jena*

Hyperhalogens: A New Class of Highly Electronegative Species

V. Mazumder, M. Chi, K. L. More, S. Sun*

**Synthesis and Characterization of Multimetallic Pd/Au and
Pd/Au/FePt Core/Shell Nanoparticles**

P. Chakraborty, I. Krivokapic, R. Bronisz, C. Enachescu, A. Hauser*
**Giant Variation of the Singlet–Quintet Intersystem Crossing Rate
Constant in an Iron(II) High-Spin Complex as a Function of
Temperature**

H. Li, A. C. Fahrenbach, S. K. Dey, S. Basu, A. Trabolsi, Z. Zhu,
Y. Y. Botros, J. F. Stoddart*

Mechanical Bond Formation by Radical Templatation

G. Yao, C. Deng,* X. Zhang, P. Yang

**Efficient Tryptic Proteolysis Accelerated by Laser Radiation for
Peptide Mapping in Proteome Analysis**

K. P. Neupane, V. L. Pecoraro*

**Probing a Homoleptic PbS₃ Coordination Environment in a
Designed Peptide Using ²⁰⁷Pb NMR Spectroscopy: Implications
for Understanding the Molecular Basis of Lead Toxicity**



*“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.

Author Profile

Bernhard Kräutler _____ 7620



C. Cummins



K. Suzuki



E. N. Jacobsen

News

Alexander von
Humboldt Research Awards:
C. Cummins and K. Suzuki _____ 7621

Janssen Pharmaceutica Prize:
E. N. Jacobsen _____ 7621

Books

Organotransition Metal Chemistry

John F. Hartwig

reviewed by B. F. Straub _____ 7622

Highlights

Insulin

H.-J. Musiol, L. Moroder* — 7624–7626

Two-Chain Insulin from a Single-Chain Branched Depsipeptide Precursor: The End of a Long Journey



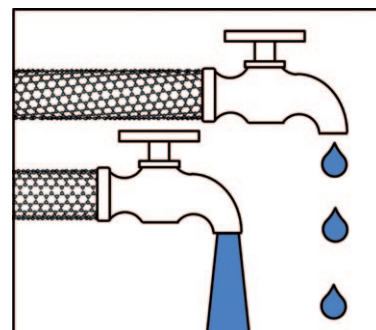
Coupled chains: A fully synthetic single-chain branched depsipeptide precursor lacking a proinsulin-like tethering of the A and B chains leads, by oxidative folding to the insulin characteristic cystine topology and by subsequent saponification of the ester bond, to the target two-chain insulin molecule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

Nanofluidics

S. G. Lemay* — 7627–7628

Fluidics Meets Electronics: Carbon Nanotubes as Nanopores

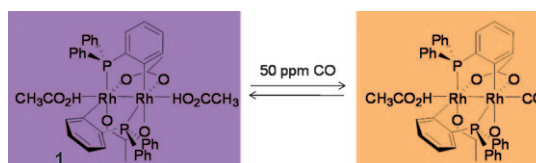
Go with the flow: The transport of salt ions and single-stranded DNA through individual single-walled carbon nanotubes marks the advent of a new type of solid-state nanopore. Surprisingly, the transport process shows a marked dependence on the electronic properties of the nanotubes: two nanotube “pipes”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



Sensors

S. Heylen, J. A. Martens* — 7629–7630

Progress in the Chromogenic Detection of Carbon Monoxide



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 H₂O, CO₂, O₂, CH₄, SO₂, NO_x, and volatile organic compounds do not interfere with the CO sensing.

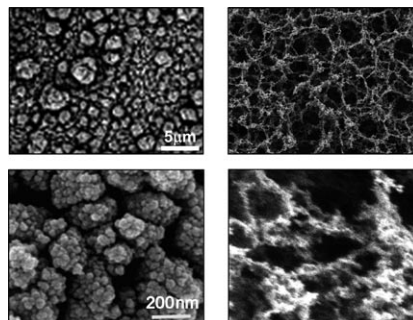
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individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Reviews

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– μ m 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

A. Tricoli,* M. Righettoni,
A. Teleki* ————— 7632–7659

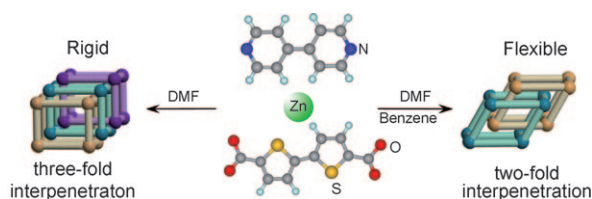
Semiconductor Gas Sensors: Dry
Synthesis and Application

Communications

Coordination Polymers

S. Bureekaew, H. Sato, R. Matsuda,*
Y. Kubota, R. Hirose, J. Kim, K. Kato,
M. Takata, S. Kitagawa* — 7660–7664

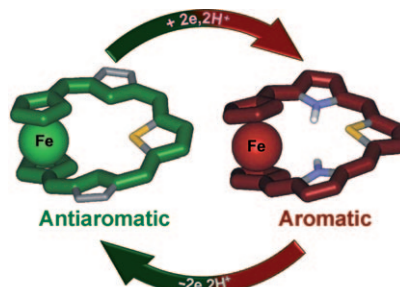
Control of Interpenetration for Tuning
Structural Flexibility Influences Sorption
Properties



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.

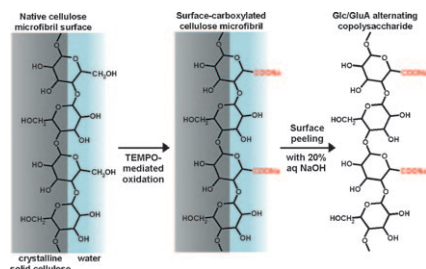
Setting the 'cene: The structural features of ferrocenophanes and porphyrinoids are combined in ferrocene–porphyrin hybrids. Ferrocenothiaporphyrin (see picture, green) and dihydroferrocenothiaporphyrin (red) are macrocyclic antiaromatic and aromatic systems, respectively. These two systems provide evidence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



Porphyrinoids

I. Simkova, L. Latos-Grażyński,*
M. Stępień ————— 7665–7669

π Conjugation Transmitted across a
d-Electron Metallocene in Ferro-
cenothiaporphyrin Macrocycles



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 $\rightarrow$ 4)- β -linked glucose/glucuronic acid (Glc/GluA) alternating copolysaccharides (see scheme; TEMPO = 2,2,6,6-tetramethylpiperidin-1-ylxyl).

Alternating Copolysaccharides

M. Hirota, K. Furihata, T. Saito, T. Kawada,
A. Isogai* ————— 7670–7672

Glucose/Glucuronic Acid Alternating Co-
polysaccharides Prepared from TEMPO-
Oxidized Native Celluloses by Surface
Peeling

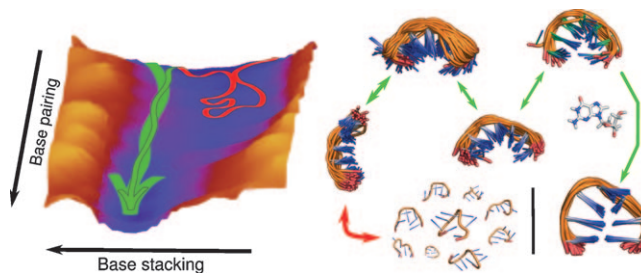


Molecular Dynamics

G. Portella, M. Orozco* — 7673–7676



Multiple Routes to Characterize the Folding of a Small DNA Hairpin



DNA perming: Folding of a small DNA hairpin from an extended conformation follows two main folding pathways: direct folding (green arrows) and de-trapping

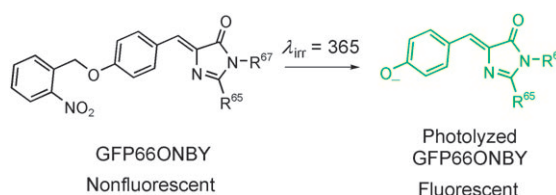
from non-native compact structures (red arrows). (Also shown: guanosine 5'G *anti* form.)

Molecular Highlighters

D. Groff, F. Wang, S. Jockusch, N. J. Turro,* P. G. Schultz* — 7677–7679



A New Strategy to Photoactivate Green Fluorescent Protein



A bright idea: A photoactivatable GFP variant has been developed by mutagenesis of the fluorophore tyrosine to a photocaged *o*-nitrobenzyl tyrosine. This protein is practically nonfluorescent until exposed to 365 nm light, which increases

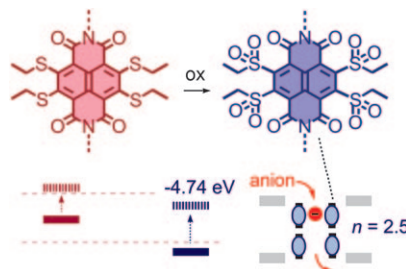
fluorescence nearly 100-fold. The quenching mechanism as suggested by crystallography and time-resolved UV/Vis spectroscopy is most likely due to photon-induced electron transfer to the nitrobenzyl group.

Functional Supramolecular Systems

J. Míšek, A. Vargas Jentzsch, S. Sakurai, D. Emery, J. Marek, S. Matile* — 7680–7683



A Chiral and Colorful Redox Switch: Enhanced π Acidity in Action



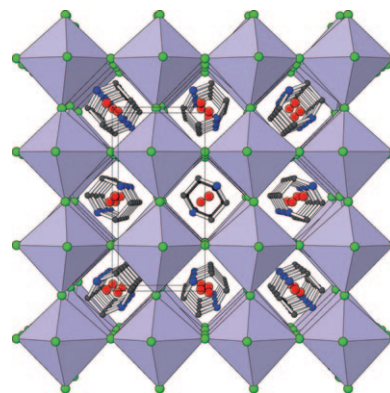
Deep blue diving: π Acidities up to a new record of -4.74 eV are made possible with simple sulfur redox chemistry (see scheme). This attractive method is able to generate exceptional electron affinities and anion transport efficiencies for applications in optoelectronic devices, medicinal chemistry, and anion– π catalysis.

Perovskites

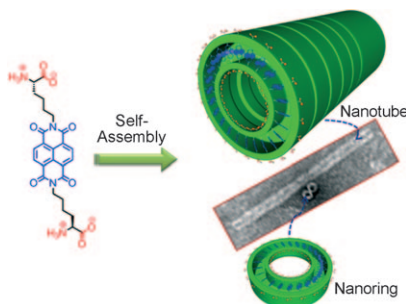
L. A. Paton, W. T. A. Harrison* — 7684–7687

Structural Diversity in Non-Layered Hybrid Perovskites of the RMCl_3 Family

A novel family: Besides thousands of metal oxide perovskites (simplest formula ABO_3) layered hybrid perovskites exist, in which slabs of vertex-sharing metal halide octahedra are separated by organic cations. Here, a “missing link” between these two families is described: nonlayered hybrid perovskite networks containing both inorganic (alkali metal and chloride ions) and organic constituents (see, for example, $\text{C}_4\text{H}_{12}\text{N}_2 \cdot \text{KCl}_3 \cdot \text{H}_2\text{O}$; KCl_6 octahedra lilac, Cl green, C dark gray, N blue, O red).



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

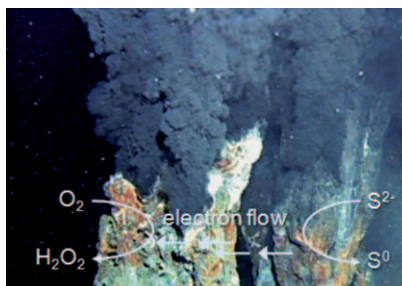


H. Shao, J. Seifert, N. C. Romano, M. Gao, J. J. Helmus, C. P. Jaroniec, D. A. Modarelli, J. R. Parquette* — 7688 – 7691

Amphiphilic Self-Assembly of an n-Type Nanotube



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.



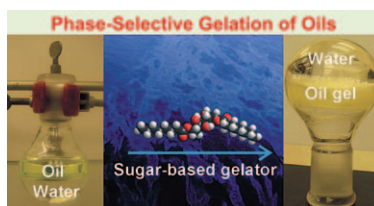
Marine Chemistry

R. Nakamura,* T. Takashima, S. Kato, K. Takai, M. Yamamoto, K. Hashimoto — 7692 – 7694

Electrical Current Generation across a Black Smoker Chimney



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.



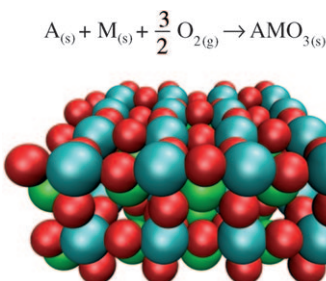
Molecular Gelators

S. R. Jadhav, P. K. Vemula, R. Kumar, S. R. Raghavan, G. John* — 7695 – 7698

Sugar-Derived Phase-Selective Molecular Gelators as Model Solidifiers for Oil Spills



Trends in formation energies $\Delta G_{\text{exptl}}^{\text{form}}$ of 41 perovskites AMO_3 at 298 K are reproduced by $\Delta G_{\text{DFT}}^{\text{form}}$ 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

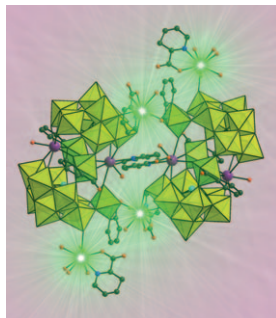
F. Calle-Vallejo, J. I. Martínez, J. M. García-Lastra, M. Mogensen, J. Rossmeisl* — 7699 – 7701

Trends in Stability of Perovskite Oxides



Polyoxometalate Hybrids

C. Ritchie, E. G. Moore, M. Speldrich,
P. Kögerler, C. Boskovic* — 7702–7705



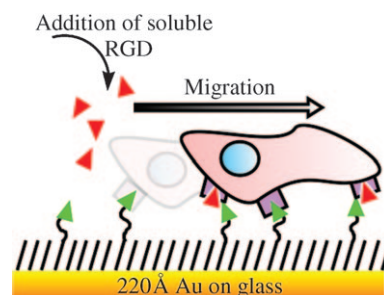
Light up the POMs: A luminescent lanthanoid complex with polyoxometalate (POM) and organic ligands has been structurally characterized (see picture). Comparison of this octanuclear Tb^{III} complex of 2-picolinate and tungsto-arsenate ligands with a dinuclear relative reveals the role of the organic ligands as chromophores, identifies the luminescent Tb centers, and determines the relationship between POM coordination mode and luminescence quenching.

Cell Migration

S. H. Shabbir, J. L. Eisenberg,
M. Mrksich* — 7706–7709

An Inhibitor of a Cell Adhesion Receptor Stimulates Cell Migration

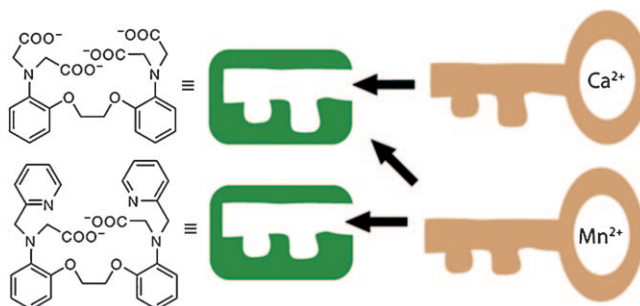
Making cells get a move on: The integrins are cell-surface receptors that mediate the adhesion and migration of cells on a protein matrix. An open question is whether addition of an inhibitor of the receptor slows or accelerates cell migration. By using self-assembled monolayers presenting a cell adhesion ligand as a model system it is found that an inhibitor (RGD peptide) can stimulate cell migration.



Molecular Recognition

J. Liang, J. W. Canary* — 7710–7713

Discrimination between Hard Metals with Soft Ligand Donor Atoms: An On-Fluorescence Probe for Manganese(II)

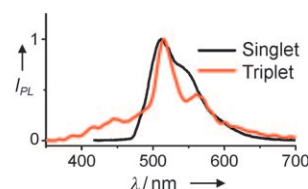
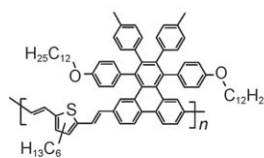


A backwards strategy for achieving Mn²⁺/Ca²⁺ selectivity was demonstrated: Instead of optimizing binding of Mn²⁺, the bapta ligand (upper structure in scheme) was modified by changing O to

N donors to discourage association by unwanted competitor Ca²⁺. Attachment of a fluorophore gave a Mn²⁺-selective on-fluorescent probe for use in live cell imaging.

π-Conjugated Polymers

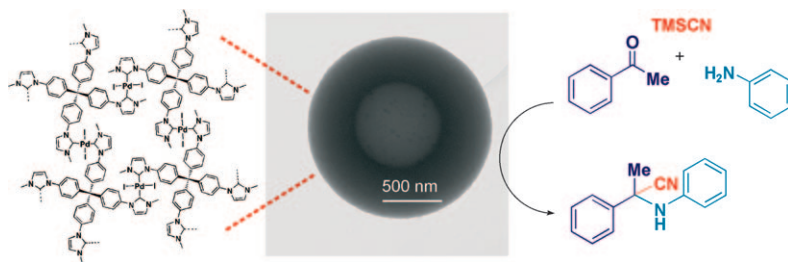
D. Chaudhuri, H. Wettach,
K. J. van Schooten, S. Liu, E. Sigmund,
S. Höger,* J. M. Lupton* — 7714–7717



Tuning the Singlet–Triplet Gap in Metal-Free Phosphorescent π-Conjugated Polymers

Glow in the dark: A tunable singlet–triplet exchange gap arises in optically active conjugated polymers that exhibit both strong fluorescence from the singlet state

and pronounced phosphorescence from triplet excitations (see picture). The polymers were incorporated into organic light-emitting diodes (OLEDs).



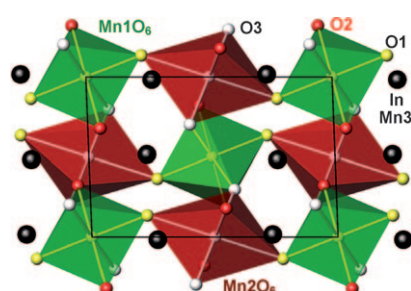
Hollow-sphere catalysts were prepared by means of 3D network formation between a tetraimidazolium building block and palladium acetate. The bis(*N*-heterocyclic carbene)–palladium species that were concomitantly formed during growth of

the hollow spheres showed excellent activity as heterogeneous catalysts in one-pot three-component Strecker reactions of ketones (see picture; TMS = trimethylsilyl).

Organometallic Hollow Spheres

J. Choi, H. Y. Yang, H. J. Kim,
S. U. Son* — 7718–7722

Organometallic Hollow Spheres Bearing Bis(*N*-Heterocyclic Carbene)–Palladium Species: Catalytic Application in Three-Component Strecker Reactions



More Mn: New perovskite oxides ($(\text{In}_{1-y}\text{Mn}_y)\text{MnO}_3$ ($1/9 \leq y \leq 1/3$, see picture) were prepared by using a high-pressure technique. The A site is doped with Mn^{2+} ions, and $(\text{In}_{1-y}\text{Mn}_y)\text{MnO}_3$ is similar to $(\text{Lu}_{1-y}\text{Ca}_y)\text{MnO}_3$. The B-site-ordered structure is realized through the ordering of Mn^{3+} and Mn^{4+} ions. Materials with $y \leq 0.25$ demonstrate spin-glass-like properties, while $(\text{In}_{2/3}\text{Mn}_{1/3})\text{MnO}_3$ shows magnetic properties typical for canted antiferromagnets.

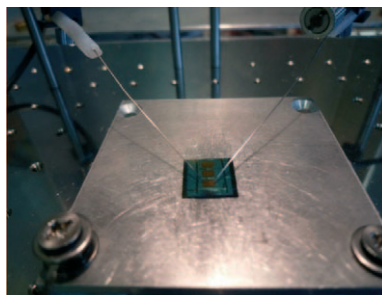
Perovskites

A. A. Belik,* Y. Matsushita, M. Tanaka,
E. Takayama-Muromachi — 7723–7727

$(\text{In}_{1-y}\text{Mn}_y)\text{MnO}_3$ ($1/9 \leq y \leq 1/3$): Unusual Perovskites with Unusual Properties



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

T. Kawase,* T. Fujiwara, C. Kitamura,
A. Konishi, Y. Hirao, K. Matsumoto,
H. Kurata, T. Kubo, S. Shinamura, H. Mori,
E. Miyazaki, K. Takimiya* — 7728–7732

Dinaphthopentalenes: Pentalene Derivatives for Organic Thin-Film Transistors



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

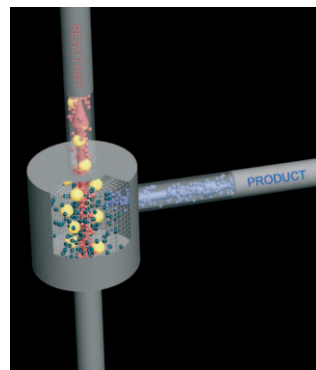
J. Lindh, P. J. R. Sjöberg,
M. Larhed* — 7733–7737

Synthesis of Aryl Ketones by Palladium(II)-Catalyzed Decarboxylative Addition of Benzoic Acids to Nitriles



Homogeneous Catalysis

M. Janssen, J. Wilting, C. Müller,*
D. Vogt* 7738–7741



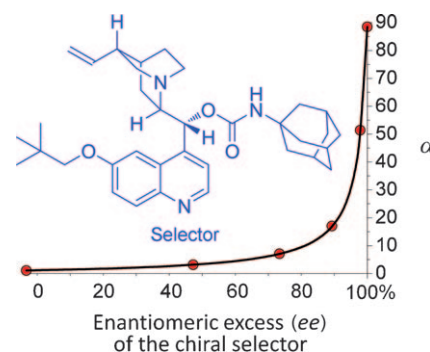
Go with the flow: Homogeneous catalyst recycling can be applied to the production of aldehydes in a continuous flow nano-filtration reactor (see picture) that can operate for an unprecedented period of up to two weeks without showing typical deactivation or leaching phenomena. The catalyst is based on a bulky, rigid, and robust silsesquioxane-modified PPh_3 ligand, and combines efficient recovery with high activity and selectivity.

Enantioseparation

P. A. Levkin, N. M. Maier, V. Schurig,
W. Lindner* 7742–7744

Strong Detrimental Effect of a Minute Enantiomeric Impurity of a Chiral Selector on the Enantioselectivity Factor

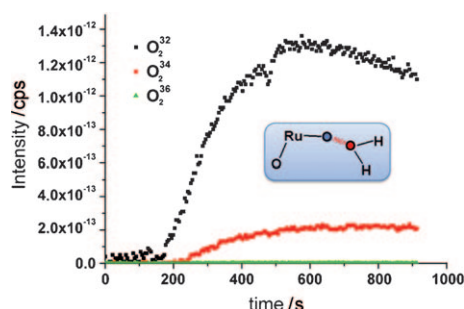
Without a trace? The higher the enantioselectivity of a chiral selector, the more it is sensitive to enantiomeric impurities. Therefore, the enantiomeric purity of a chiral selector affects the enantioseparation factor α (see picture).



Water Oxidation

X. Sala, M. Z. Ertem, L. Vigarà,
T. K. Todorova, W. Chen, R. C. Rocha,
F. Aquilante, C. J. Cramer,* L. Gagliardi,*
A. Llobet* 7745–7747

The $\text{cis-}[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{H}_2\text{O})_2]^{2+}$ Water-Oxidation Catalyst Revisited



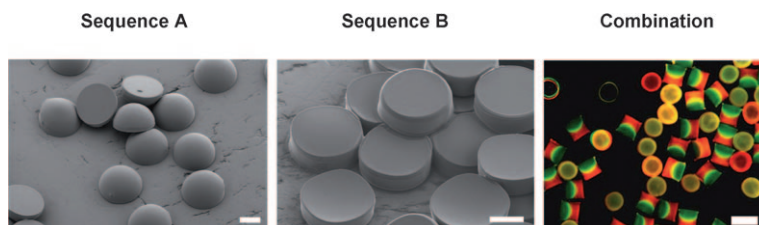
The only operating mechanism in the oxidation of water to dioxygen catalyzed by the mononuclear $\text{cis-}[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{H}_2\text{O})_2]^{2+}$ complex when treated with excess Ce^{IV} was unambiguously estab-

lished. Theoretical calculations together with ^{18}O -labeling experiments (see plot) revealed that it is the nucleophilic attack of water on a Ru-O group.

Monodisperse Particles

C.-H. Choi, J. Lee, K. Yoon, A. Tripathi,
H. A. Stone, D. A. Weitz,
C.-S. Lee* 7748–7752

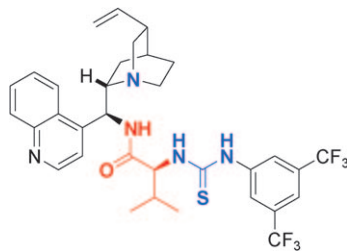
Surface-Tension-Induced Synthesis of Complex Particles Using Confined Polymeric Fluids



Resolving the tension: Complex particles with various shapes such as bullets, cylinders, discs, hearts, hexagons, and Janus particles can be synthesized by two different surface-tension-induced flow sequences (A and B; see picture, scale

bars = 100 μm). The particles produced by using this approach can be exploited as anisotropic building blocks for the fabrication of complex systems by combination of the two sequences.

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-di-substituted oxindoles and indolines with an all-carbon quaternary stereogenic center.



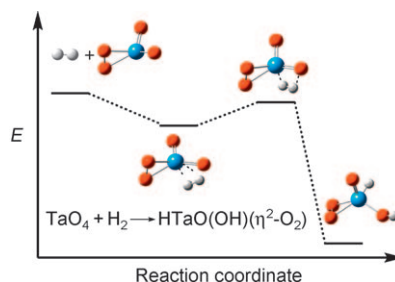
Asymmetric Catalysis

Q. Zhu, Y. Lu* 7753 – 7756

Stereocontrolled Creation of All-Carbon Quaternary Stereocenters by Organocatalytic Conjugate Addition of Oxindoles to Vinyl Sulfone



Get active: Neutral TaO₄ d⁰ complex is able to cleave dihydrogen heterolytically and spontaneously to form [HTaO(OH)(η²-O₂)] in solid argon at cryogenic temperatures. Theoretical calculations predict that the hydrogen atoms in [HTaO(OH)(η²-O₂)] can easily be transferred to organic compounds. Thus, TaO₄ can serve as a model catalyst for hydrogenation reactions.



Small-Molecule Activation

M. F. Zhou,* C. X. Wang, Z. H. Li, J. Zhuang, Y. Y. Zhao, X. M. Zheng, K. N. Fan 7757 – 7761

Spontaneous Dihydrogen Activation by Neutral TaO₄ Complex at Cryogenic Temperatures



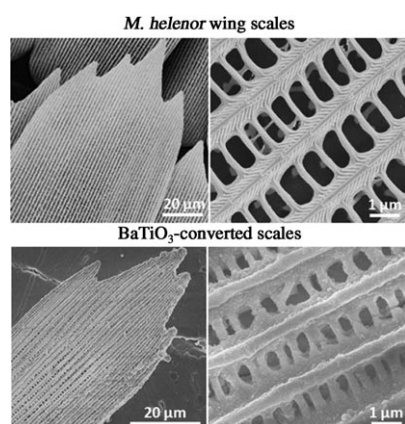
Getting up to speed: Both LiCl and the YCl₃/MeLi catalyst system have an acceleration effect upon the substitution of silanes using Grignard reagents (see

scheme). The method provides access to benzyl-, allyl-, and arylsilanes in good yields from the starting silanes.

Synthetic Methods

N. Hirone, H. Sanjiki, R. Tanaka, T. Hata, H. Urabe* 7762 – 7764

Acceleration of the Substitution of Silanes with Grignard Reagents by Using either LiCl or YCl₃/MeLi



Chitinous wing scales of *Morpho helenor* butterflies were converted into BaTiO₃ 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

J. P. Vernon, Y. Fang, Y. Cai, K. H. Sandhage* 7765 – 7768

Morphology-Preserving Conversion of a 3D Bioorganic Template into a Nanocrystalline Multicomponent Oxide Compound

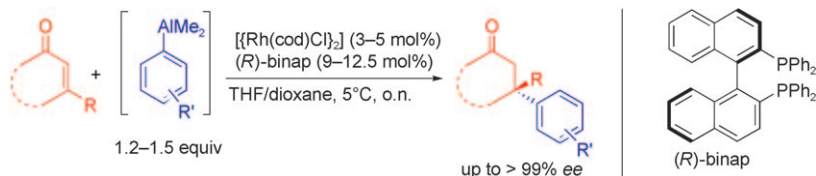


Asymmetric Catalysis

C. Hawner, D. Müller, L. Gremaud,
A. Felouat, S. Woodward,*
A. Alexakis* — 7769–7772



Rhodium-Catalyzed Asymmetric 1,4-Addition of Aryl Alanes to Trisubstituted Enones: Binap as an Effective Ligand in the Formation of Quaternary Stereocenters



All for one and 1,4-all: Readily available aryl alanes are used in the rhodium-catalyzed asymmetric conjugate addition reaction with a variety of cyclic and acyclic enones. The enhanced reactivity of the

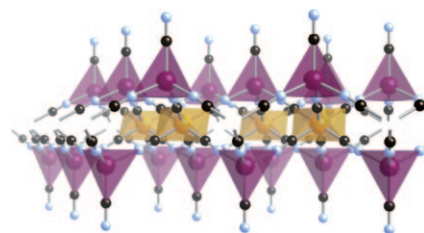
system allows the use of the common binap ligand for the generation of quaternary benzylic stereocenters in excellent enantioselectivity (see scheme).

Prussian Blue Materials

J.-H. Her, P. W. Stephens, C. M. Kareis,
J. G. Moore, J. S. Miller* — 7773–7775

Anomalous Stoichiometry, Layered Structure, and Magnetic Ordering for the Prussian Blue Analogue $[\text{NEt}_4]_2[\text{Mn}^{\text{II}}_3(\text{CN})_8]$

Unprecedented: Atypical of Prussian blue structured materials, Mn^{II} and $[\text{NEt}_4]\text{CN}$ react to form $[\text{NEt}_4]_2\text{Mn}_3(\text{CN})_8$ possessing layers of octahedral $[\text{Mn}^{\text{II}}(\text{CN})_6]^{4-}$ bonded to two high-spin tetrahedral Mn^{II} sites (see structure; yellow and red Mn, black C, blue N).



Solid Acids

J. Huang, N. van Vegten, Y. Jiang,
M. Hunger, A. Baiker* — 7776–7781



Increasing the Brønsted Acidity of Flame-Derived Silica/Alumina up to Zeolitic Strength

Feel the burn: Silica/alumina was prepared in milliseconds by flame-spray pyrolysis (see picture) with a homogeneous composition and at super-high calcination temperatures. This solid acid has tunable acidity ranging from weak or moderate to strong Brønsted acidity. This unique property makes this material versatile for desired industrial applications.

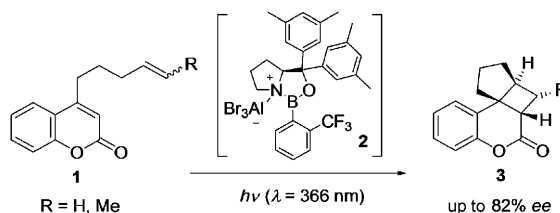


Photochemistry

H. Guo, E. Herdtweck,
T. Bach* — 7782–7785

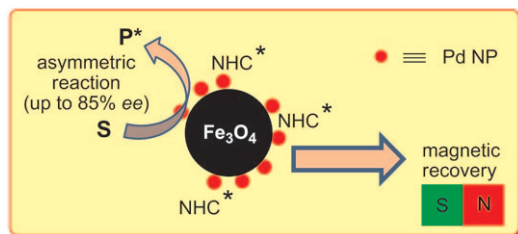


Enantioselective Lewis Acid Catalysis in Intramolecular [2+2] Photocycloaddition Reactions of Coumarins



Photochemistry goes acidic! In the presence of the chiral Lewis acid catalyst **2** the intramolecular [2+2] photocycloaddition of 4-(alk-4-enyl)coumarins (**1**) provides the corresponding products **3** with up to four stereogenic centers in a highly

chemo- (84–89% yield) and stereoselective fashion. For R = H, enantioselectivities up to 82% ee are possible with 50 mol% catalyst **2** and up to 78% ee with only 20 mol% of catalyst **2**.



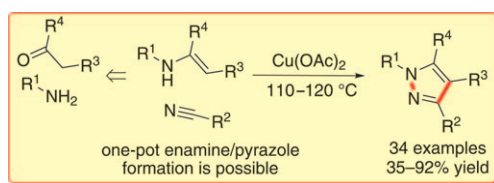
Superficial success: A chiral N-heterocyclic carbene (NHC*) is used to modify $\text{Fe}_3\text{O}_4/\text{Pd}$ nanoparticles, which then catalyze asymmetric α -arylations. This successful synthesis of a heterogeneous

catalyst and its application in asymmetric catalysis is in stark contrast to the simple immobilization of an established chiral homogeneous catalyst.

Nanocatalysis

K. V. S. Ranganath, J. Klosesges,
A. H. Schäfer, F. Glorius* — 7786–7789

Asymmetric Nanocatalysis:
N-Heterocyclic Carbenes as Chiral
Modifiers of $\text{Fe}_3\text{O}_4/\text{Pd}$ nanoparticles



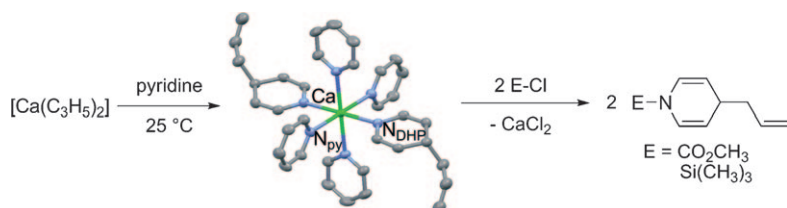
Golden section: A novel synthetic strategy for the synthesis of tetrasubstituted pyrazoles is provided. In an efficient C–C/N–N bond-formation cascade, enamines and nitriles are oxidatively coupled to deliver pyrazoles in good yields

(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

J. J. Neumann, M. Suri,
F. Glorius* — 7790–7794

Efficient Synthesis of Pyrazoles: Oxidative
C–C/N–N Bond-Formation Cascade



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 cal-

cium 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.

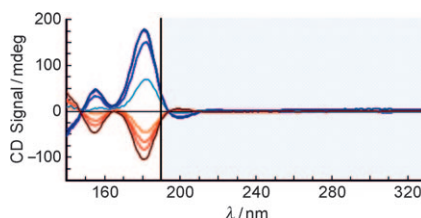
Organocalcium Chemistry

P. Jochmann, T. S. Dols, T. P. Spaniol,
L. Perrin, L. Maron,*
J. Okuda* — 7795–7798

Insertion of Pyridine into the Calcium Allyl
Bond: Regioselective 1,4-Dihydropyridine
Formation and C–H Bond Activation



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

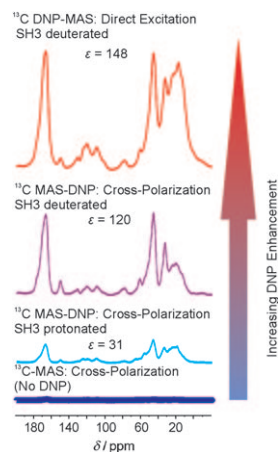
U. J. Meierhenrich,* J.-J. Filippi,
C. Meinert, J. H. Bredehöft,
J.-i. Takahashi, L. Nahon, N. C. Jones,
S. V. Hoffmann — 7799–7802

Circular Dichroism of Amino Acids in the
Vacuum-Ultraviolet Region

NMR Spectroscopy

Ü. Akbey, W. T. Franks, A. Linden,
S. Lange, R. G. Griffin
B.-J. van Rossum,
H. Oschkinat* _____ **7803 – 7806**

Dynamic Nuclear Polarization of
Deuterated Proteins



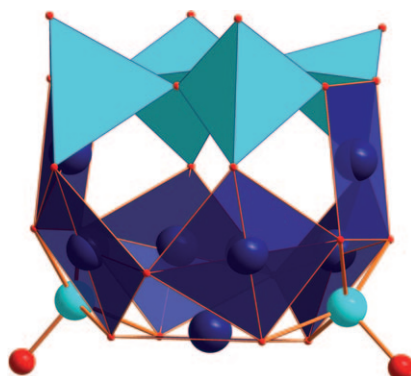
For D's a jolly good fellow: Deuteration of proteins significantly increases the signal enhancements observed in dynamic nuclear polarization (DNP) magic-angle spinning (MAS) NMR experiments. In ^{13}C CP-MAS spectra an enhancement of 120 is observed for perdeuterated SH3 with an exchangeable proton ratio of 50%, whereas the enhancement is only 31 for the fully protonated SH3. The direct ^{13}C excitation of the perdeuterated sample increases the enhancement to 148.

Noble Metalates

N. V. Izarova, N. Vankova, A. Banerjee,
G. B. Jameson, T. Heine, F. Schinle,
O. Hampe, U. Kortz* _____ **7807 – 7811**



A Noble-Metalate Bowl: The Polyoxo-6-
vanado(V)-7-palladate(II)
 $[\text{Pd}_7\text{V}_6\text{O}_{24}(\text{OH})_2]^{6-}$



Nobly born: The bowl-shaped noble metalate $[\text{Pd}^{\text{II}}_7\text{V}^{\text{V}}_6\text{O}_{24}(\text{OH})_2]^{6-}$ (Pd_7V_6) comprises seven square-planar $\text{Pd}^{\text{II}}\text{O}_4$ units as well as four tetrahedral $\text{V}^{\text{V}}\text{O}_4$ and two square-pyramidal $\text{V}^{\text{V}}\text{O}_5$ addenda units (see picture). The solution stability of Pd_7V_6 has been demonstrated by ^{51}V NMR spectroscopy, ESI mass spectrometry, and DFT calculations.



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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