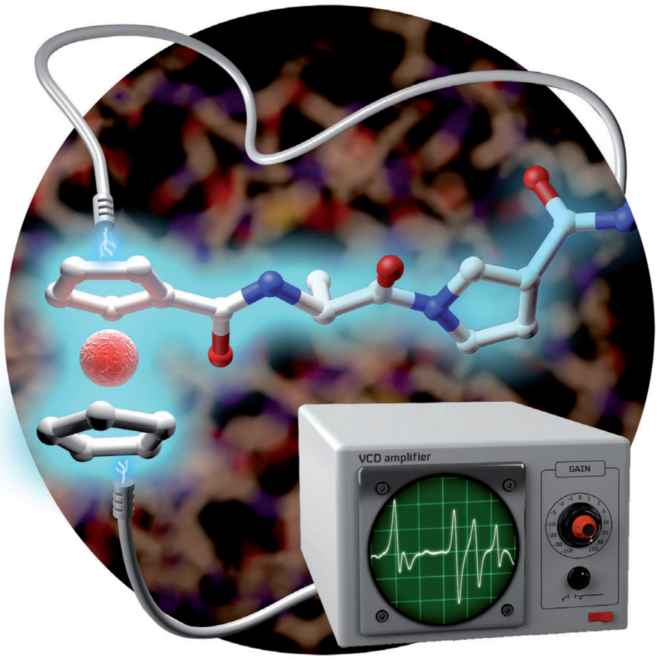
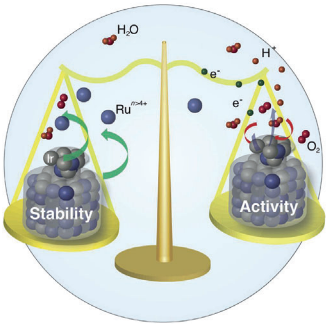
Vibration circular dichroism ...

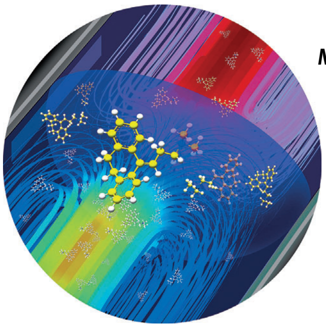


… (VCD) spectroscopy is used to determine the absolute configuration and conformation of chiral molecules in solution but low signal intensities and spectral congestion often prohibit the investigation of local structure. In their Communication on page 14042 ff., F. Hartl, W. J. Buma, S. Woutersen et al. describe the attachment of a ferrocene-based electrochemically switchable amplifier to a molecular system, which enables the local amplification of the VCD signal.

Surface Analysis

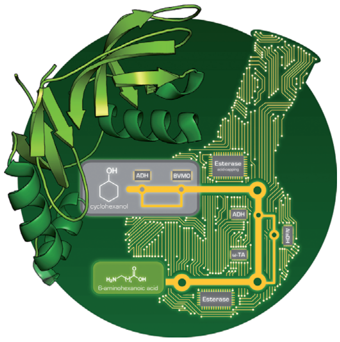
N. M. Markovic et al. describe in their Communication on page 14016 ff. how the activity of bimetallic oxide materials for the oxygen evolution reaction can be tuned through surface segregation of the elements into nanosegregated domains.





Mass Spectrometry

A highly sensitivity single-step method based on slug-flow microextraction for the mass spectrometric analysis of organic compounds in only 5 µL of a biofluid is described by Z. Ouyang and coworkers in their Communication on page 14124 ff.



Enzyme Catalysis

The preparation of a nylon-6 monomer, 6-aminohexanoic acid, from cyclohexanol at the expense of only NH_3 and O_2 by using two biocatalytic self-sufficient redox modules is described by W. Kroutil et al. in their Communication on page 14153 ff.

How to contact us:

Editorial Office:
E-mail: angewandte@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-315

Reprints, E-Prints, Posters, Calendars:
Carmen Leitner
E-mail: chem-reprints@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-327

Copyright Permission:
Bettina Loycke
E-mail: rights-and-licences@wiley-vch.de
Fax: (+49) 6201–606-332
Telephone: (+49) 6201–606-280

Online Open:
Margitta Schmitt, Carmen Leitner
E-mail: angewandte@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-315

Subscriptions:
www.wileycustomerhelp.com
Fax: (+49) 6201–606-184
Telephone: 0800 1800536 (Germany only)
+44(0) 1865476721 (all other countries)

Advertising:
Marion Schulz
E-mail: mschulz@wiley-vch.de
jspiess@wiley-vch.de
Fax: (+49) 6201–606-550
Telephone: (+49) 6201–606-565

Courier Services:
Boschstrasse 12, 69469 Weinheim

Regular Mail:
Postfach 101161, 69451 Weinheim

Angewandte Chemie International Edition is a journal of the Gesellschaft Deutscher Chemiker (GDCh), the largest chemistry-related scientific society in continental Europe. Information on the various activities and services of the GDCh, for example, cheaper subscription to *Angewandte Chemie International Edition*, as well as applications for membership can be found at **www.gdch.de** or can be requested from GDCh, Postfach 900440, D-60444 Frankfurt am Main, Germany.

GDCh
GESELLSCHAFT
DEUTSCHER CHEMIKER

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Get the Angewandte App
International Edition

Available on the App Store

Enjoy Easy Browsing and a New Reading Experience on the iPad or iPhone
- Keep up to date with the latest articles in Early View.
- Download new weekly issues automatically when they are published.
- Read new or favorite articles anytime, anywhere.

Service

Author Profile

"My favorite places on earth are Xiamen, Hong Kong, and Guangzhou.
I would have liked to have discovered revolutionary new materials or catalysts …"
This and more about Haiping Xia can be found on page 13968.

Books

Highlights

A big honor for small objects: The Nobel Prize in Chemistry 2014 was jointly awarded to Eric Betzig, Stefan Hell, and William E. Moerner "*for the development of super-resolved fluorescence microscopy*". This Highlight describes how the field of super-resolution microscopy developed from the first detection of a single molecule in 1989 to the sophisticated techniques of today.

Super-resolved Microscopy

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

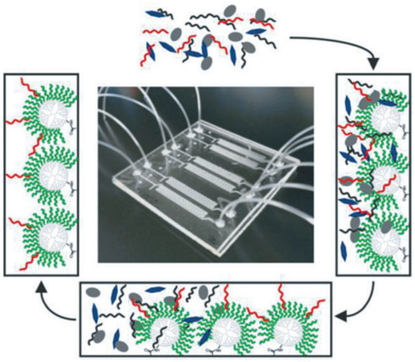
Significant gains in energy savings now underway can be traced to a single invention—the blue light-emitting diode. GaN-based blue LED technology not only resulted in efficient white light sources, but continues to enable a host of applications and scientific inquiries. The researchers primarily responsible for the development of the blue LED were awarded the 2014 Nobel Prize in Physics.

Essays

T. W. Richards

In recognition of his exact determinations of the atomic weights of a large number of the chemical elements, T. W. Richards received the Nobel Prize in Chemistry in 1914. His meticulous techniques resulted in “a degree of accuracy never before attained”. This Essay follows Richards from his precocious youth to becoming a celebrated chemist and emphasizes his dedication to forseeing likely sources of error and how to avoid them.

Reviews



It's a small world: Many nucleic acid isolation techniques have been miniaturized and integrated into microfluidic devices, each having their own advantages and disadvantages, as well as (potential) applications. The techniques presented include using silica-based surfaces, functionalized paramagnetic beads, oligonucleotide-modified polymer surfaces, pH-dependent charged surfaces, and aluminum oxide membranes.

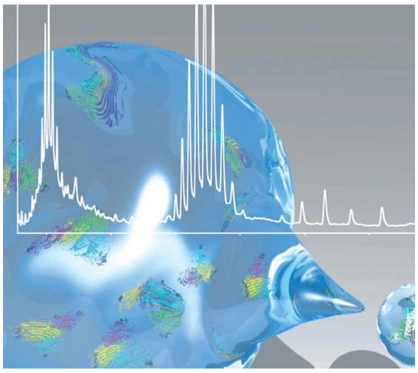
For the USA and Canada: ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. US mailing agent: SPP, PO Box 437, Emigsville, PA 17318. Periodicals postage paid at Emigsville, PA. US POSTMASTER: send address changes to *Angewandte Chemie*, John Wiley & Sons Inc., C/O The Sheridan Press, PO Box 465, Hanover, PA 17331. Annual subscription price for institutions: US$ 11.738/10.206 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Protein Interactions

J. T. S. Hopper,
C. V. Robinson* ———— **14002 – 14015**

Mass Spectrometry Quantifies Protein Interactions—From Molecular Chaperones to Membrane Porins



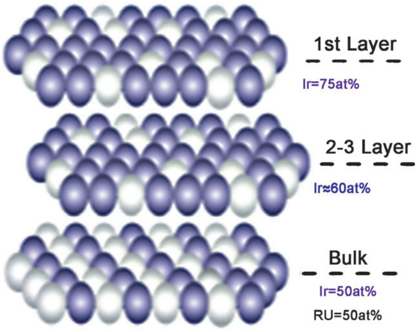
Mass information: Mass spectrometry can provide new insight into dynamic interaction networks, dissociation mechanisms, and the cooperativity of ligand binding. This Review focuses on recent studies that provide quantitative information on dynamic protein interactions in both soluble and membrane-embedded assemblies and discusses potential pitfalls in data interpretation.

Communications

Surface Analysis

N. Danilovic, R. Subbaraman,
K.-C. Chang, S. H. Chang, Y. J. Kang,
J. Snyder, A. P. Paulikas, D. Strmcnik,
Y.-T. Kim, D. Myers, V. R. Stamenkovic,
N. M. Markovic* ———— **14016 – 14021**

Using Surface Segregation To Design Stable Ru-Ir Oxides for the Oxygen Evolution Reaction in Acidic Environments



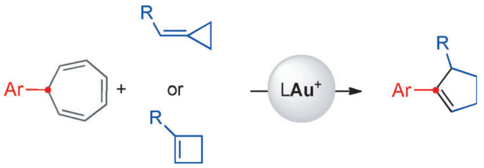
A hive of activity: Tuning the near-surface composition of Ru and Ir elements in a bimetallic oxide by surface segregation results in the formation of a nanosegregated domain (see picture) that balances the stability and activity of surface atoms. A $Ru_{0.5}Ir_{0.5}$ alloy prepared by this method exhibited a stability four-times higher than the best Ru-Ir oxygen evolution reaction materials, but the same activity.

Frontispiece

Gold Catalysis

Y. Wang, M. E. Muratore, Z. Rong,
A. M. Echavarren* ———— **14022 – 14026**

Formal (4+1) Cycloaddition of Methylenecyclopropanes with 7-Aryl-1,3,5-cycloheptatrienes by Triple Gold(I) Catalysis

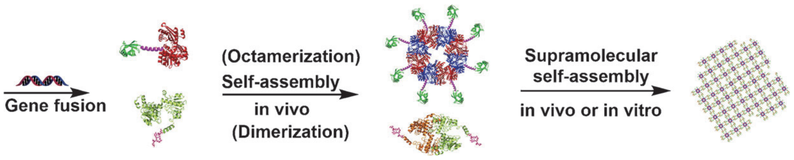


Gold carbenes: 7-Aryl-1,3,5-cycloheptatrienes react intermolecularly with methylenecyclopropanes in a triple gold(I)-catalyzed reaction to form cyclopentenes. The same (4+1) cycloaddition occurs with cyclobutenes.

Biocatalysis

X. Gao, S. Yang, C. Zhao, Y. Ren,*
D. Wei* ———— **14027 – 14030**

Artificial Multienzyme Supramolecular Device: Highly Ordered Self-Assembly of Oligomeric Enzymes In Vitro and In Vivo



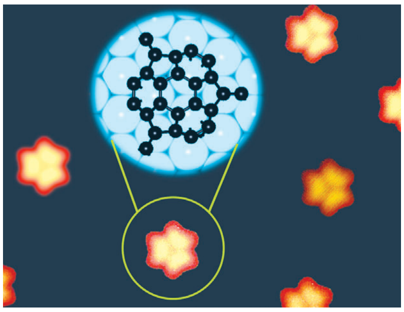
The more the merrier: A two-dimensional layer-like supramolecular assembly of octameric leucine dehydrogenase and dimeric formate dehydrogenase was generated in vitro and in vivo by combining enzyme oligomerization and protein–protein interaction properties. This multienzyme structure had greater stability and higher NAD(H) recycling efficiency than unassembled enzymes when applied to a coenzyme recycling system.

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Carbon Clusters

J. Gao, F. Ding* ________ **14031 – 14035**

The Structure and Stability of Magic Carbon Clusters Observed in Graphene Chemical Vapor Deposition Growth on Ru(0001) and Rh(111) Surfaces

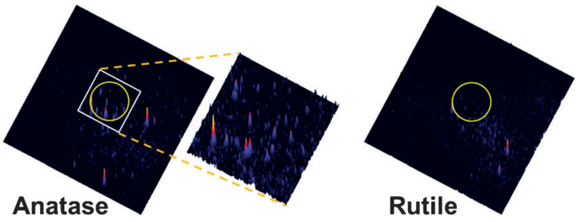


Nucleation of graphene: A new carbon cluster, composed of a C_{21} core and three dangling carbon atoms, is found to be exceptionally stable (see picture). This cluster is the most probable carbon cluster observed during the growth of graphene on Ru(0001) and Rh(111) surfaces by chemical vapor deposition.

Photocatalysis

W. Kim, T. Tachikawa, G.-h. Moon, T. Majima, W. Choi* ____ **14036 – 14041**

Molecular-Level Understanding of the Photocatalytic Activity Difference between Anatase and Rutile Nanoparticles

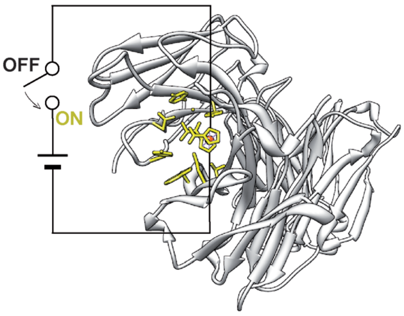


Diffusing free hydroxyl radicals ($^{\bullet}OH_f$) in water are responsible for the higher activity of anatase compared to rutile. A single-molecule detection system was used to directly observe the diffusion of $^{\bullet}OH_f$ from the anatase surface to the bulk solution. In contrast, rutile did not create $^{\bullet}OH_f$ at all.

Structure Elucidation

S. R. Domingos, H. J. Sanders, F. Hartl,* W. J. Buma,* S. Woutersen* ________ **14042 – 14045**

Switchable Amplification of Vibrational Circular Dichroism as a Probe of Local Chiral Structure



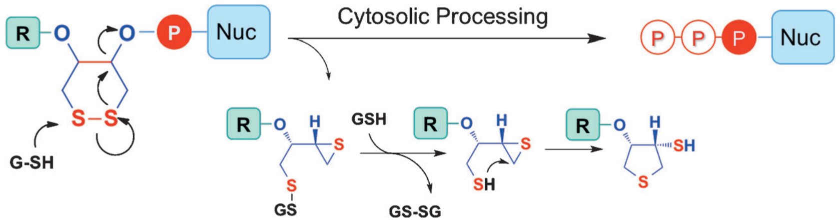
Turn ON the amp: Vibrational circular dichroism (VCD) signals of a spatially restricted part of a molecule can be detected by employing a local VCD amplifier that can be turned ON and OFF electrochemically. The amplification is localized in the neighborhood of the amplifier and can thus be used to locally probe chiral molecular structure.

Front Cover

Drug Design

G. Butora,* N. Qi, W. Fu, T. Nguyen, H.-C. Huang, I. W. Davies **14046 – 14050**

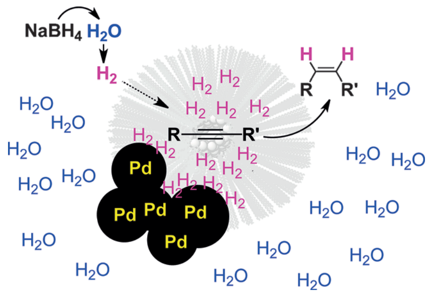
Cyclic-Disulfide-Based Prodrugs for Cytosol-Specific Drug Delivery



Open on delivery: Cyclic-disulfide-based prodrugs are especially suitable for the highly efficient intracellular delivery of antiviral and antimetabolic nucleoside monophosphates. The key feature of this design is a reduction-triggered charge-dissipating cyclodeesterification of an alicyclic disulfide, followed by facile intramolecular self-quenching of the transient thiirane (see scheme; GSH = glutathione).

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Nano, meet nano! The addition of $NaBH_4$ to $Pd(OAc)_2$ in water containing nanomicelles leads to generation of H_2 and Pd nanoparticles. This combination leads to clean and highly selective conversion of alkynes to *Z*-alkenes at room temperature. The aqueous mixture is smoothly recycled without loss of reagent activity, stereochemical outcome, or yield. Furthermore, many functional groups are tolerated under these green conditions.



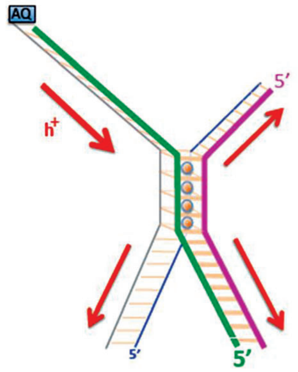
Semihydrogenation

E. D. Slack, C. M. Gabriel,
B. H. Lipshutz* ———— 14051 – 14054

A Palladium Nanoparticle–Nanomicelle Combination for the Stereoselective Semihydrogenation of Alkynes in Water at Room Temperature

---

A mechatronic DNA nanoswitch is composed of a tight, topologically constrained composite of four DNA strands, in which a core of four guanine-rich single strands structurally and electronically links together four DNA double helices. The addition and removal of K^+ or Sr^{2+} cations promote the formation of alternative conformers, which show strikingly distinct electronic properties.

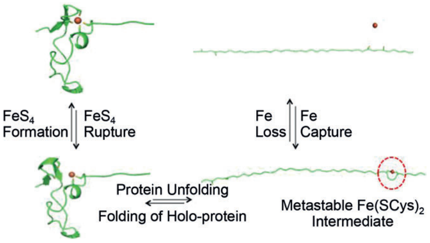


Nanostructures

Y. C. Huang, D. Sen* —— 14055 – 14059

A Twisting Electronic Nanoswitch Made of DNA

Folding technique: A study employing single-molecule force spectroscopy showed that a metastable $Fe(SCys)_2$ intermediate is key to the refolding of holo-rubredoxin and the reconstitution of the FeS_4 center. The study also provides experimental evidence for the iron-priming mechanism for the folding of rubredoxin.

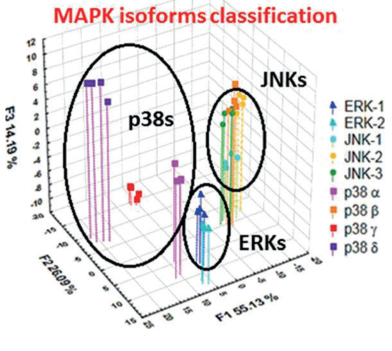


Protein Folding

P. Zheng, Y. Wang, H. Li* 14060 – 14063

Reversible Unfolding–Refolding of Rubredoxin: A Single-Molecule Force Spectroscopy Study

---



SOX it to the kinases: Five SOX peptides are used to classify groups of mitogen-activated protein kinases (MAPK) and their isoforms using chemometrics. The score plots show excellent classification and accuracy, while support vector machine analysis serves to quantify ERK and an ERK inhibitor concentration in kinase mixtures. Examination of the loading plots reveals cross-reactivity among the peptides, and some unexpected results.

Kinase Sensing

D. Zamora-Olivares, T. S. Kaoud, J. Jose,
A. Ellington, K. N. Dalby,*
E. V. Anslyn* ———— 14064 – 14068

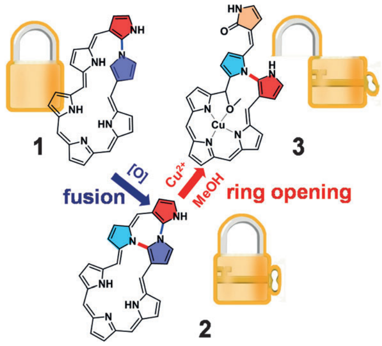
Differential Sensing of MAP Kinases Using SOX-Peptides

Porphyrinoids

P. C. Wei, K. Zhang, X. Li, D. Y. Meng, H. Ågren, Z. P. Ou, S. W. Ng, H. Furuta,* Y. S. Xie* ______ **14069 – 14073**

Neo-Fused Hexaphyrin: A Molecular Puzzle Containing an N-Linked Pentaphyrin

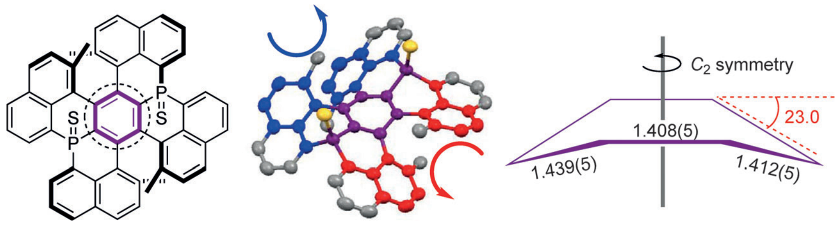
Fusion, confusion? Ring fusion of neo-confused hexaphyrin (1.1.1.1.1.0) **1** led to the bicyclic neo-fused hexaphyrin **2**, and subsequent Cu^{II} coordination triggered a ring opening reaction to afford a contracted N-linked pentaphyrin **3**. The reactive N—C bonds in the porphyrinoid macrocycles play an important role.



Helical Structures

S. Hashimoto, S. Nakatsuka, M. Nakamura,* T. Hatakeyama* ______ **14074 – 14076**

Construction of a Highly Distorted Benzene Ring in a Double Helicene



Bent on helices: A P-fused double helicene consisting of a highly distorted benzene, with a bending angle of 23°, has been synthesized by a tandem intramolecular phospha-Friedel–Crafts reaction. Despite distortion and reduced aromaticity, the proposed molecule shows thermal and chemical stability, and can be converted into the corresponding C_2-symmetric bis(phosphine).

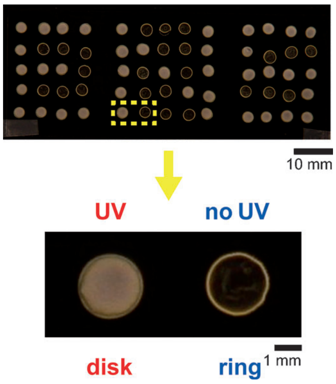
Particle Patterning

M. Anyfantakis, D. Baigl* **14077 – 14081**

Dynamic Photocontrol of the Coffee-Ring Effect with Optically Tunable Particle Stickiness

Inside Cover

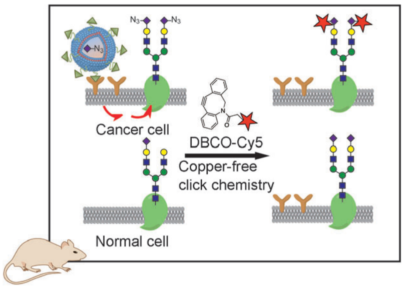
Coffee stain: The dynamic photocontrol of the coffee-ring effect in a particle-laden evaporating drop is achieved through optical tuning of the particle stickiness. Reversible light-dependent modulation of surfactant–particle interactions dictates particle attraction and trapping at the liquid–gas interface, so that particles can be deposited into a wide range of patterns from rings to homogeneous disks.



Tumor Imaging

R. Xie, L. Dong, R. Huang, S. Hong, R. Lei, X. Chen* ______ **14082 – 14086**

Targeted Imaging and Proteomic Analysis of Tumor-Associated Glycans in Living Animals



Sweet target: A strategy for the targeted imaging of tumor-associated glycans is reported and makes use of ligand-targeted liposomes encapsulating azidosugars. The azidosugars were selectively incorporated into the melanoma glycans in a xenograft mouse model and were then reacted with fluorophores by using copper-free click chemistry for in vivo imaging or with affinity tags for proteomic analysis.

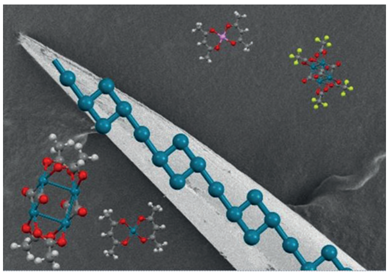
© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Metal Atom Wires

X. Yin, S. A. Warren, Y.-T. Pan, K.-C. Tsao, D. L. Gray, J. Bertke, H. Yang* ________ 14087 – 14091

A Motif for Infinite Metal Atom Wires

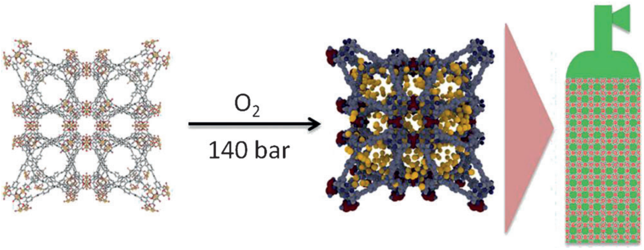
Totally wired: A new motif for the synthesis of 1D metal atom wire crystal is described in which Pd/Pt heterometallic and Pd atom chain structures were formed. The picture depicts an SEM micrograph of a needle-like crystal of the metal atom wire compound and representations of its molecular building blocks.



Oxygen Storage

J. B. DeCoste,* M. H. Weston, P. E. Fuller, T. M. Tovar, G. W. Peterson, M. D. LeVan,* O. K. Farha* ________ 14092 – 14095

Metal–Organic Frameworks for Oxygen Storage



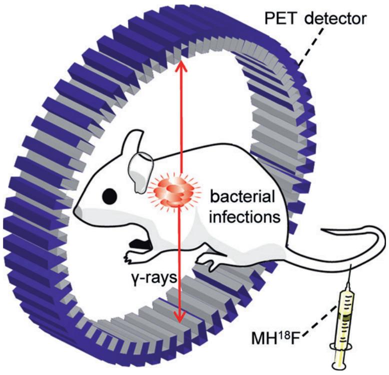
MOFs store oxygen too: Two metal–organic frameworks with open metal sites store oxygen at capacities far greater than that of an empty cylinder and are comparable to the state-of-the-art oxygen storage materials. Self-assembled materials allow for rational design of materials for adsorption of specific gases.

Imaging of Bacteria

X. Ning, W. Seo, S. Lee, K. Takemiya, M. Rafi, X. Feng, D. Weiss, X. Wang, L. Williams, V. M. Camp, M. Eugene, W. R. Taylor,* M. Goodman,* N. Murthy* ________ 14096 – 14101

PET Imaging of Bacterial Infections with Fluorine-18-Labeled Maltohexaose

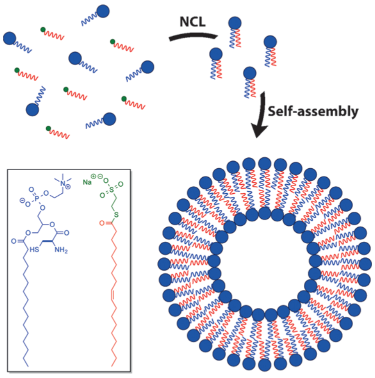
Highly sensitive: A positron emission tomography (PET) tracer composed of ^{18}F-labeled maltohexaose (MH^{18}F) can be used to image bacteria in vivo with a sensitivity and specificity that are orders of magnitude higher than those of fluorodeoxyglucose. MH^{18}F can detect early-stage infections composed of as few as 10^5 *E. coli* colony-forming units (CFUs), and can identify drug resistance in bacteria in vivo.



Phospholipid Membranes

R. J. Brea, C. M. Cole, N. K. Devaraj* ________ 14102 – 14105

In Situ Vesicle Formation by Native Chemical Ligation

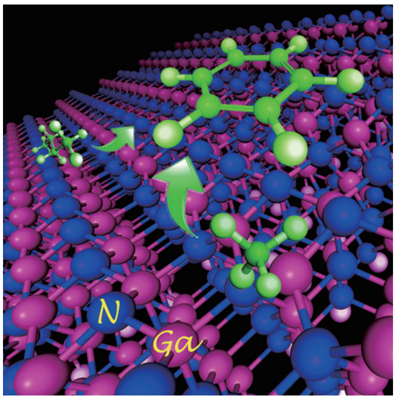


Spontaneous growth: Native chemical ligation (NCL) can be used to prepare phospholipids spontaneously at neutral pH from thioesters. The lipids self-assemble in situ to form vesicles up to several micrometers in diameter. Thanks to the chemoselectivity of NCL, this method of membrane formation in situ is compatible with biological materials.

Heterogeneous Catalysis

L. Li, X. Y. Mu, W. B. Liu, X. H. Kong, S. Z. Fan, Z. T. Mi,* C.-J. Li* ———— **14106 – 14109**

Thermal Non-Oxidative Aromatization of Light Alkanes Catalyzed by Gallium Nitride



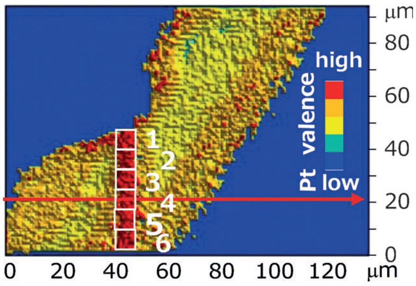
Light weights: The readily available non-doped GaN material possesses superior thermal stability and catalytic activity towards the non-oxidative aromatization of light alkanes (from C_1 to C_6) at elevated temperature. Theoretical calculations suggest an energetically favorable adsorption interaction between methane and the *m*-plane of GaN.

Fuel Cells

S. Takao, O. Sekizawa, S. Nagamatsu, T. Kaneko, T. Yamamoto, G. Samjeské, K. Higashi, K. Nagasawa, T. Tsuji, M. Suzuki, N. Kawamura, M. Mizumaki, T. Uruga, Y. Iwasawa* ——— **14110 – 14114**

Mapping Platinum Species in Polymer Electrolyte Fuel Cells by Spatially Resolved XAFS Techniques

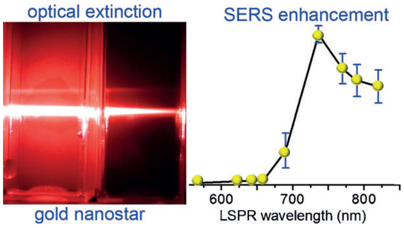
Catalyst characterization: Platinum species in a Pt/C cathode catalyst layer were mapped by spatially resolved X-ray absorption fine structure (XAFS) methods. Information on the oxidation and leaching of Pt cathode nanoparticles in degraded polymer electrolyte fuel cells (PEFCs) is obtained, which is relevant for the mechanism of PEFC degradation.



Plasmonics

M. Li, J. W. Kang, R. R. Dasari, I. Barman* ———— **14115 – 14119**

Shedding Light on the Extinction-Enhancement Duality in Gold Nanostar-Enhanced Raman Spectroscopy

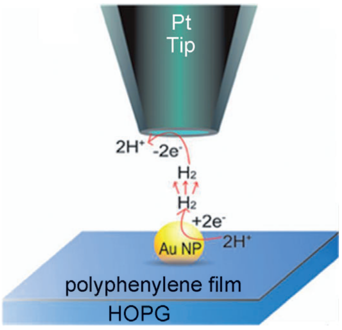


Gold nanostars: The relationship between the enhancement by surface-enhanced Raman spectroscopy (SERS) and the localized surface plasmon resonance (LSPR) band is investigated (see picture). The competition between the field enhancement and the optical extinction causes the maximum enhancement factor occurring at a blue-shifted LSPR band from the excitation wavelength rather than at the on-resonance position.

Electrocatalysis

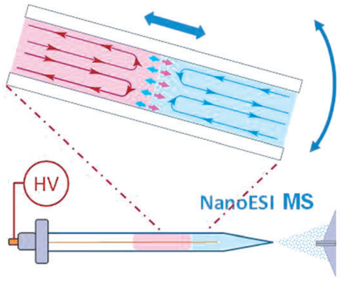
T. Sun, Y. Yu, B. J. Zacher, M. V. Mirkin* ———— **14120 – 14123**

Scanning Electrochemical Microscopy of Individual Catalytic Nanoparticles



Tip size matters: Extremely small polished platnium electrodes were used as scanning electrochemical microscopy tips to attain spatial resolution higher than that of ordinary atomic force microscopy imaging or super-resolution optical techniques. Electron transfer and catalytic hydrogen evolution at individual metal nanoparticles were visualized (HOPG = highly ordered pyrolytic graphite).

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



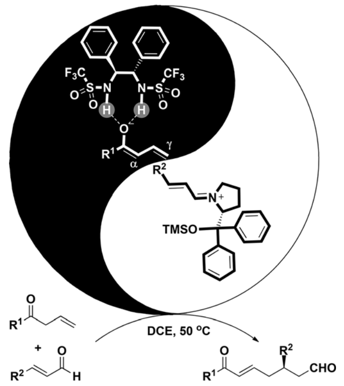
Go with the flow: High sensitivity and quantitation precision have been achieved by using a single-step method based on slug-flow microextraction and nano-electrospray ionization (Nano-ESI) for the MS analysis of organic compounds in only 5 μL of a biofluid. Real-time chemical derivatization allows the analysis of anabolic steroids, and monitoring the enzymatic functions of wet blood is also possible.

Mass Spectrometry

Y. Ren, M. N. McLuckey, J. Liu, Z. Ouyang* ________ **14124–14127**

Direct Mass Spectrometry Analysis of Biofluid Samples Using Slug-Flow Microextraction Nano-Electrospray Ionization

Inside Back Cover



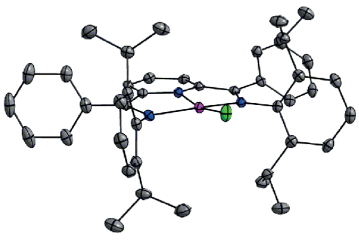
Fall into line: The title catalysis strategy was developed for addressing the long-standing problem of the direct vinylogous Michael addition of unmodified linear dienol substrates. The desired 1,7-dioxo compounds were obtained with good yields and excellent regio- and enantioselectivity. DCE = 1,2-dichloroethane, TMS = trimethylsilyl.

Asymmetric Catalysis

Y. Gu, Y. Wang, T.-Y. Yu, Y.-M. Liang, P.-F. Xu* ________ **14128–14131**

Rationally Designed Multifunctional Supramolecular Iminium Catalysis: Direct Vinylogous Michael Addition of Unmodified Linear Dienol Substrates

---



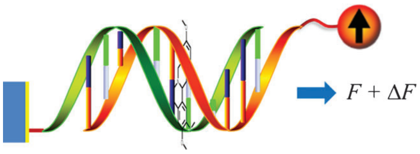
On a plain: Two square-planar complexes of aluminum(III) with chloride and hydride ligands have been synthesized (see picture; C gray, N blue, Al crimson, Cl green). These are supported by tridentate bis(imino)pyridine ligands that are reduced by two electrons. The Al^{III} ion in each is Lewis acidic enough to bind 2,6-lutidine.

Coordination Complexes

E. J. Thompson, T. W. Myers, L. A. Berben* ________ **14132–14134**

Synthesis of Square-Planar Aluminum(III) Complexes

A force to be reckoned with: Intercalation of a drug molecule in a DNA duplex causes a variation in the binding force of the duplex. The differential binding force (ΔF) can be probed precisely using the force-induced remnant magnetization spectroscopy technique. The technique allows the sequence specificity of DNA and chiral selectivity of drug molecules to be revealed.



Noncovalent Interactions

Q. Hu, S. Xu* ________ **14135–14138**

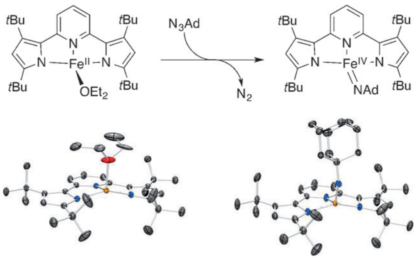
Sequence and Chiral Selectivity of Drug–DNA Interactions Revealed by Force Spectroscopy

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Iron(IV) Complexes

K. Searles, S. Fortier,* M. M. Khusniyarov,
P. J. Carroll, J. Sutter, K. Meyer,*
D. J. Mindiola,*
K. G. Caulton* ———— **14139 – 14143**

A *cis*-Divacant Octahedral and Mononuclear Iron(IV) Imide

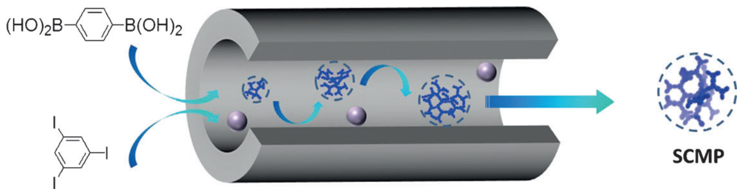


The iron-y of an imide: A rare low-spin Fe^{IV} imide complex [(pyrr$_2$py)Fe=NAd] (pyrr$_2$py^{2-} = bis(pyrrolyl)pyridine; Ad = 1-adamantyl) confined to a *cis*-divacant octahedral geometry was prepared by reduction of N$_3$Ad with the Fe^{II} precursor [(pyrr$_2$py)Fe(OEt$_2$)]. The complex exhibits temperature-independent paramagnetism. In comparison to an authentic Fe^{III} complex, such as [(pyrr$_2$py)FeCl], the pyrr$_2$py^{2-} ligand is virtually redox innocent.

Nanostructures

S. Deng, J. Zhi, X. Zhang, Q. Wu, Y. Ding,*
A. Hu* ———— **14144 – 14148**

Size-Controlled Synthesis of Conjugated Polymer Nanoparticles in Confined Nanoreactors

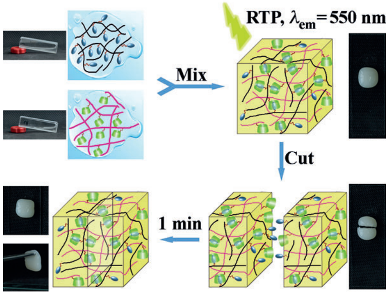


Size matters: Soluble conjugated polymeric nanoparticles are synthesized by Suzuki-type polycondensation of two monomers in the channel of ordered mesoporous silica-supported carbon nanomembranes. These synthesized soluble conjugated microporous polymers (SCMPs) exhibit uniform particle-size distributions and well-controlled particle sizes. The SCMPs are particularly attractive in light-emitting and other optoelectronic applications.

Self-Healing Materials

H. Chen, X. Ma,* S. Wu,
H. Tian* ———— **14149 – 14152**

A Rapidly Self-Healing Supramolecular Polymer Hydrogel with Photostimulated Room-Temperature Phosphorescence Responsiveness



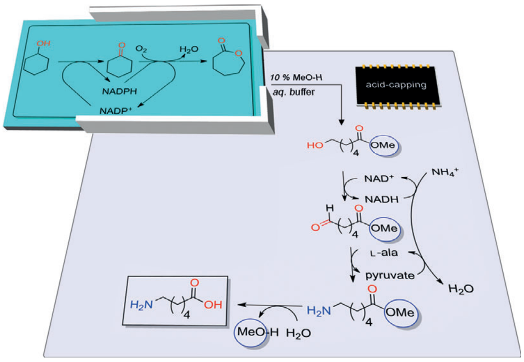
A supramolecular polymeric hydrogel forms by host–guest recognition between a β-cyclodextrin polymer and an α-bromonaphthalene polymer without any additional gelators. This hydrogel can self-heal within only about one minute under ambient atmosphere without any additive, and can be excited to engender photostimulated room temperature phosphorescence (RTP) emission when azobenzene polymer is introduced.

Enzyme Catalysis

J. H. Sattler, M. Fuchs, F. G. Mutti,
B. Grischek, P. Engel, J. Pfeffer,
J. M. Woodley,
W. Kroutil* ———— **14153 – 14157**

Introducing an In Situ Capping Strategy in Systems Biocatalysis To Access 6-Aminohexanoic acid

Get a cap: A nylon-6 monomer was prepared by two biocatalytic self-sufficient redox modules from cyclohexanol at the expense of NH$_3$ and O$_2$. To circumvent an inhibiting intermediate, in situ capping of a carboxylic acid functionality was introduced by opening the intermediate ε-caprolactone to the corresponding methyl ester in buffer.



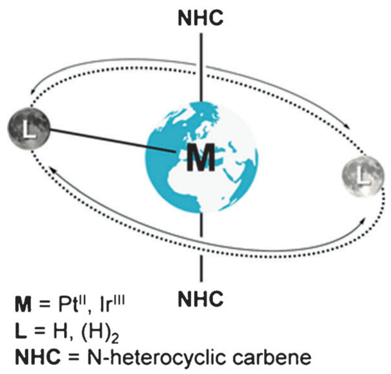
Back Cover

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Metal Hydrides

M. A. Ortuño, P. Vidossich, S. Conejero,*
A. Lledós* ______ 14158 – 14161

Orbital-Like Motion of Hydride Ligands around Low-Coordinate Metal Centers

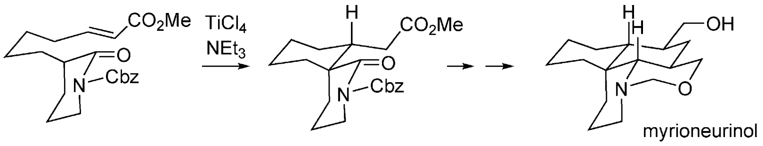


Mobile hydrides: A new type of dynamic process involving hydrides in low-coordinate NHC-based complexes has been computationally characterized. This dynamics can be described as an orbital-like motion of hydride ligands around the metal center. This novel insight leads to a better interpretation of NMR spectra.

Natural Product Synthesis

A. J. Nocket,
S. M. Weinreb* ______ 14162 – 14165

Total Synthesis of the Tetracyclic Antimalarial Alkaloid (±)-Myrioneurinol

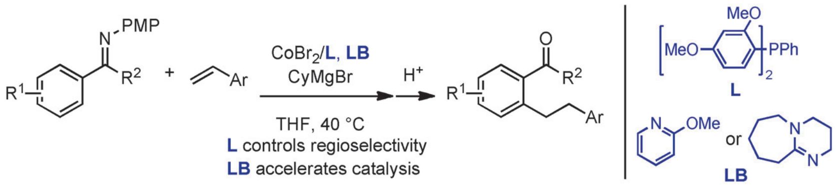


Malaria's worst nightmare: A total synthesis of the tetracyclic antimalarial *Myrioneuron* alkaloid (±)-myrioneurinol features three highly diastereoselective reactions as the key steps: an intramolecular Michael addition of a lactam titanium enolate to an α,β-unsaturated ester, a conjugate addition of a malonate enolate to a nitrosoalkene, and an intramolecular aza-Sakurai reaction.

C−H Activation

W. Xu, N. Yoshikai* ______ 14166 – 14170

Highly Linear Selective Cobalt-Catalyzed Addition of Aryl Imines to Styrenes: Reversing Intrinsic Regioselectivity by Ligand Elaboration

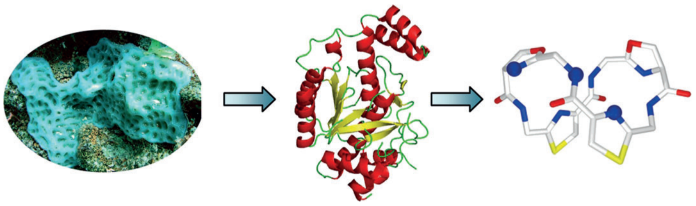


Paired off: The title reaction has been achieved with cobalt-based catalytic systems featuring bis(2,4-dimethoxyphenyl)(phenyl)phosphine (**L**) and either 2-methoxypyridine or DBU (**LB**), thus affording a variety of 1,2-diarylethanes in good yields. Ligand screening and deuterium-labeling studies show the ligand and Lewis base to be important in the crucial C−C reductive elimination step. Cy = cyclohexyl, PMP = *para*-methoxyphenyl.

Enzymatic Route to Cyclic Peptides

W. E. Houssen, A. F. Bent, A. R. McEwan,
N. Pieiller, J. Tabudravu, J. Koehnke,
G. Mann, R. I. Adaba, L. Thomas,
U. W. Hawas, H. Liu, U. Schwarz-Linek,
M. C. M. Smith, J. H. Naismith,*
M. Jaspars* ______ 14171 – 14174

An Efficient Method for the In Vitro Production of Azol(in)e-Based Cyclic Peptides

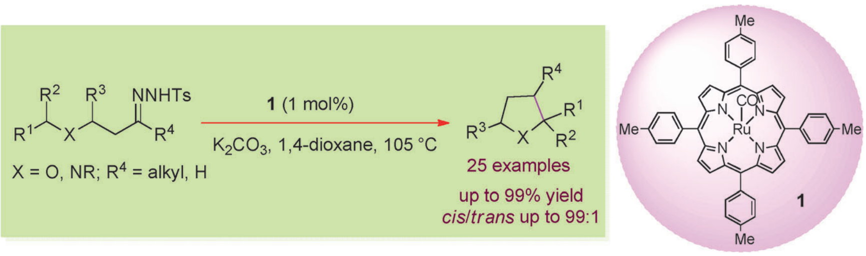


Heterocycle-containing cyclic peptides are promising scaffolds for the pharmaceutical industry, but their chemical synthesis is very challenging. A new universal method has been devised to prepare these compounds by using a set of engineered marine-derived enzymes and substrates.

C–H Functionalization

A. R. Reddy, C.-Y. Zhou, Z. Guo, J. Wei, C.-M. Che* ———— **14175 – 14180**

Ruthenium–Porphyrin-Catalyzed Diastereoselective Intramolecular Alkyl Carbene Insertion into C–H Bonds of Alkyl Diazomethanes Generated In Situ from *N*-Tosylhydrazones

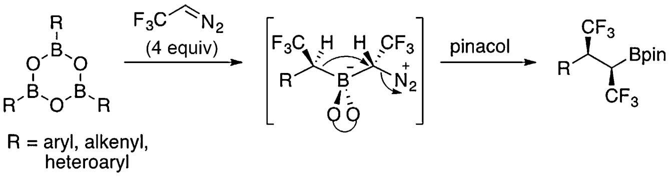


Nose to tail: With a ruthenium–porphyrin catalyst, alkyl diazomethanes generated in situ from *N*-tosylhydrazones underwent efficient intramolecular C(sp^3)–H insertion to give substituted tetrahydrofurans and pyrrolidines (see scheme) in a reaction that can be viewed as a reductive coupling between C=O and C–H bonds to form a new C–C bond. This transformation was applied in a concise synthesis of (±)-pseudoheliotridane.

Trifluoromethylation

G. A. Molander,* D. Ryu **14181 – 14185**

Diastereoselective Synthesis of Vicinally Bis(trifluoromethylated) Alkylboron Compounds through Successive Insertions of 2,2,2-Trifluorodiazoethane

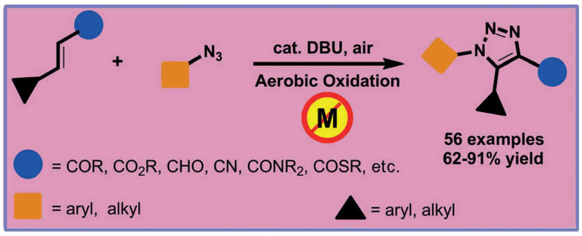


Why stop at one? A recently reported route to α-trifluoromethylated alkylboron compounds by an α-transfer mechanism has now been extended to the synthesis of unprecedented vicinally bis(trifluoromethylated) alkylboron compounds with high diastereoselectivity (see scheme). The utility of these products, each of which was isolated as a single diastereomer, is highlighted by their functionalization through transformation of the C–B bond.

Organocatalysis

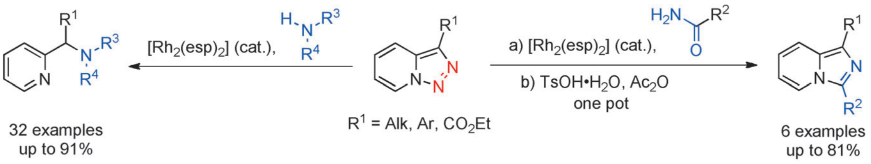
W. Li, J. Wang* ———— **14186 – 14190**

Lewis Base Catalyzed Aerobic Oxidative Intermolecular Azide–Zwitterion Cycloaddition



The works: The discovery of a novel aerobic oxidative intermolecular azide–zwitterion reaction catalyzed by an organocatalyst is presented. It is demonstrated that the merger of the Lewis base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and electron-deficient olefins generates reactive zwitterion intermediates, which readily participate in cycloaddition reactions with an array of azides, thus providing facile entry to fully or highly substituted 1,2,3-triazole frameworks.

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



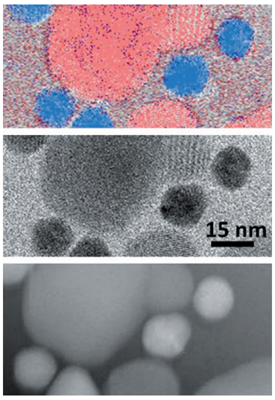
Insert here: A general and efficient NH insertion reaction of rhodium pyridyl carbenes derived from pyridotriazoles was developed. Various NH-containing compounds, including amides, anilines, enamines, and aliphatic amines, smoothly underwent the NH insertion reaction to afford 2-picolylamine derivatives. The developed transformation was further utilized in a facile one-pot synthesis of imidazo[1,5-a]pyridines. esp = α,α,α′,α′-tetramethyl-1,3-benzenedipropionic acid, Ts = 4-toluenesulfonyl.

Heterocycle Synthesis

Y. Shi, A. V. Gulevich,
V. Gevorgyan* ______ **14191 – 14195**

Rhodium-Catalyzed NH Insertion of Pyridyl Carbenes Derived from Pyridotriazoles: A General and Efficient Approach to 2-Picolylamines and Imidazo[1,5-*a*]pyridines

---



A mesoporous photoanode consisting of WO_3 decorated with polyoxometalate-capped Au nanoparticles (NPs) showed a significant enhancement of the visible-light-assisted photoelectrolysis of water. Shielding of the NPs prevents the formation of recombination centers at the photoanode surface. The large increase of water splitting photocurrents is assigned to a combined plasmonic and catalytic effect of the Au NPs on the WO_3 surface.

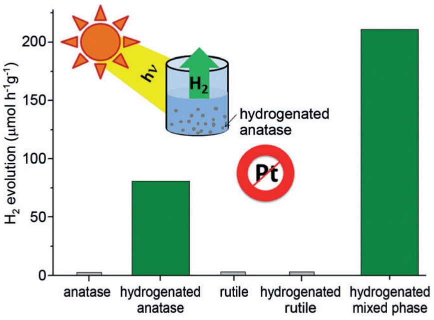
Water Splitting

R. Solarska,* K. Bienkowski, S. Zoladek,
A. Majcher, T. Stefaniuk, P. J. Kulesza,
J. Augustynski ______ **14196 – 14200**

Enhanced Water Splitting at Thin Film Tungsten Trioxide Photoanodes Bearing Plasmonic Gold–Polyoxometalate Particles

---

Without a noble metal: The high-pressure hydrogenation of commercially available anatase or mixed-phase anatase/rutile TiO_2 powder resulted in a highly effective and stable photocatalyst for H_2 evolution without the need for an additional co-catalyst. This activation was not observed for rutile, but for anatase/rutile mixtures, a strong synergistic effect was found.

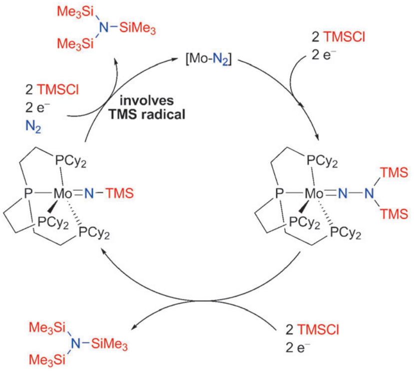


H_2 Production

N. Liu, C. Schneider, D. Freitag,
U. Venkatesan, V. R. R. Marthala,
M. Hartmann, B. Winter, E. Spiecker,
A. Osvet, E. M. Zolnhofer, K. Meyer,
T. Nakajima, X. Zhou,
P. Schmuki* ______ **14201 – 14205**

Hydrogenated Anatase: Strong Photocatalytic Dihydrogen Evolution without the Use of a Co-Catalyst

---



Stoichiometric N_2 reduction at a Mo center stabilized by bulky tetradentate phosphine ligand allowed the isolation of Mo–aminoimide and Mo–imido complexes. Both are suitable catalysts for the synthesis of $NTMS_3$ from N_2 and TMSCl through a mechanism involving a TMS radical.

Dinitrogen Conversion

Q. Liao, N. Saffon-Merceron,
N. Mézailles* ______ **14206 – 14210**

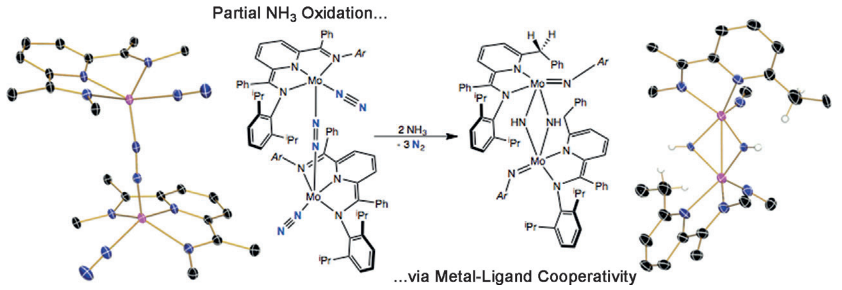
Catalytic Dinitrogen Reduction at the Molybdenum Center Promoted by a Bulky Tetradentate Phosphine Ligand

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Cooperative Effects

G. W. Margulieux, Z. R. Turner,
P. J. Chirik* ______ **14211 – 14215**

Synthesis and Ligand Modification Chemistry of a Molybdenum Dinitrogen Complex: Redox and Chemical Activity of a Bis(imino)pyridine Ligand

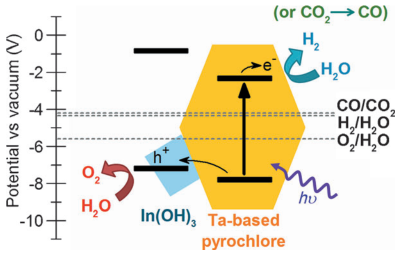


Good golly Miss ‘Moly’: A molybdenum dinitrogen complex supported by a redox-active bis(imino)pyridine ligand has been synthesized and structurally characterized. Unique N—H addition chemistry involving metal–ligand cooperativity has been observed with ammonia and aryl hydrazines, as well as primary and secondary amines. Such transformations are of relevance for synthetic schemes for the interconversion of ammonia and its elements.

Photocatalysis

M.-C. Hsieh, G.-C. Wu, W.-G. Liu,
W. A. Goddard, III,
C.-M. Yang* ______ **14216 – 14220**

Nanocomposites of Tantalum-Based Pyrochlore and Indium Hydroxide Showing High and Stable Photocatalytic Activities for Overall Water Splitting and Carbon Dioxide Reduction

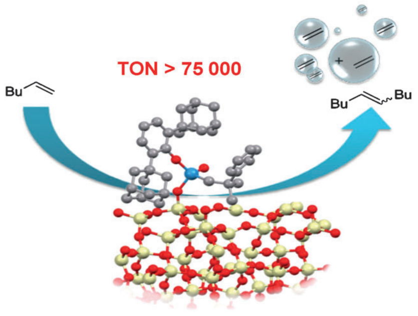


Teamwork: The nanocomposite of Ta-based pyrochlore and $In(OH)_3$ exhibits high and stable photoactivity for water splitting and CO_2 reduction and generates stoichiometric amounts of H_2 (or CO) and O_2. The pyrochlore nanoparticles alone are highly active for H_2 production from methanol. Experiments and DFT calculations suggest that the pyrochlore catalyzes the reduction of water or CO_2, whereas $In(OH)_3$ is the component for water oxidation.

Supported Catalysts

M. P. Conley, W. P. Forrest, V. Mougel,
C. Copéret,*
R. R. Schrock* ______ **14221 – 14224**

Bulky Aryloxide Ligand Stabilizes a Heterogeneous Metathesis Catalyst



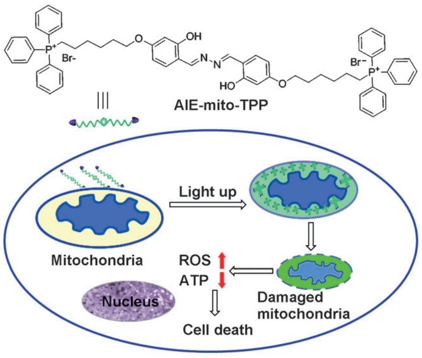
Like a rock: Grafting a W-oxo alkylidene, containing bulky adamantyl-substituted phenoxy ligands, onto partially dehydroxylated silica generates a very active and stable metathesis catalyst. This large ligand allows efficient terminal alkene homocoupling with a turnover number (TON) exceeding 75 000.

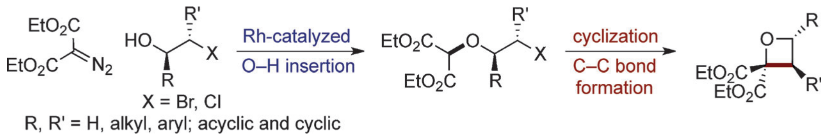
Bioimaging

Q. Hu, M. Gao, G. Feng,
B. Liu* ______ **14225 – 14229**

Mitochondria-Targeted Cancer Therapy Using a Light-Up Probe with Aggregation-Induced-Emission Characteristics

Lighting up mitochondria: A mitochondria-targeting probe (AIE-mito-TPP) has been developed, comprising a triphenylphosphine (TPP) moiety conjugated to a fluorogen, which can undergo aggregation-induced emission (AIE). The preferential aggregation and subsequent emission of AIE-mito-TPP within cancer-cell mitochondria makes them a potential agent for cancer-cell imaging and therapy.



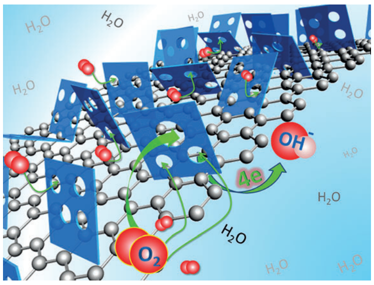


It only takes two (steps): Highly substituted oxetanes and fused oxetane bicycles were generated by a mild, functional-group-tolerant O–H insertion and cyclization strategy. Enantioenriched oxetanes were obtained with complete retention of configuration from enantioenriched bromohydrins. These oxetanes present interesting building blocks for medicinal chemistry and were further functionalized, while the oxetane ring remained intact.

Oxetanes

O. A. Davis, J. A. Bull* ——— **14230 – 14234**

Synthesis of Di-, Tri-, and Tetrasubstituted Oxetanes by Rhodium-Catalyzed O–H Insertion and C–C Bond-Forming Cyclization

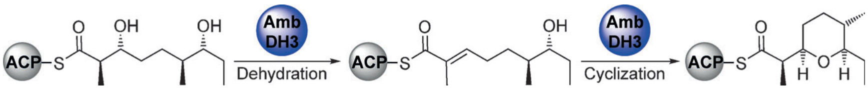


Nitrogen-doped: A new oxygen reduction reaction electrocatalyst was obtained from ZIF-derived porous carbon and graphene. The catalyst exhibits high activity, superior tolerance to methanol, and good stability in comparison to commercial Pt/C catalyst.

Electrocatalysts

H.-x. Zhong, J. Wang, Y.-w. Zhang, W.-l. Xu, W. Xing, D. Xu, Y.-f. Zhang, X.-b. Zhang* ——— **14235 – 14239**

ZIF-8 Derived Graphene-Based Nitrogen-Doped Porous Carbon Sheets as Highly Efficient and Durable Oxygen Reduction Electrocatalysts

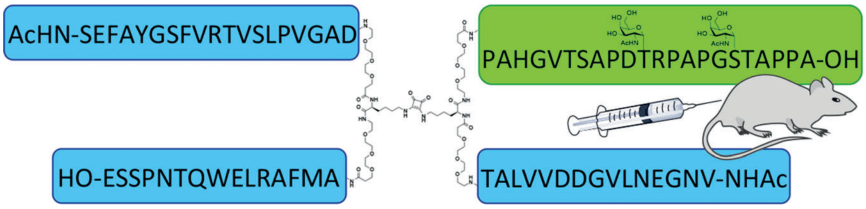


Two birds with one stone: Through reaction of the recombinant polyketide synthase domain AmbDH3 with synthetic substrate surrogates, this domain was shown to have an unprecedented dual role as a dehydratase and a pyran-forming cyclase. The domain shows high stereoselectivity and relaxed substrate specificity, thus making it a potential tool for the chemoenzymatic synthesis of chiral oxygen-containing heterocycles.

Enzyme Catalysis

G. Berkhan, F. Hahn* ——— **14240 – 14244**

A Dehydratase Domain in Ambruticin Biosynthesis Displays Additional Activity as a Pyran-Forming Cyclase



The criss-cross formation of squaric acid diamides was used in the synthesis of anticancer vaccines in which a tumor-associated MUC1 glycopeptide antigen is combined with three different bacterial T-helper-cell epitopes. Without support by complete Freund's adjuvant, the four-component vaccine elicits strong a immune responses in mice and predominantly protective IgG antibodies that recognize human breast cancer cells.

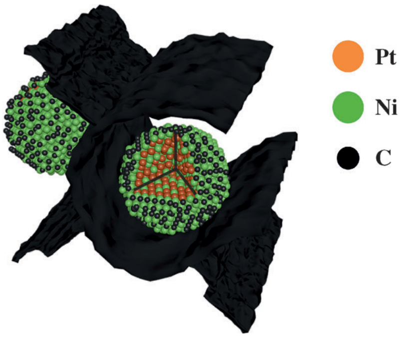
Antitumor Vaccines

B. Palitzsch, S. Hartmann, N. Stergiou, M. Glaffig, E. Schmitt, H. Kunz* ——— **14245 – 14249**

A Fully Synthetic Four-Component Antitumor Vaccine Consisting of a Mucin Glycopeptide Antigen Combined with Three Different T-Helper-Cell Epitopes

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

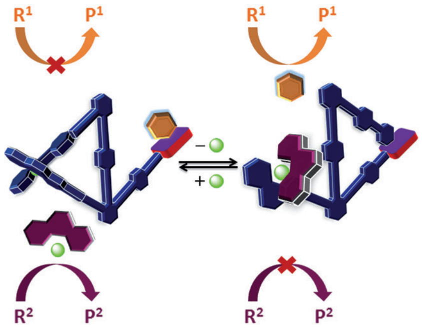
Fuel Cells



Forever young catalysts: An excellently performing electrocatalyst for the oxygen reduction reaction (ORR) is prepared by confined-space alloying of nanoparticles in the pores of a carbon support. Owing to the high specific activity and the small particle size even after thermal annealing, the catalyst has a high mass activity. The nanoparticles are also highly stable in accelerated aging tests.

Switchable Catalysis

Much more than ON and OFF! Like a switch used to toggle between two lamps, the molecular two-state nanoswitch may control two catalytic processes alternately. Here, in the two switching states the catalytically active substances are liberated and bound in alternation.



DOI: 10.1002/anie.201485114

Flashback: 50 Years Ago ...

The chemical effects of nuclear reactions, which can involve “recoil atoms” that have high kinetic energies, were first reported in 1934. 30 years later, the recoil chemistry of tritium was of particular interest as it could be easily produced and was the only radioactive isotope with the chemical properties of hydrogen, and Friedrich Schmidt-Bleek and F. Sherwood Rowland summarized the recoil reactions of tritium with organic compounds in a Review. Rowland shared the Nobel Prize in Chemistry 1995 with Paul J. Crutzen and Mario J. Molina for their work on the formation and decomposition of ozone.

Diazonium species were the subject of two Communications. In the first report, T. Severin and J. Dählstrom described the synthesis of quinonoid diazo compounds from 2-(*p*-nitrophenyl)dimedone. In the second report, K. Bott discussed the synthesis of three stable aliphatic diazonium ions. The identities of these compounds were confirmed by the characteristic signals for the $N\equiv N$ group in the infrared spectrum and by elemental analysis.

Siegfried Hünig and Helmut Quast reported on the detection of a heterocyclic nucleophilic carbene, which was produced by deprotonation of 3-methylbenzthiazolium salts. At that time, there was no reported reaction that could be proved to proceed via a carbene and not the corresponding dimer. In this case, the presence of the carbene was confirmed by comparing the reaction products of the carbene or the dimer with azidinium salts.

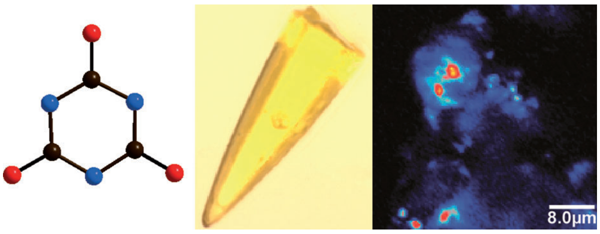
Read more in Issue 12/1964.

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Nonlinear Optical Materials

M. Kalmutzki, M. Ströbele, F. Wackenhut,
A. J. Meixner,
H.-J. Meyer* **14260 – 14263**

Synthesis, Structure, and Frequency-Doubling Effect of Calcium Cyanurate

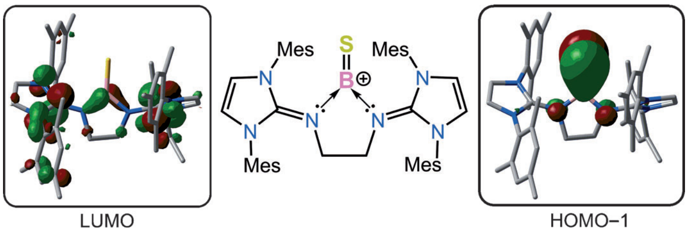


The alkaline-earth cyanurate $Ca_3(O_3C_3N_3)_2$ (CCY) was produced in a solid-state metathesis reaction through the cyclotrimerization of cyanate ions. The crystal structure of CCY is closely related to the structure of β-BBO. Crystalline CCY promises to be amongst the most efficient frequency doubling materials.

Boron Compounds

D. Franz, E. Irran,
S. Inoue* **14264 – 14268**

Isolation of a Three-Coordinate Boron Cation with a Boron–Sulfur Double Bond



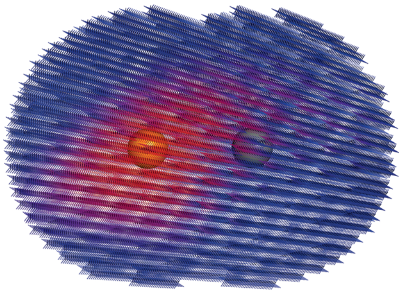
A healthy relationship: The first three-coordinate boron cation with a boron–sulfur double bond has the shortest B–S distance reported for a molecular complex. In the calculated LUMO, the contribution from the boron center confirms that the compound is a boron-centered cation. The HOMO−1 reveals the π interaction which is the cause of the close contact between B and S.

Metalloenzymes

T. J. Carruthers, P. D. Carr, C.-T. Loh,
C. J. Jackson, G. Otting* **14269 – 14272**

Iron(III) Located in the Dinuclear Metallo-β-Lactamase IMP-1 by Pseudocontact Shifts

Metal detector: Pseudocontact shifts measured by NMR spectroscopy allow the accurate determination of the location of paramagnetic metal ions in the active site of dinuclear metalloenzymes. Using this method a [FeZn]-complex of the metallo-β-lactamase IMP-1 could be identified and characterized.



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).

This article is available online free of charge (Open Access).

This article is accompanied by a cover picture (front or back cover, and inside or outside).

The Very Important Papers, marked VIP, have been rated unanimously as very important by the referees.

The Hot Papers are articles that the Editors have chosen on the basis of the referee reports to be of particular importance for an intensely studied area of research.