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:

*A. Elahi, T. Fowowe, D. J. Caruana**
Dynamic Electrochemistry in Flame Plasma Electrolyte

*T. Köchner, T. A. Engesser, H. Scherer, D. A. Plattner, A. Steffani, I. Krossing**
Positive at Last: $[P_9]^+[Al(OR^F)_4]^-$, the First Pure Phosphorus Cation Salt

R. Liu, G. Yuan, C. L. Joe, T. E. Lightburn, K. L. Tan, D. Wang**
Silicon Nanowires as Photoelectrodes for Carbon Dioxide Fixation

*L. M. H. Lai, I. Y. Goon, K. Chuah, M. Lim, F. Braet, R. Amal, J. J. Gooding**
Biochemical Resistor: An Ultrasensitive Biosensor for Small Organic Molecules

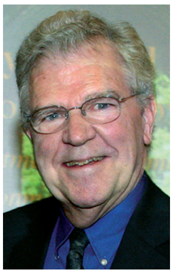
Author Profile

"When I was eighteen I wanted to be Bruce Lee, or at least Chuck Norris.
My motto is give serendipity a chance! …"
This and more about V. Gevorgyan can be found on page 6562.

News

J. M. DeSimone

J. B. Goodenough



J. T. Groves

U. T. Bornscheuer

Obituaries

Robert E. Ireland (1929–2012)

Books

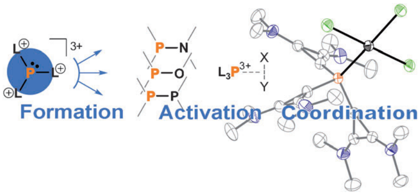
Writing Chemistry Patents and Intellectual Property — Francis J. Waller

Highlights

Phosphorus Chemistry

K.-O. Feldmann,
J. J. Weigand* **6566 – 6568**

Multiple-Charged P_1-Centered Cations: Perspectives in Synthesis



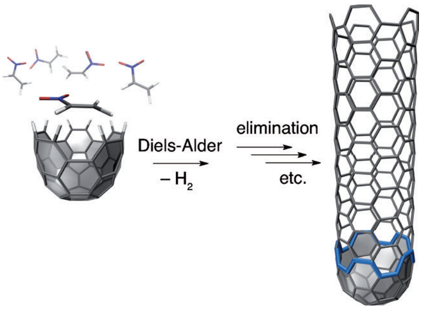
Taking center stage: Several new features of the title compounds were recently uncovered. P_1-centered cations are employed as reagents for the preparation of unprecedented phosphorus compounds and transition-metal complexes. This represents a remarkable extension of their chemistry, which might make an impact on the field of homogeneous catalysis.

Nanocarbons

S. Schrettl, H. Frauenrath* **6569 – 6571**

Elements for a Rational Polymer Approach towards Carbon Nanostructures

Growth spurt: A recent series of publications promises to pave the way for a polymer approach towards well-defined carbon nanostructures by combining the stepwise organic synthesis of carbon nanotube (CNT) end caps and their use as templates for CNT growth by Diels–Alder addition of nitroethylene as a masked acetylene derivative.

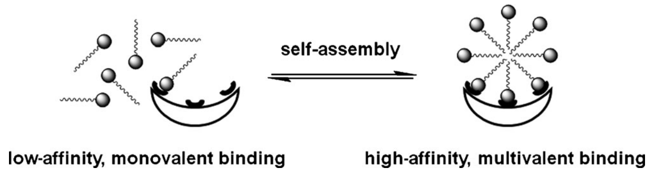


Minireviews

Supramolecular Chemistry

A. Barnard, D. K. Smith* **6572 – 6581**

Self-Assembled Multivalency: Dynamic Ligand Arrays for High-Affinity Binding



The power of many: The use of self-assembly to create dynamic multivalency (see scheme) is a powerful strategy, with some significant advantages over the use of static multivalent arrays. It mimics processes which occur naturally within cell membranes, and has a wide range of potential applications, both in nanomaterials science and nanomedicine.

For the USA and Canada:
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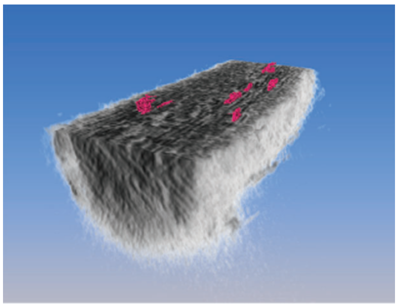
Reviews

Materials Synthesis

F. Nudelman,
N. A. J. M. Sommerdijk* ___ **6582 – 6596**

Biomineralization as an Inspiration for Materials Chemistry

Living organisms build special organic–inorganic hybrid materials such as bones, teeth, and shells that are highly sophisticated in terms of their adaptation to function. Chemists and materials scientists mimic these natural strategies to build biominerals and to tune their properties for biomedical and technical applications.



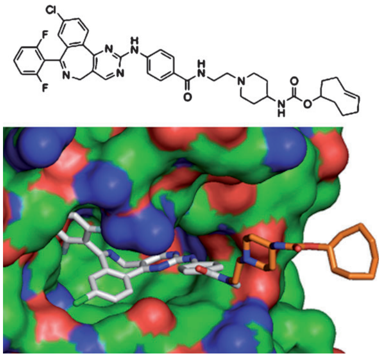
Communications

Protein Labeling

K. S. Yang, G. Budin, T. Reiner,
C. Vinegoni, R. Weissleder* **6598 – 6603**

Bioorthogonal Imaging of Aurora Kinase A in Live Cells

Frontispiece



In living color: Aurora kinase A (AKA) was imaged in live cells using a bioorthogonal two-step reaction with a small molecule AKA inhibitor (see scheme) and a fluorescent reporter. The fluorescent molecule was localized to spindle poles and microtubules during metaphase, consistent with the localization of both endogenous and green fluorescent protein tagged AKA. By using this approach, changes in AKA distribution during mitosis were also observed.

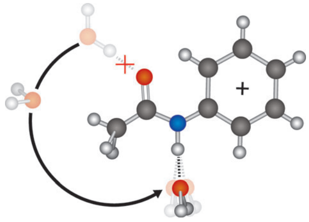
Hydrogen Bonds

VIP

K. Tanabe, M. Miyazaki, M. Schmies,
A. Patzer, M. Schütz, H. Sekiya, M. Sakai,
O. Dopfer,* M. Fujii* ______ **6604 – 6607**

Watching Water Migration around a Peptide Bond

Inside Cover



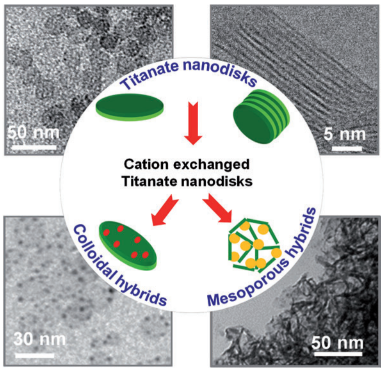
A long and winding road: The motion of a single water ligand around a peptide bond in acetanilide was probed in real time by time-resolved IR spectroscopy. Triggered by photoionization, the H_2O ligand is released from the CO site of the peptide linkage and trapped after a migration time of 5 ps at the NH site of the same peptide bond (see picture).

Hybrid Materials

C.-T. Dinh, Y. Seo, T.-D. Nguyen, F. Kleitz,*
T.-O. Do* ________________ **6608 – 6612**

Controlled Synthesis of Titanate Nanodisks as Versatile Building Blocks for the Design of Hybrid Nanostructures

Back Cover

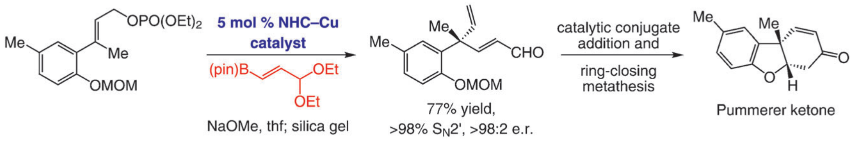


Building with nanobricks: Uniform titanate nanodisks with a controlled diameter of 12–35 nm were synthesized by a nonaqueous method. These nanodisks were used for the design of various titanate-based mesoporous hybrids with a high specific surface area and tailored porosity. They could also be used as efficient stabilizers for the synthesis of small, uniform metal nanoparticles that exhibit enhanced catalytic activity.

Enantioselective Catalysis

F. Gao, J. L. Carr,
A. H. Hoveyda* ______ **6613 – 6617**

Copper-Catalyzed Enantioselective Allylic Substitution with Readily Accessible Carbonyl- and Acetal-Containing Vinylboron Reagents

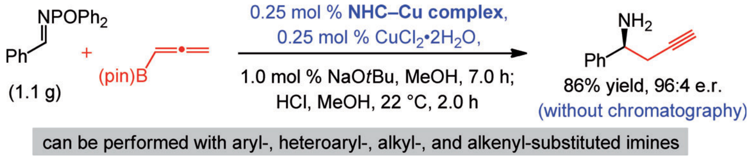


More with boron: The title reaction was developed to generate quaternary carbon stereogenic centers through the use of commercially available vinylboron reagents (see scheme, MOM = methoxymethyl, NHC = N-heterocyclic carbene, pin = pinacolato). Application of the method to the two isomeric forms of an intermediate in morphine biosynthesis demonstrates its utility.

Enantioselective Catalysis

E. M. Vieira, F. Haeffner, M. L. Snapper,
A. H. Hoveyda* ______ **6618 – 6621**

A Robust, Efficient, and Highly Enantioselective Method for Synthesis of Homopropargyl Amines

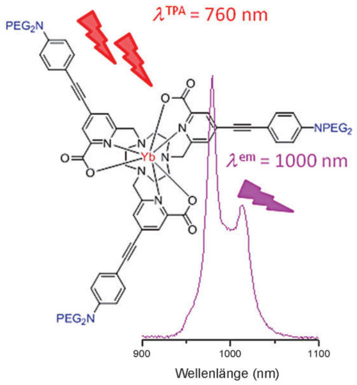


Fast, robust, selective: Copper-catalyzed enantioselective additions of homopropargyl groups to a wide range of aldimines proceed readily and with high enantioselectivity. The catalytic method is scalable and practical, the allenylboron reagent is commercially available, and conversion into amines is inexpensive and high-yielding.

Bioimaging

A. D'Aléo, A. Bourdolle, S. Brustlein,
T. Fauquier, A. Grichine, A. Duperray,
P. L. Baldeck, C. Andraud,* S. Brasselet,*
O. Maury* ______ **6622 – 6625**

Ytterbium-Based Bioprobes for Near-Infrared Two-Photon Scanning Laser Microscopy Imaging

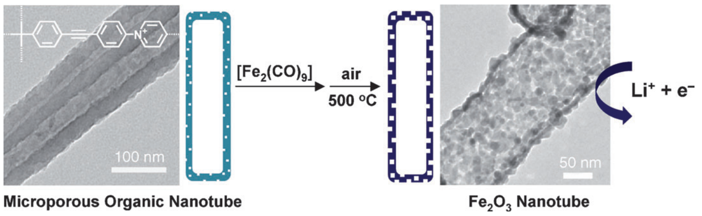


Cleanly separated by two photons: The design and photophysical characterization of a new highly stable macrocyclic ytterbium complex featuring a two-photon antenna ligand is described (see picture). The biphotonic sensitization of the near-infrared ytterbium(III) luminescence and the conception of an unconventional near-infrared biphotonic microscope allow performing in-depth imaging of thick tissues.

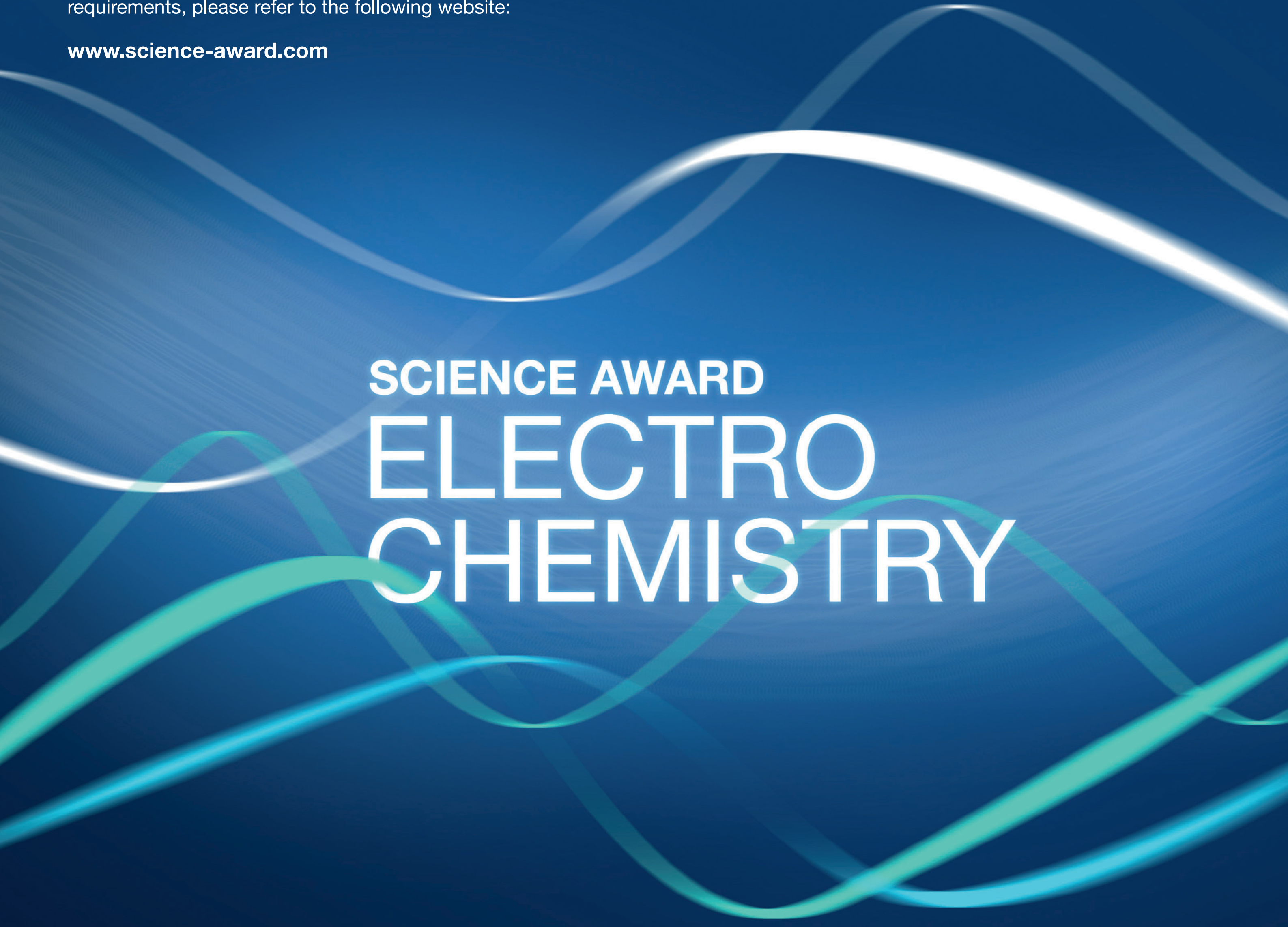
Nanomaterials

N. Kang, J. H. Park, J. Choi, J. Jin, J. Chun,
I. G. Jung, J. Jeong, J.-G. Park, S. M. Lee,
H. J. Kim, S. U. Son* ______ **6626 – 6630**

Nanoparticulate Iron Oxide Tubes from Microporous Organic Nanotubes as Stable Anode Materials for Lithium Ion Batteries



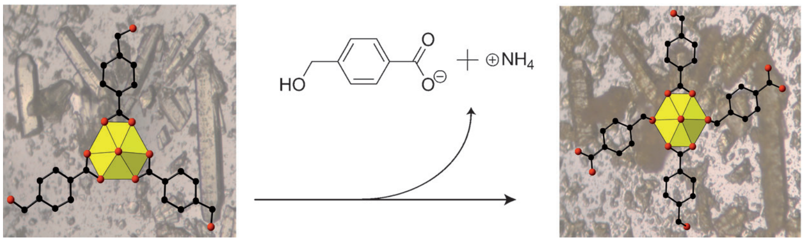
Tubes from tubes: Microporous organic nanotubes were prepared by Sonogashira coupling between tetrakis(4-ethynylphenyl)methane and *N*,*N*′-di(4-iodophenyl)-4,4′-bipyridinium dichloride. These nanotubes were used as a template for secondary inorganic materials, namely Fe$_2$O$_3$ nanotubes with a high discharge capacity and excellent stability.


SCIENCE AWARD
ELECTRO
CHEMISTRY

Crystal Engineering

M. B. Andrews, C. L. Cahill* **6631 – 6634**

Uranyl Hybrid Material Derived from In Situ Ligand Synthesis: Formation, Structure, and an Unusual Phase Transformation



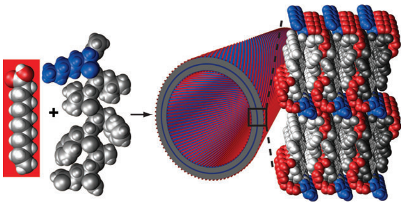
Phase to phase: The in situ hydrolysis of 4-(bromomethyl)benzoic acid to 4-(hydroxymethyl)benzoic acid (HMBA) in the presence of the uranyl cation has resulted in the novel hybrid material (A)-$[UO_2(HMBA)_3]$ ($A = NH_4^+$ or H_3O^+), which was characterized by X-ray diffraction. On exposure to ethanol the material undergoes a solid-state phase transformation, accompanied by the loss of a ligand and counterion to form $[UO_2(HMBA)_2]$ (see scheme; O red, C black).

Peptide Amphiphile Self-Assembly

R. Ni, W. S. Childers, K. I. Hardcastle, A. K. Mehta,* D. G. Lynn* **6635 – 6638**

Remodeling Cross-β Nanotube Surfaces with Peptide/Lipid Chimeras

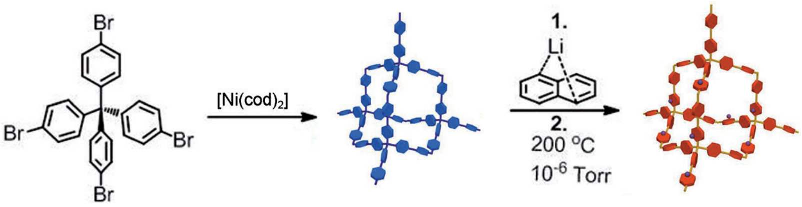
Between the sheets: A unique cross-β-peptide amphiphile assembly positions the acyl chain within the hydrophobic cross-β laminate (see picture; acyl chain: red, peptide: gray, lysine: blue). The atomic-level structure of the self-assembled surface can also be systematically altered, opening the possibility to create a wide range of nanostructured biomaterials.



Porous Aromatic Frameworks

K. Konstas,* J. W. Taylor, A. W. Thornton, C. M. Doherty, W. X. Lim, T. J. Bastow, D. F. Kennedy, C. D. Wood, B. J. Cox, J. M. Hill, A. J. Hill, M. R. Hill* **6639 – 6642**

Lithiated Porous Aromatic Frameworks with Exceptional Gas Storage Capacity

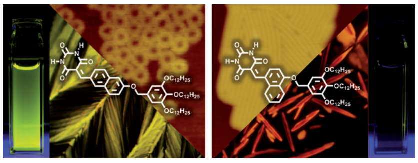


A porous treasure: Porous aromatic framework PAF-1 (see picture, blue structure) has been lithiated, giving a reduced framework with an increased gas storage capacity compared to native PAF-1 (by 22, 71, and 320% for H_2, CH_4, and CO_2, respectively). The reduced framework was examined spectroscopically, and the potential hydrogen storage capacity was calculated.

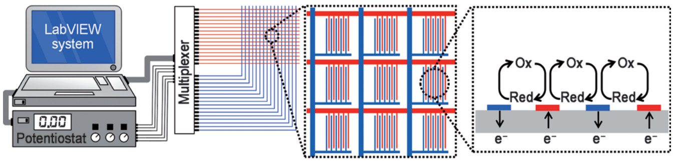
Self-Assembly

S. Yagai,* Y. Goto, X. Lin, T. Karatsu, A. Kitamura, D. Kuzuhara, H. Yamada, Y. Kikkawa, A. Saeki, S. Seki **6643 – 6647**

Self-Organization of Hydrogen-Bonding Naphthalene Chromophores into J-type Nanorings and H-type Nanorods: Impact of Regioisomerism



Regioisomers of self-assembling molecules resulted in the evolution of distinct 0D and 1D nanostructures, namely nanorings and nanorods (see picture). J- and H-type excitonic coupling of naphthalene chromophores was found in the nanostructures. The bulk liquid-crystalline states contain hydrogen-bonded rosettes, which explains how the observed regioisomers generate distinct nanostructures with characteristic excitonic interactions.



Monitoring cellular activity: A local redox-cycling-based electrochemical chip device (see picture) has been used to entrap three-dimensional culture cells and evaluate their activity. Deep microwells were incorporated into the chip device for the trapping of embryoid bodies. This chip device is useful for the evaluation of 3D organ tissues.

Electrochemical Imaging

K. Ino,* T. Nishijo, T. Arai, Y. Kanno,
Y. Takahashi, H. Shiku,
T. Matsue* ____ **6648 – 6652**

Local Redox-Cycling-Based Electrochemical Chip Device with Deep Microwells for Evaluation of Embryoid Bodies

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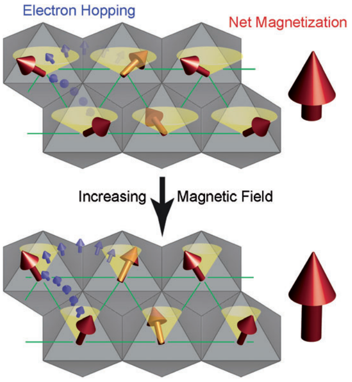

Spin frustration and the unusual electronic state of Cr^{4+} ions are the origins of unconventional colossal magnetoresistance (CMR) in $NaCr_2O_4$, a new member of the rare mixed-valence chromium oxides. CMR materials have previously been limited to almost only manganese oxides; the discovery of the CMR in a non-manganese-based material opens a new dimension in the quest for novel CMR materials.

Magnetic Properties

H. Sakurai,* T. Kolodiazhnyi, Y. Michiue,
E. Takayama-Muromachi, Y. Tanabe,
H. Kikuchi ____ **6653 – 6656**

Unconventional Colossal Magnetoresistance in Sodium Chromium Oxide with a Mixed-Valence State

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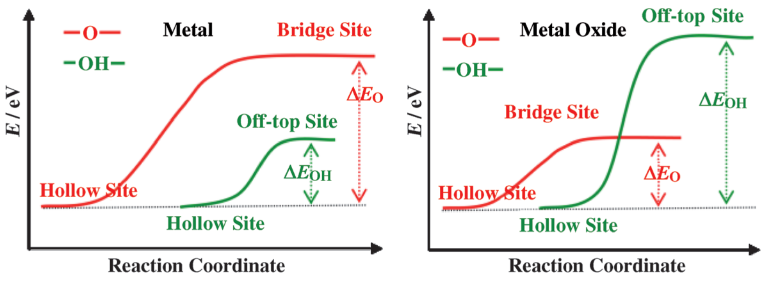

Test the water: Calculations have been used to investigate why water deactivates Co_3O_4 to CO oxidation and activates platinum group metals in the same reaction. The significant difference in the potential energy surfaces of OH on metal versus metal oxides is the origin of the different effects water has in these systems.

Heterogeneous Catalysis

H.-F. Wang, R. Kavanagh, Y.-L. Guo,
Y. Guo, G. Lu,* P. Hu* ____ **6657 – 6661**

Structural Origin: Water Deactivates Metal Oxides to CO Oxidation and Promotes Low-Temperature CO Oxidation with Metals

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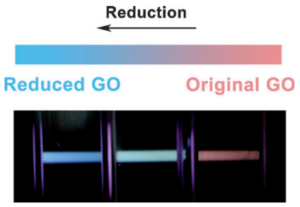


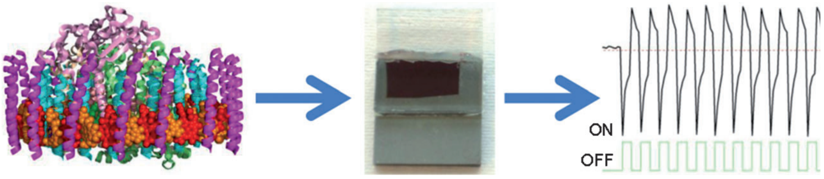
Tuning to G(O) flat: Photoluminescence in graphene oxide (GO) suspensions can be tuned from red to blue emission (see scheme) by gradually changing the amounts of sp^2- and sp^3-bonded carbon atoms through reduction of the surface oxide groups. Electron–hole recombination from two different types of excited states is proposed to explain the luminescence in GO at varying degrees of reduction.

Tunable Luminescence

C. T. Chien, S. S. Li, W. J. Lai, Y. C. Yeh,
H. A. Chen, I. S. Chen, L. C. Chen,
K. H. Chen, T. Nemoto, S. Isoda, M. Chen,
T. Fujita, G. Eda, H. Yamaguchi,
M. Chhowalla, C. W. Chen* **6662 – 6666**

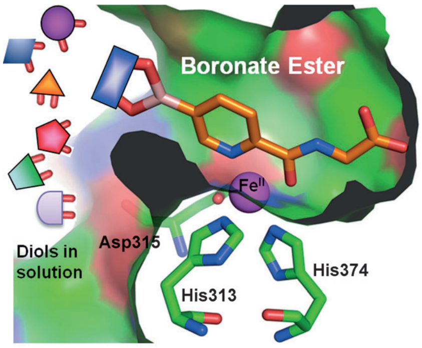
Tunable Photoluminescence from Graphene Oxide

Solar Cells



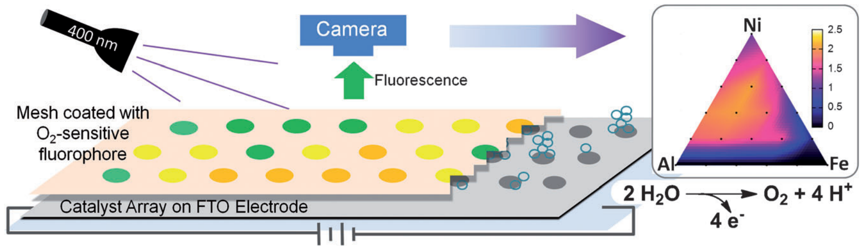
AC or DC? Protein-based photoelectrochemical cells that were constructed using a photosynthetic reaction center (left) generated a conventional direct current (DC) output during continuous illumination but an alternating current (AC) during regular light-on/light-off cycles (right). The mechanism of AC generation exploits the ability of nature's reaction centers to store charge as well as to catalyze highly efficient photochemical charge separation.

Boron Chemistry



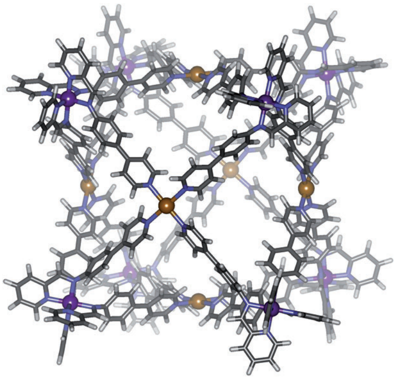
Dynamic duo: The reversible reaction of boronic acids with alcohols to form boronate esters, coupled to protein mass spectrometry analyses, was used to discover potent oxygenase inhibitors. This dynamic combinatorial mass spectrometry technique could potentially be applied to the identification of other protein inhibitors.

Water Splitting



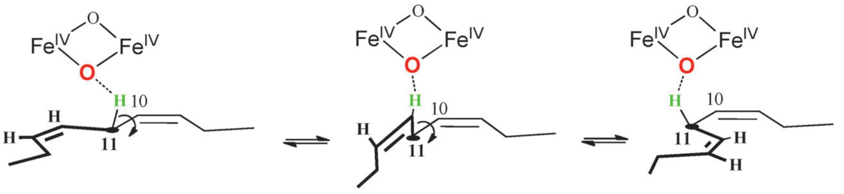
Realizing their potential: The title assay has enabled rapid screening of diverse mixed-metal oxide electrocatalysts composed exclusively of earth-abundant metal ions. Several newly discovered catalyst compositions (e.g., Ni/Al/Fe oxides) exhibit substantially lower overpotentials for water oxidation than known, widely used electrocatalysts.

Self-Sorting



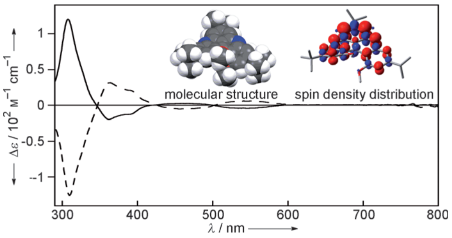
96 bonds were formed when 62 building blocks (heterotopic ligands with Fe^{II} and Pt^{II} ions) self-assembled in a one-pot reaction into a heterometallic $Fe_8Pt_6L_{24}$ cubic cage (see model, Fe purple, Pt orange, N blue). The dynamic nature of this method also allowed an efficient cage-to-cage conversion: a tetrahedral Fe_4L_6 cage was converted into the $Fe_8Pt_6L_{24}$ cube, which was subsequently converted into a second tetrahedral $Fe_4L'_6$ cage.

Enzyme Mechanisms



Variations on an oxidative theme: The precision with which FAD2-type desaturases carry out $C-H$ activation reactions on flexible lipidic substrates is astonishing. The conformational space available within the active site of these enzymes has been explored using deuterium-labeled substrates, and evidence for a novel quasi-eclipsed conformer has been uncovered. The scheme shows some prototypical substrate conformations.

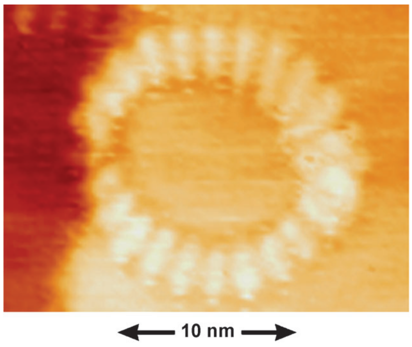
Phenalenyl Radicals



A new spin on an old system: The title neutral radicals have been synthesized and characterized for the first time. Thanks to two terminal methoxy groups and three *tert*-butyl groups, the chiral radicals are configurationally and chemically stable. The three-dimensional π-electron network shows extensive spin delocalization, and the distinct CD properties are attributed to the chirality of the helicene unit (see picture).

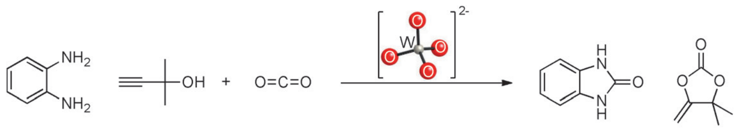
Giant Conjugated Macrocycles

VIP



Many hands make light work: Small templates working together have directed the formation of a giant π-conjugated macrocycle with a diameter of 10 nm—larger than many enzymes. The 24 porphyrin subunits of the nanoring are well resolved in the STM image. The conformation of the nanoring can be controlled by self-assembly of a stable 2:24 double-strand sandwich complex with 1,4-diazabicyclo[2.2.2]octane (DABCO).

Homogeneous Catalysis

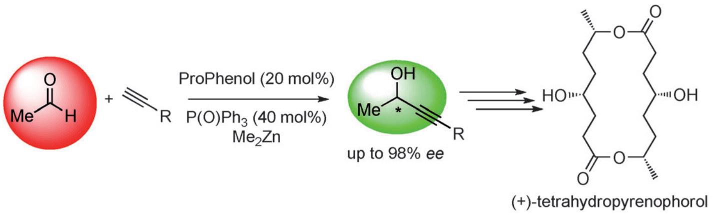


No pressure: A simple monomeric tungstate, [WO$_4$]$^{2-}$, serves as a highly efficient homogeneous catalyst for various transformations of CO$_2$ at atmospheric pressure. The tungsten-oxo moiety activates CO$_2$ and the substrate simultaneously. The catalyst system is high yielding and applicable to a wide range of substrates such as amines (see scheme), 2-aminobenzonitriles, and propargylic alcohols.

Synthetic Methods

B. M. Trost,* A. Quintard ___ **6704 – 6708**

Asymmetric Catalytic Alkynylation of Acetaldehyde: Application to the Synthesis of (+)-Tetrahydropyrenophorol



In control: By controlling the kinetics of alkynylation over aldolization, the challenging asymmetric catalytic alkynylation of acetaldehyde has been realized. The resulting products are attractive synthons which are produced with good to excellent enantiocontrol, and show broad tolerance and applicability, as demonstrated by the synthesis (+)-tetrahydropyrenophorol.

VIP

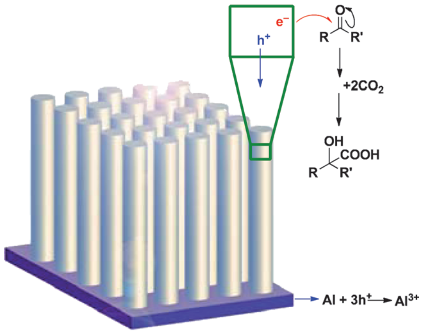
CO$_2$ Photochemistry

R. Liu, G. Yuan, C. L. Joe, T. E. Lightburn, K. L. Tan,* D. Wang* ___ **6709 – 6712**

Silicon Nanowires as Photoelectrodes for Carbon Dioxide Fixation

Front Cover

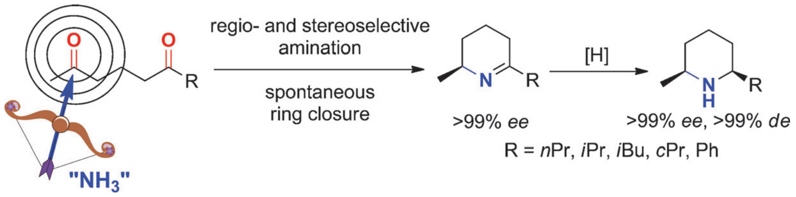
Lights on: When illuminated, p-type Si nanowires donate photogenerated electrons to aromatic ketones, producing reactive radicals that can harvest CO$_2$ to yield α-hydroxy acids (see scheme). The reaction scheme closely resembles that of natural photosynthesis and gives up to 98 % yield and selectivity. Products obtained by this reaction include important precursors for nonsteroidal anti-inflammatory drugs, such as ibuprofen and naproxen.



Regioselective Bioamination

R. C. Simon, B. Grischek, F. Zepeck, A. Steinreiber, F. Belaj, W. Kroutil* ___ **6713 – 6716**

Regio- and Stereoselective Monoamination of Diketones without Protecting Groups

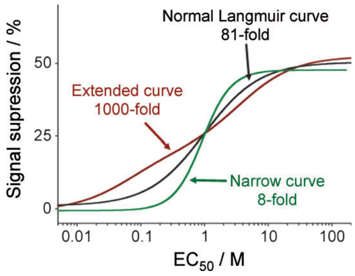


Hitting the right target: Differentiation between two keto moieties was accomplished by a regio- and enantioselective bioamination employing ω-transaminases. Using 1,5-diketones as substrates gave access to the optically pure 2,6-disubstituted piperidine scaffold. The approach allowed the shortest synthesis of the alkaloid dihydropinidine, as well as its enantiomer, by choosing an appropriate ω-transaminase.

Biosensors

D. Kang, A. Vallée-Bélisle, A. Porchetta, K. W. Plaxco, F. Ricci* ___ **6717 – 6721**

Re-engineering Electrochemical Biosensors To Narrow or Extend Their Useful Dynamic Range

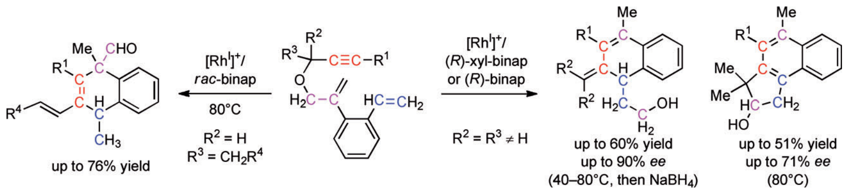


By combining DNA probes having different target affinities, but with similar specificity on the same electrode, an extended dynamic response of a biosensor spanning three orders of magnitude in target concentration was obtained. By using a different strategy, the useful dynamic range of an electrochemical DNA sensor was narrowed to only an 8-fold range of target concentrations.

Cascade Reactions

E. Okazaki, R. Okamoto, Y. Shibata,
K. Noguchi, K. Tanaka* ____ **6722 – 6727**

Rhodium-Catalyzed Cascade Reactions of Dienynes Leading to Substituted Dihydronaphthalenes and Naphthalenes

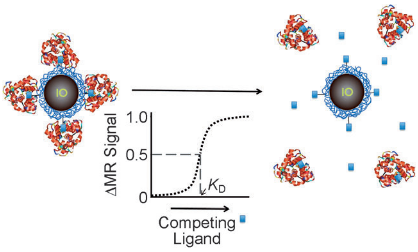


Five in one: Catalytic cascade reactions of dienynes catalyzed by cationic rhodium(I)–binap complexes lead to the formation of 1,2-dihydronaphthalenes, naphthalenes, and 1,4-dihydronaphthalenes. These cascade reactions involve up to five fundamentally different transformations, including the catalytic enantioselective carboformylation of alkenes with aldehydes or the cycloisomerization of enallenes.

Protein–Ligand Interactions

O. J. Santiesteban, C. Kaittanis,
J. M. Perez* ____________ **6728 – 6732**

Assessment of Molecular Interactions through Magnetic Relaxation

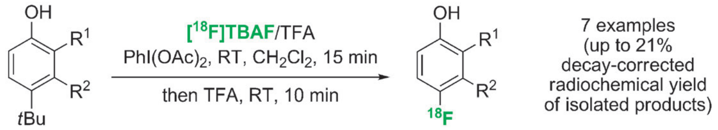


Just relax: The dissociation constants (K_D) of various molecular interactions can be determined using a novel competition assay with binding magnetic relaxation nanosensors. In this assay, changes in the magnetic relaxation (MR) of an aqueous suspension of the nanosensors facilitate the fast determination of K_D values by using nanomolar protein concentrations (see picture).

Radiochemistry

Z. Gao, Y. H. Lim, M. Tredwell, L. Li,
S. Verhoog, M. Hopkinson, W. Kaluza,
T. L. Collier, J. Passchier, M. Huiban,
V. Gouverneur* __________ **6733 – 6737**

Metal-Free Oxidative Fluorination of Phenols with [^{18}F]Fluoride

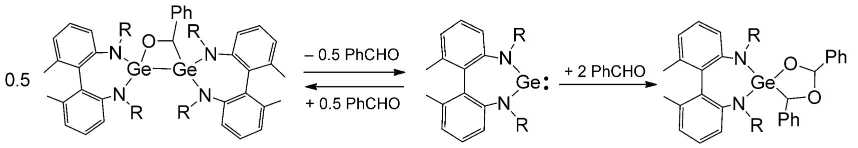


The radiochemical synthesis of [^{18}F]4-fluorophenols is based on phenol umpolung under oxidative conditions and direct nucleophilic fluorination with [^{18}F]fluoride (see scheme, TBAF = tetra-*n*-butylammonium fluoride, TFA = trifluoroacetic acid). Readily available O-unprotected 4-*tert*-butyl phenols are used as precursors in this one-pot protocol. The reaction is completed in less than 30 minutes at room temperature and can be performed using standard or microfluidic technology.

Main Group Chemistry

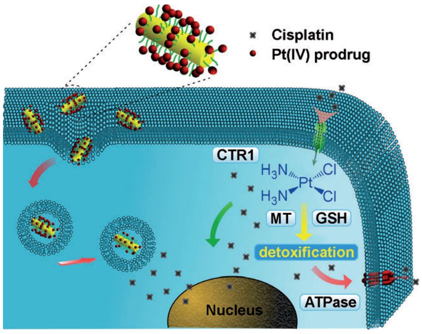
H. Arii, T. Amari, J. Kobayashi,
K. Mochida,* T. Kawashima **6738 – 6741**

Low-Coordinate Germanium(II) Centers Within Distorted Axially Chiral Seven-Membered Chelates: Stereo- and Enantioselective Cycloadditions



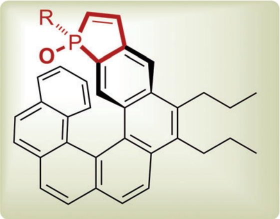
Distorted germylene: A distorted seven-membered N-heterocyclic germylene, which has a germanium center of relatively high Lewis acidity, reacts with benzaldehyde to give (2+1+1) or (2+2+1) cycloadducts. The type of cycloadduct produced in the reaction is dependent on the ratio of substrates used. It is considered that the reactions involve stereoselective 1,3-dipolar cycloadditions of an in situ generated carbonyl germaylide.

Platinum Drugs



Resistance is futile: A platinum(IV) prodrug conjugated to a gold-nanorod-based delivery agent avoids the type of drug resistance that is associated with cisplatin (see picture). This conjugate is taken up into cells through endocytosis, thus avoiding the resistance-associated uptake mediated by the copper transport protein Ctr1. The platinum(IV) prodrug is more inert than cisplatin to glutathione and metallothionein, which cause deactivation.

Phosphorus Heterocycles



Building helicenes: A photochemical cyclization approach affords helicenes in which the fused ring sequence ends with a phosphole unit (see scheme). The stereogenic phosphorus centers of the substrates control the screw sense of helical chirality. The terminal phosphole units undergo photochemical [2+2] annulations to give dimeric helical structures.

DOI: 10.1002/anie.201203982

50 Years Ago . . .

Angewandte Chemie International Edition was first published in 1962, the mother journal first in 1888. In this monthly flashback, we feature some of the articles that appeared 50 years ago. This look back can open our eyes, stimulate discussion, or even raise a smile.

Issue 7 in 1962 literally contained some explosive chemistry in the form of not one but two reports of unexpected explosions. H. Wilms and A. Dorlars described how they heated mesitylene with concentrated nitric acid in an autoclave. Several minutes after reaching 115°C and 10 atm gauge pressure, an explosion occurred that tore the autoclave apart lengthwise and ripped the steel doors from a safety cover. In a separate Communication, P. G. Ferrini and A. Marxer reported how tropylium perchlorate exploded when being manipulated with a glass rod. The explosion shattered the bench top, which broke the solvent bottles that were stored beneath it. The spilt solvent then caught fire. 50 years ago, reports such as this were a good way of making researchers more aware of the risks involved in these reactions, and thus helped to reduce the number of laboratory accidents.

The ethylene ketal of cyclopentadienone was the subject of two back-to-back Communications that described different routes to this product. The approach reported by E. Vogel and E.-G. Wyes involved capturing the desired product as its maleic anhydride adduct, while C. H. DePuy, B. W. Ponder, and J. D. Fitzpatrick described how the dimer of the target compound was produced by elimination of a substituted cyclopentanone ketal.

In a Review, U. Hofmann discussed the chemical basis of ancient Greek vase painting. A range of studies showed that illitic clay was used as a black paint and a kaolinitic clay was used as a red paint, and electron microscopy was used to examine the vase surfaces and elucidate the processes that occurred during the firing stage.

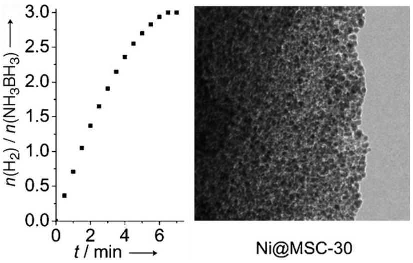
Read more in Issue 7/1962

Heterogeneous Catalysis

P.-Z. Li, A. Aijaz, Q. Xu* ___ **6753 – 6756**

Highly Dispersed Surfactant-Free Nickel Nanoparticles and Their Remarkable Catalytic Activity in the Hydrolysis of Ammonia Borane for Hydrogen Generation

Highly active: Surfactant-free Ni nanocatalysts were highly dispersed into the nanoporous carbon support MSC-30 through a dry process, and the obtained Ni@MSC-30 catalyzed the generation of H_2 from the hydrolysis of ammonia borane at room temperature (see picture). The improvement of the performance of surfactant-free non-noble metal nanocatalysts is a promising step toward the application of NH_3BH_3 as an applicable chemical hydrogen storage material.

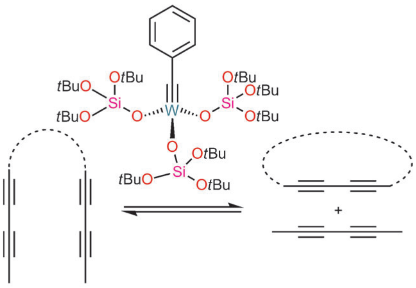


Diyne Metathesis

S. Lysenko, J. Volbeda, P. G. Jones, M. Tamm* ___ **6757 – 6761**

Catalytic Metathesis of Conjugated Diynes

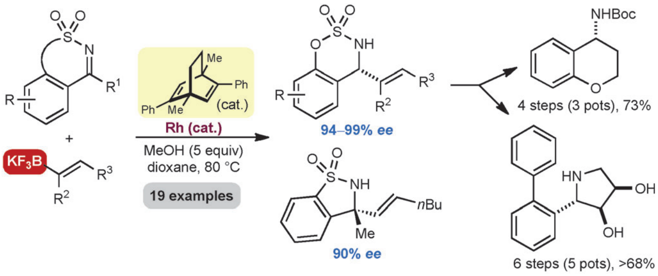
The tungsten benzylidyne complex [PhC≡W{OSi(O*t*Bu)$_3$}$_3$] efficiently catalyzes the metathesis of conjugated diynes and ring-closing diyne metathesis (see scheme). Although this reaction implies C−C single-bond activation, ^{13}C labeling studies reveal that it proceeds by classical alkylidyne group exchange and involves cleavage and formation of carbon–carbon triple bonds.



Asymmetric Catalysis

Y. Luo, A. J. Carnell, H. W. Lam* ___ **6762 – 6766**

Enantioselective Rhodium-Catalyzed Addition of Potassium Alkenyltrifluoroborates to Cyclic Imines



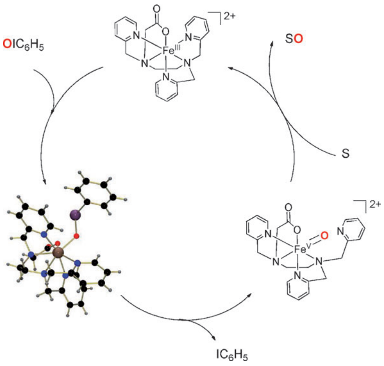
Fixed: Cyclic imines, in which the C=N bond is constrained in the *Z* geometry, have been identified as highly effective substrates for enantioselective rhodium-catalyzed additions of potassium alkenyltrifluoroborates. Not only is the alkene in the products a useful functional handle for subsequent manipulations, products containing aryl sulfamates may be employed in nickel-catalyzed Suzuki–Miyaura and Kumada coupling reactions to generate further compounds of interest.

Biomimetic Synthesis

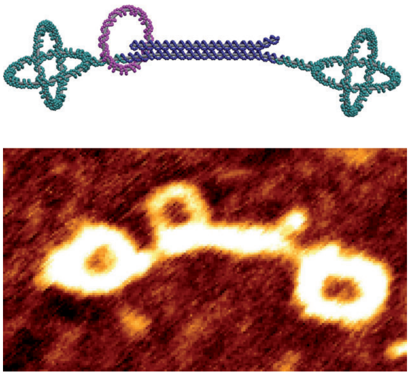
A. Lennartson, C. J. McKenzie* ___ **6767 – 6770**

An Iron(III) Iodosylbenzene Complex: A Masked Non-Heme Fe^{V}O

Coordinative flexibility and ligand bifunctionality play important roles in a biomimetic iron complex of a hexadentate ligand (see picture). This system can bind an auxiliary iodosylbenzene ligand to give the first structurally characterized metal complex of this important oxidizing agent. The complex is a protected precursor for Fe^{V}O species, and the selective high-yielding catalytic oxygenation of a sulfide is demonstrated.



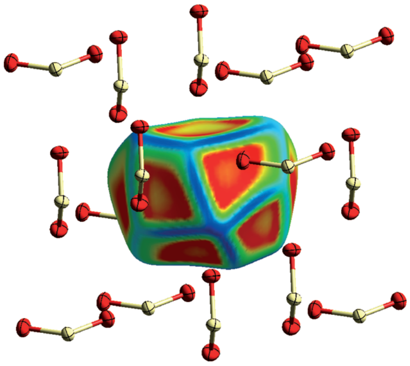
DNA Nanostructures



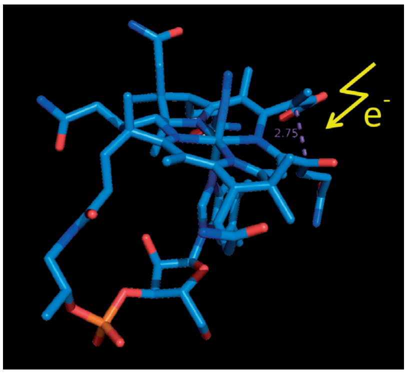
Non-deformable axles based on paranemic crossover DNAs can serve as components for mechanically stable DNA rotaxanes. The required design strategies provide generally applicable guidelines for the incorporation of mechanically interlocked DNA architectures or even DNA origami structures. DNA rotaxanes with mechanically reinforced axles can serve as precursors for complex molecular machines capable of force transmission.

Experimental Bond Orders

A novel refinement technique for X-ray diffraction data has been employed to derive S—O bond orders in sulfur dioxide experimentally. The results show that ionic S—O bonding dominates over hypervalency.



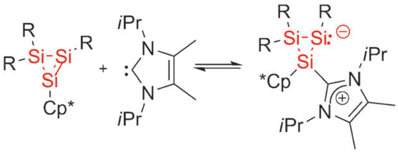
Vitamin B_{12}



A radical B12 synthesis: A recently described blue 7,8-secocorrinoid, a degradation product of vitamin B_{12}, has a remarkable structural predisposition for ring closure. Reductive reconstitution of the corrin macrocycle by means of a stereospecific radical reaction leads to a 7-epicobalamin. Human B_{12}-binding proteins bind this vitamin B_{12} analogue significantly less strongly than natural cobalamins.

Si=Si Double Bonds

Si=Si activation: Reversible formation of a donor–acceptor complex between an N-heterocyclic carbene and a cyclotrisilene with carbon-based substituents shifts the electron density of the double bond and thus induces strong polarization, as shown by the significantly pyramidal tricoordinate silicon atom.



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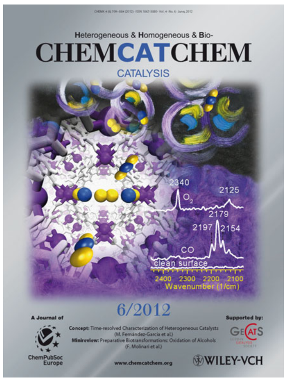

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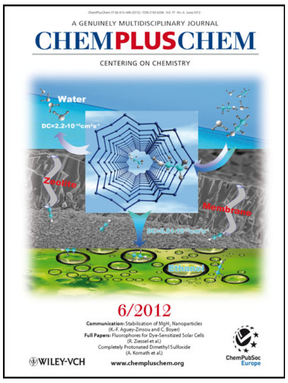

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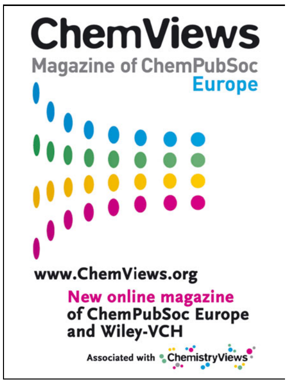

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