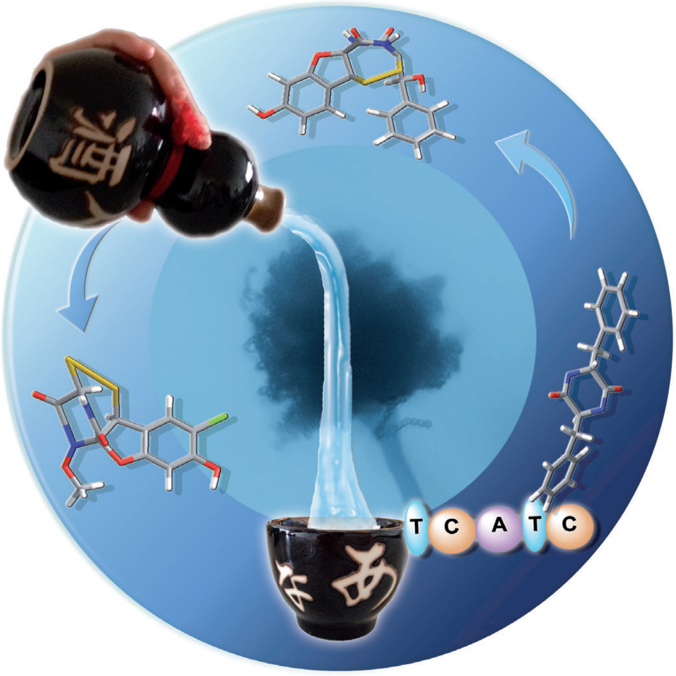
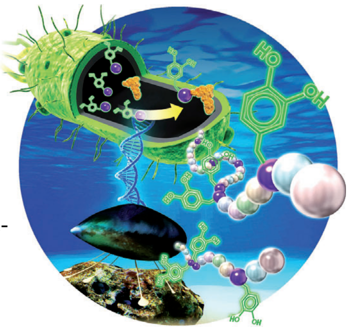
The Koji Mold *Aspergillus oryzae*, …

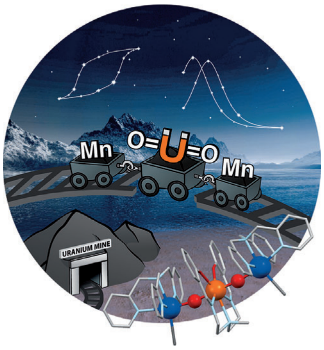


… which is widely used in food fermentations (e.g., sake production), produces the toxin aspirochlorine. C. Hertweck et al. elucidated in their Communication on page 13409 ff. the biosynthetic pathway of this chlorinated epipolythiodioxopiperazine. An iterative non-ribosomal peptide synthetase assembles the diketopiperazine core from two phenylalanine units, one of which then undergoes an unprecedented conversion to glycine. Enzymatic halogenation of the second Phe unit significantly contributes to the biological activity of aspirochlorine.

Adhesive Proteins

Mussel glue with a very high Dopa content was engineered through residue-specific Dopa incorporation in *Escherichia coli*, as described by H. J. Cha et al. in their Communication on page 13360 ff. The bioglue exhibits strong adhesion and water-resistance.





Single-Molecule Magnets

In their Communication on page 13434 ff., M. Mazzanti et al. report a trinuclear {Mn−O=U=O−Mn} complex that behaves as a single-molecule magnet with the highest effective relaxation barrier (81 ± 0.5 K) for a mono-uranium system.

Lithium-Ion Batteries

The aspect ratio of the nanostructures used to fabricate electrode materials correlates with the electrochemical performance in lithium-ion batteries. The findings of Z. Chen, X. Chen, et al. in their Communication on page 13488 ff. may lead to efficient devices based on nanomaterials.

How to contact us:

Editorial Office:
E-mail: angewandte@wiley-vch.de
Fax: (+49) 62 01–606-331
Telephone: (+49) 62 01–606-315

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Service

Author Profile

"I can never resist good food.
My biggest motivation is to understand the principles behind interesting phenomena …"
This and more about Xi Zhang can be found on page 13322.

News

J.-P. Sauvage

A. Sekiguchi

M. Köhn

J. Roithová

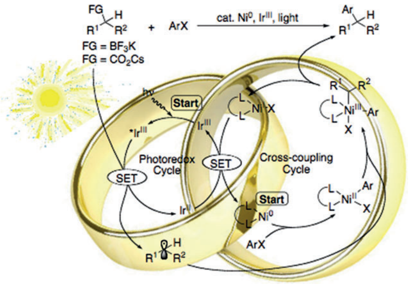
Books

Highlights

Photoredox Catalysis

E. Jahn, U. Jahn* ______ **13326 – 13328**

Oxidative Photoredox-Catalytic Activation of Aliphatic Nucleophiles for C(sp^3)–C(sp^2) Cross-Coupling Reactions



In the light you will find the road (Led Zeppelin): Visible-light photoredox catalysis leads the way in overcoming the reactivity limitations of alkyl nucleophiles in cross-coupling reactions. Iridium-triggered oxidative photoredox activation of alkyltrifluoroborate or carboxylic acids affords alkyl radicals, which undergo nickel-catalyzed cross-coupling reactions.

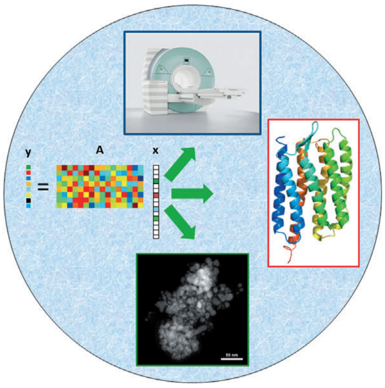
Minireviews

Signal Processing

D. J. Holland,*
L. F. Gladden ______ **13330 – 13340**

Less is More: How Compressed Sensing is Transforming Metrology in Chemistry

A mathematical concept known has compressed sensing has emerged recently that is leading to faster, higher resolution measurements from an array of instruments, as well as leading to the development of entirely new measurement approaches. This Minireview highlights the principles and key applications of compressed sensing across chemistry, physics, and medicine.

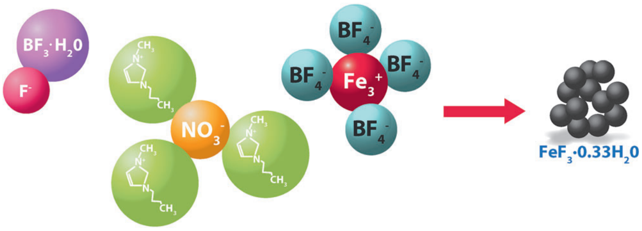


Reviews

Energy Materials

G. Gebresilassie Eshetu, M. Armand,
B. Scrosati,*
S. Passerini* ______ **13342 – 13359**

Energy Storage Materials Synthesized from Ionic Liquids



Functional ionic liquids (ILs) are appealing eco-friendly solvents for the synthesis of tailor-made inorganic compounds of use in energy storage devices. Their peculiar properties, such as low volatility, wide liquidus range, high thermal stability, and large electrochemical window, make them suitable as functional advanced materials, media for materials production, and components for preparing highly engineered functional products.

For the USA and Canada:
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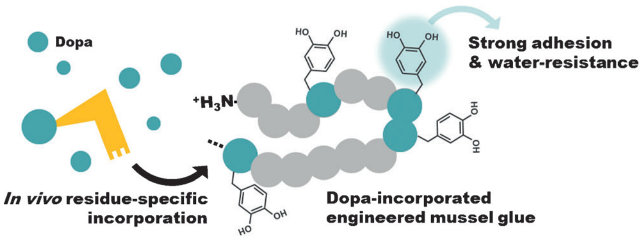
Communications

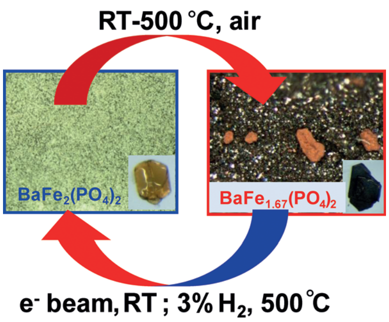
Mussel Adhesive

Frontispiece



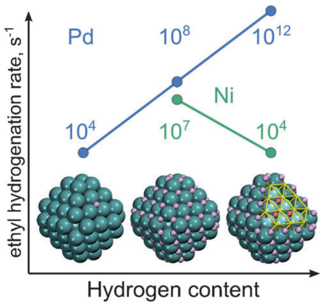
Engineered mussel glue with a very high 3,4-dihydroxyphenylalanine (Dopa) content close to that of natural protein was created through in vivo residue-specific Dopa incorporation method in *Escherichia coli*. This bioglue exhibited strong adhesion and water-resistance, which shows great potential in underwater applications.

Reversible Iron Exsolution



Digging holes and refilling them: $BaFe_2(PO_4)_2$ is the first 2D-Ising ferromagnetic oxide, and it has a unique re-entrant structural transition at low temperature. Furthermore, it topochemically oxidizes into a variety of fully ordered 2D Fe-depleted compounds with mixed Fe^{2+}/Fe^{3+} valence, even at room temperature, with modified properties. This process is reversible, and Fe can be reincorporated under H_2 flux or electron beam.

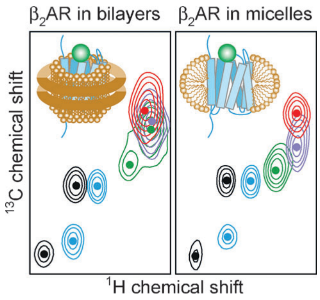
Surface Chemistry



Understanding hydrogenation on transition metals: Subsurface hydrogen, H^{sub}, is shown to significantly influence the stability and the reactivity of the adsorbed hydrogen in two different ways. Calculations on a representative reaction, ethyl hydrogenation, show that it is accelerated on Pd and Pt, but slowed down on Ni and Rh in the presence of H^{sub}.

Membrane Proteins

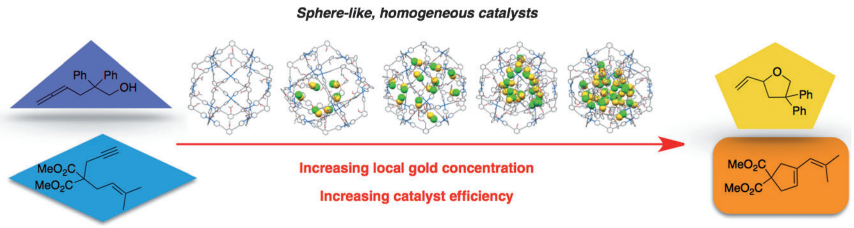
Functional dynamics: NMR analyses revealed that the exchange rates and populations in the conformational equilibrium between the active and inactive states of the β_2-adrenergic receptor (β_2AR), a G-protein-coupled receptor (GPCR), were remarkably different in a lipid bilayer than in detergents. The fast timescale of activation of intracellular signaling by GPCRs, as calculated from the exchange rates, enables rapid neurotransmission and sensory perception.



Homogeneous Catalysis

R. Gramage-Doria, J. Hessels,
S. H. A. M. Leenders, O. Tröppner,
M. Dürr, I. Ivanović-Burmazović,
J. N. H. Reek* ________ **13380 – 13384**

Gold(I) Catalysis at Extreme Concentrations Inside Self-Assembled Nanospheres

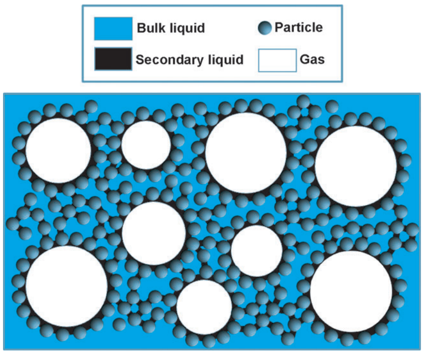


A(u)ll in!! A self-assembly strategy which allows catalysis at extremely high local catalyst concentration inside a well-defined nanosphere is reported. The resulting intrinsically inactive gold(I) chloride complexes become catalytically active with high selectivities.

Surface Chemistry

Y. Zhang, J. Wu, H. Wang, J. C. Meredith,*
S. H. Behrens* ________ **13385 – 13389**

Stabilization of Liquid Foams through the Synergistic Action of Particles and an Immiscible Liquid

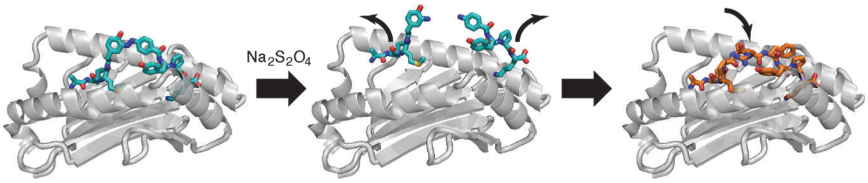


Capillary foams are a new class of foams, in which particles and a secondary liquid jointly adsorb at the surface of gas bubbles within a bulk liquid. Particles that adsorb preferentially at the interface of the secondary liquid can mediate its spreading around the gas bubbles. The bubbles are further entrapped in a network of excess secondary-liquid-bridged particles in the primary liquid.

Immunology

J. A. L. Choo, S. Y. Thong, J. Yap,
W. J. E. van Esch, M. Raida, R. Meijers,
J. Lescar, S. H. L. Verhelst,
G. M. Grotenbreg* ________ **13390 – 13394**

Bioorthogonal Cleavage and Exchange of Major Histocompatibility Complex Ligands by Employing Azobenzene-Containing Peptides



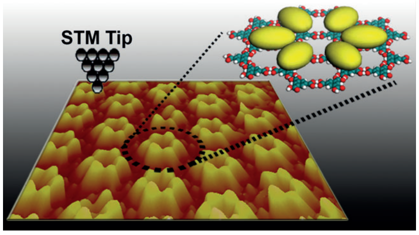
As easy as Abc: Replacement of an azobenzene-containing (Abc) peptide with novel MHC ligands can be triggered by sodium dithionite. The Abc peptide (turquoise) is cleaved into two fragments, which are released from the binding groove. A novel epitope (orange) can then reoccupy the protein complex. This strategy enables the parallel generation of an array of MHCs with novel antigen-specificities for use in high-throughput studies of T cell responses.

Surface Molecular Engineering

Q.-N. Zheng, X.-H. Liu, X.-R. Liu, T. Chen,
H.-J. Yan, Y.-W. Zhong, D. Wang,*
L.-J. Wan* ________ **13395 – 13399**

Bilayer Molecular Assembly at a Solid/Liquid Interface as Triggered by a Mild Electric Field

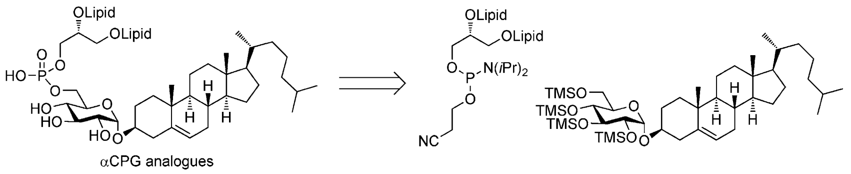
Flowers that bloom and fade: An electric field applied between an STM tip and the substrate triggered the formation of a hetero-bilayer structure of flower-shaped clusters of triazole-substituted pyrene molecules on top of a trimesic acid matrix (see picture). The bilayer structure could be transformed into a monolayer kagome structure by changing the polarity of the electric field.



Natural Products

H. Q. Nguyen, R. A. Davis,
J. Gervay-Hague* ———— **13400 – 13403**

Synthesis and Structural Characterization of Three Unique *Helicobacter pylori* α-Cholesteryl Phosphatidyl Glucosides

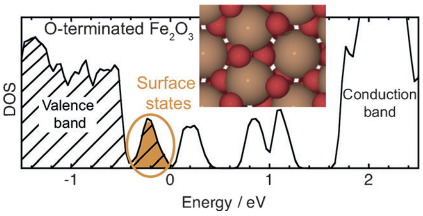


Analogues of α-cholesteryl phosphoglycolipids (αCPGs), which are immunostimulants produced by *H. pylori* bacteria, were synthesized in a step-economical manner. The approach relies upon the regioselective deprotection of per-*O*-trimethylsilyl-α-D-cholesterylglucoside at C6 followed by the phosphorylation with a phosphoramidite. TMS = trimethylsilyl.

Water Splitting

B. Iandolo,* A. Hellman **13404 – 13408**

The Role of Surface States in the Oxygen Evolution Reaction on Hematite



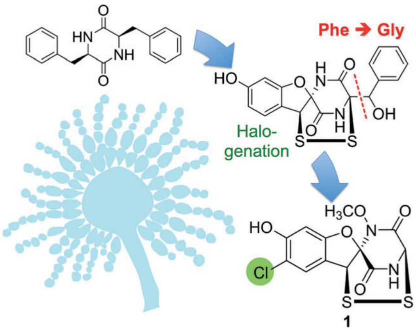
Riding on the surface states highway: First-principles calculations and photoelectrochemical measurements provide a framework for deepened understanding of the oxygen evolution reaction from water splitting on hematite. The reaction takes place on the O-terminated hematite surface via surface states close in energy to the top of the valence band.

Mycotoxin Biosynthesis

P. Chankhamjon, D. Boettger-Schmidt,
K. Scherlach, B. Urbansky, G. Lackner,
D. Kalb, H.-M. Dahse, D. Hoffmeister,
C. Hertweck* ———— **13409 – 13413**

Biosynthesis of the Halogenated Mycotoxin Aspirochlorine in Koji Mold Involves a Cryptic Amino Acid Conversion

Front Cover



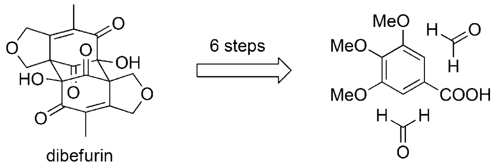
1

A delicious riddle: The koji mold *Aspergillus oryzae* is used for the production of Asian delicacies like soy sauce and sake. The biosynthesis of the toxin aspirochlorine (**1**) in *A. oryzae* was elucidated by mutagenesis, in vitro adenylation, and isotope labeling. It was found that its peptide core is not assembled from Phe and Gly, but from two Phe units: one Phe undergoes chlorination and oxygenation whereas the other one is transformed into Gly.

Total Synthesis

P. Ellerbrock, N. Armanino,
D. Trauner* ———— **13414 – 13418**

Biomimetic Synthesis of the Calcineurin Phosphatase Inhibitor Dibefurin



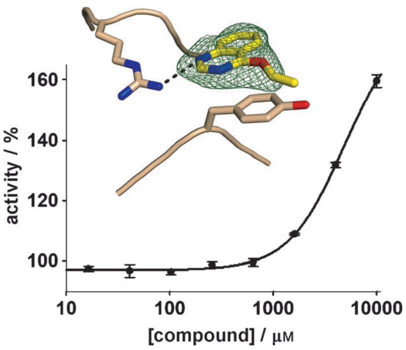
Studies in symmetric synthesis: The C_i-symmetric calcineurin phosphatase inhibitor dibefurin was synthesized in six steps, the last of which is a biomimetic homodimerization. The synthesis provides an example of the fascinating reactivity of pyrogallols under oxidative conditions.

Enzyme Catalysis

J. F. Darby, J. Landström, C. Roth, Y. He, G. J. Davies, R. E. Hubbard* ________ **13419 – 13423**

Discovery of Selective Small-Molecule Activators of a Bacterial Glycoside Hydrolase

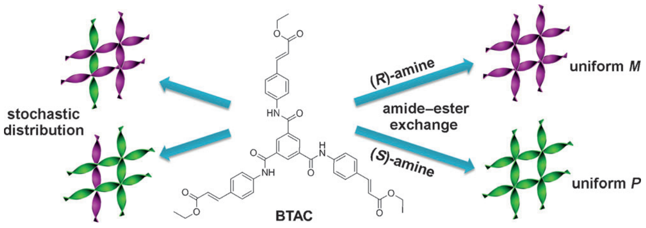
Glycosidase activators: Small-molecule activators of a glycoside hydrolase are identified from a biophysical fragment-based screening approach. In the crystal structure, the activators (yellow molecule in picture) are seen to bind close to the catalytic center of the enzyme and behave as nonessential activators. Activation potentially occurs through stabilization of a substrate-bound form of the enzyme.



Chirality

Z. Shen, T. Wang,* M. Liu* ________ **13424 – 13428**

Macroscopic Chirality of Supramolecular Gels Formed from Achiral Tris(ethyl cinnamate) Benzene-1,3,5-tricarboxamides



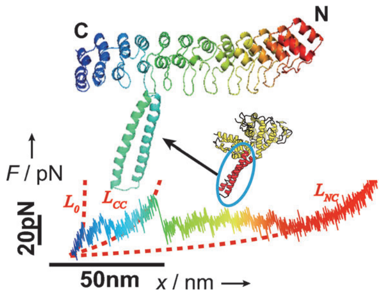
The self-assembly of achiral and C_3-symmetric benzene-1,3,5-tricarboxamides (BTAC) in DMF/H_2O mixtures without any chiral dopants led to supramolecular gels that showed macroscopic chirality. The unequal number of left- and right-handed twists and thus the macroscopic chirality of the gels could be controlled through amide–ester exchange reactions.

Protein Folding

Q. Li, Z. N. Scholl, P. E. Marszalek* ________ **13429 – 13433**

Capturing the Mechanical Unfolding Pathway of a Large Protein with Coiled-Coil Probes

An antiparallel coiled coil (CC) mechanical probe that can be used to assess the unfolding mechanism of a protein is developed. When a protein is studied by single-molecule force spectroscopy, the probe enables the assignment of force peaks to structural elements when the unfolding process passes through the location of the CC probe without significant disturbance of the host protein structure.

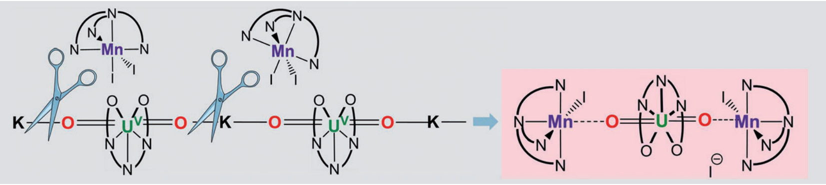


Single-Molecule Magnets

L. Chatelain, J. P. S. Walsh, J. Pécaut, F. Tuna, M. Mazzanti* ___ **13434 – 13438**

Self-Assembly of a 3d–5f Trinuclear Single-Molecule Magnet from a Pentavalent Uranyl Complex

Inside Back Cover

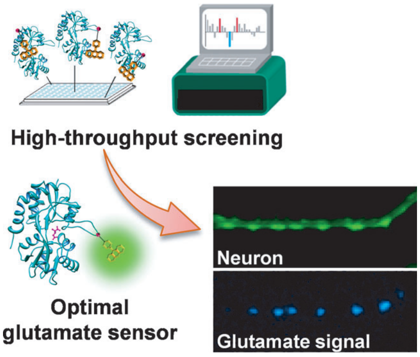


Assembling SMMs: A TPA-capped Mn^{II} complex (TPA = tris(2-pyridylmethyl)amine) is used to promote the controlled formation of a UMn_2 trinuclear complex that exhibits the behavior of a single-molecule magnet (SMM). This complex has a relaxation barrier of 81 ± 0.5 K arising from intramolecular Mn–U exchange interactions and an open magnetic hysteresis loop at $T < 3$ K.

Fluorescent Probes

K. Takikawa, D. Asanuma, S. Namiki,
H. Sakamoto, T. Ariyoshi, N. Kimpara,
K. Hirose* ———— 13439 – 13443

High-Throughput Development of a Hybrid-Type Fluorescent Glutamate Sensor for Analysis of Synaptic Transmission

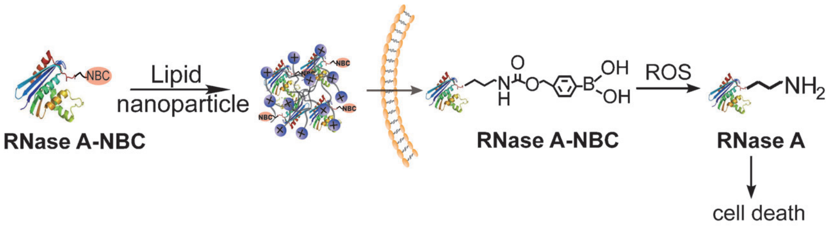


Space probes: A high-throughput screening system has been used to develop a high-performance fluorescent glutamate sensor with a dynamic range $>2400\%$, good photostability, and high selectivity. The use of this sensor enabled the spatiotemporal dynamics of glutamate release at single synapses to be reliably visualized, thereby revealing a synapse-to-synapse heterogeneity of short-term plasticity.

Drug Delivery

M. Wang, S. Sun, C. I. Neufeld,
B. Perez-Ramirez, Q. Xu* 13444 – 13448

Reactive Oxygen Species-Responsive Protein Modification and Its Intracellular Delivery for Targeted Cancer Therapy

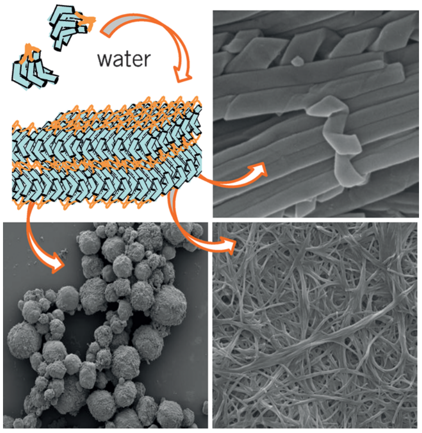


Reversible protein function modulation was achieved by a convenient chemical approach. RNase A was equipped with a boronic acid group (RNase A–NBC) that responds to reactive oxygen species (ROS). This complex shows cytotoxicity in the presence of ROS, as for example in cancer cells, whereas healthy cells are only affected at significantly higher concentrations.

Chirality Transfer

M. Cano, A. Sánchez-Ferrer, J. L. Serrano,
N. Gimeno,* M. B. Ros* 13449 – 13453

Supramolecular Architectures from Bent-Core Dendritic Molecules

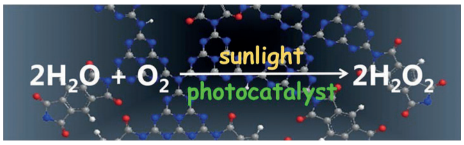


Twist of fate: Achiral, ionic bent-core dendrimers can not only lead to different bent-core liquid crystals (BCLCs) but also to a variety of aggregates in water, such as rods, spheres, nontwisted, or twisted fibers, and helical ribbons that lead to tubules. The conformational chirality of bent-core molecules in BCLCs can also be translated to chiral supramolecular architectures in the presence of a solvent.

Photocatalysis

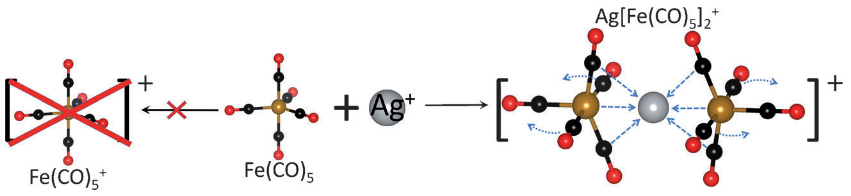
Y. Shiraishi,* S. Kanazawa, Y. Kofuji,
H. Sakamoto, S. Ichikawa, S. Tanaka,
T. Hirai ———— 13454 – 13459

Sunlight-Driven Hydrogen Peroxide Production from Water and Molecular Oxygen by Metal-Free Photocatalysts



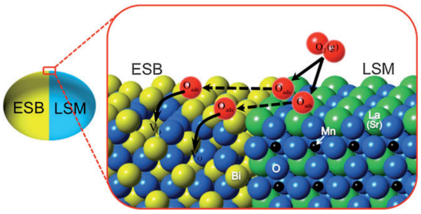
Peroxide made by sunbathing: Sunlight irradiation ($\lambda > 400$ nm) of graphitic carbon nitride ($g\text{-}C_3N_4$) containing electron-deficient aromatic diimide units successfully produces H_2O_2 from water and O_2. This metal-free H_2O_2 synthesis is driven by oxidation of water by the photoformed valence-band holes and selective two-electron reduction of O_2 by the conduction-band electrons.

Weakly Coordinating Anions



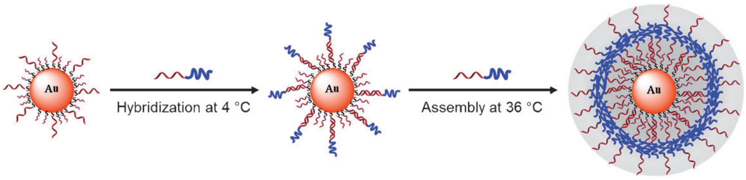
Oxidation or coordination? A simple reaction between a silver salt with a weakly coordinating anion and Fe(CO)$_5$ yields the unprecedented Ag[Fe(CO)$_5$]$_2^+$ complex. This nonclassical carbonyl cation shows unusual stability as a crystalline solid (up to 150 °C). In the crystal and in DFT calculations it shows a unique bonding pattern with four carbonyl groups with bonds bent towards Ag, breaking the expected 4-fold symmetry.

Fuel Cells



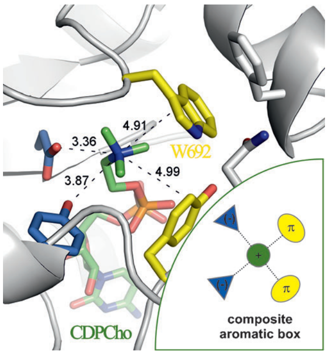
Composite electrode: A novel in situ co-assembled nanocomposite icn-LSMESB, consisting of La$_{1-x}$Sr$_x$MnO$_3$ (LSM) and Bi$_{1.6}$Er$_{0.4}$O$_3$ (ESB), with feature size of <80 nm for each phase is synthesized by conjugated wet-chemical synthesis. It exhibits a >140 times enhanced cathode polarization at 600 °C compared to conventional LSM–Y$_{0.08}$Zr$_{0.84}$O$_{1.92}$ (YSZ) cathodes and an exceptional solid oxide fuel cell performance at reduced temperature.

Vesicle Formation



You've been framed: By employing the thermally responsive poly(propylene oxide) (PPO) as the leading hydrophobic groups (LHGs) on gold nanoparticles, a frame-guided assembly strategy could be triggered by temperature change. Increasing the temperature above the low critical solution temperature (LCST), the PPO became hydrophobic allowing DNA-*b*-PPO to assemble around the nanoparticle frame by hydrophobic interactions generating vesicles.

Enzyme Recognition

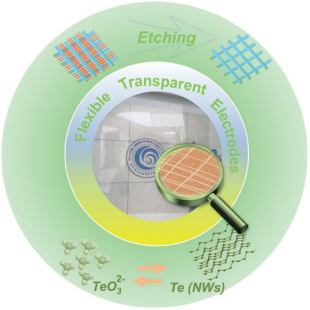


Composite aromatic box: The key functional role of both charged (blue) and cation–π (yellow in the picture) interactions within the choline-binding subsite of CTP:phosphocholine cytidylyltransferase and choline kinase from *Plasmodium falciparum* have been deciphered. The comparison of quaternary ammonium binding site structures revealed a general composite aromatic box pattern of enzyme recognition sites.

Nanowire Devices

J.-W. Liu, J.-L. Wang, Z.-H. Wang, W.-R. Huang, S.-H. Yu* **13477 – 13482**

Manipulating Nanowire Assembly for Flexible Transparent Electrodes

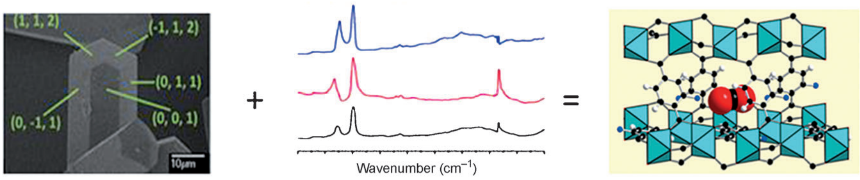


Nano networking: Silver nanowires and Te nanowires are co-assembled by the Langmuir–Blodgett technique. Etching away the Te nanowires leaves Ag nanowire networks in which the spacing between the Ag wires is controlled by the Te nanowires. By manipulating the spacing between nanowires the optical transparency and electrical conductivity of flexible Ag nanowire electrodes can be precisely tailored.

Metal–Organic Frameworks

A. Greenaway, B. Gonzalez-Santiago, P. M. Donaldson, M. D. Frogley, G. Cinque, J. Sotelo, S. Moggach, E. Shiko, S. Brandani, R. F. Howe,* P. A. Wright* **13483 – 13487**

In situ Synchrotron IR Microspectroscopy of CO_2 Adsorption on Single Crystals of the Functionalized MOF $Sc_2(BDC\text{-}NH_2)_3$



Materials for carbon capture: In situ IR microspectroscopy has been used to probe the adsorption behavior of a small-pore amino-functionalized metal–organic framework (MOF; see picture) under flowing gas conditions relevant to carbon capture. Single crystals of the MOF $Sc_2(BDC\text{-}NH_2)_3$ have been investigated during CO_2 uptake ($BDC\text{-}NH_2$ = 2-amino-1,4-benzenedicarboxylate).

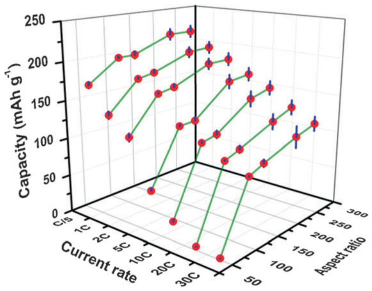
Lithium-Ion Batteries

Y. Tang, Y. Zhang, J. Deng, D. Qi, W. R. Leow, J. Wei, S. Yin, Z. Dong, R. Yazami, Z. Chen,* X. Chen* **13488 – 13492**

Unravelling the Correlation between the Aspect Ratio of Nanotubular Structures and Their Electrochemical Performance To Achieve High-Rate and Long-Life Lithium-Ion Batteries

Back Cover

A new aspect: When titanate-based nanotubes are used to fabricate electrode materials, the aspect ratio of the nanostructures correlates with the electrochemical performance in lithium-ion batteries. These insights should be useful in the development of efficient energy devices based on nanomaterials.

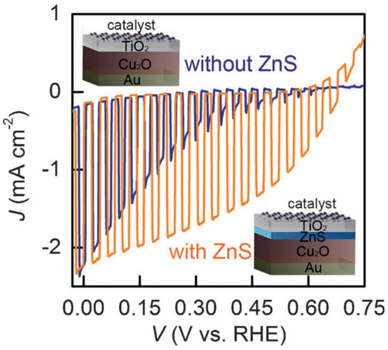


Photoelectrochemistry

P. Dai, W. Li, J. Xie, Y. He, J. Thorne, G. McMahon, J. Zhan, D. Wang* **13493 – 13497**

Forming Buried Junctions to Enhance the Photovoltage Generated by Cuprous Oxide in Aqueous Solutions

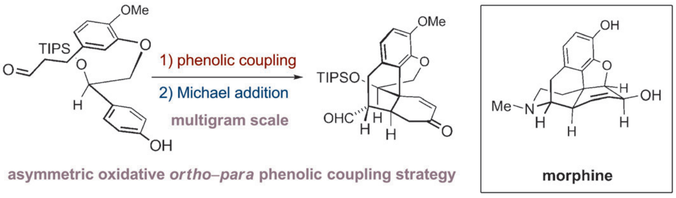
The photovoltage generated by Cu_2O in H_2O is readily increased by decorating the surface with a thin ZnS layer, which replaces the Cu_2O/H_2O interface and improves charge separation by Cu_2O. The strategy is compatible with stabilizing Cu_2O with TiO_2 and with various catalysts that promote the hydrogen evolution reaction and may enable the development of dual-absorber water splitting systems with the photocathode as the top layer.



Total Synthesis

M. Tissot, R. J. Phipps, C. Lucas,
R. M. Leon, R. D. M. Pace,
T. Ngouansavanh,
M. J. Gaunt* ________ **13498 – 13501**

Gram-Scale Enantioselective Formal Synthesis of Morphine through an *ortho*–*para* Oxidative Phenolic Coupling Strategy



Morphine formal synthesis: A catalytic enantioselective method generates gram-scale quantities of an intermediate that is common to other approaches to morphine. The key steps involve an *ortho*–*para* oxidative phenolic coupling and a highly diastereoselective “desymmetrization” of the resulting cyclohexadienone that generates three of four stereocenters in one step.

Proteomics

T. Tomohiro,* S. Morimoto, T. Shima,
J. Chiba, Y. Hatanaka ___ **13502 – 13505**

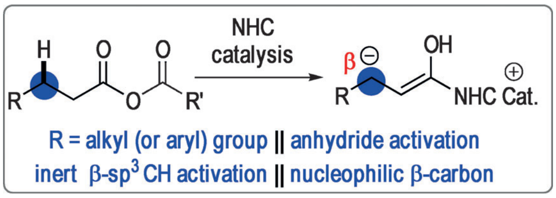
An Isotope-Coded Fluorogenic Cross-Linker for High-Performance Target Identification Based on Photoaffinity Labeling

A photoaffinity labeling (PAL)-based method is employed for the rapid identification of target proteins/interacting sites and makes use of a high-performance chemical tag, namely an isotope-coded fluorescent tag (IsoFT). The combination of PAL with multiple target selection techniques significantly reduces the amount of time and protein required for proteomic target identification.

Organocatalysis

Z. Jin, S. Chen, Y. Wang, P. Zheng,
S. Yang,* Y. R. Chi* ____ **13506 – 13509**

β-Functionalization of Carboxylic Anhydrides with β-Alkyl Substituents through Carbene Organocatalysis

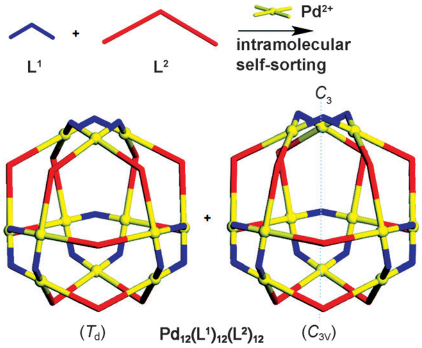


Nucleophilic carbon: NHC catalysis is used for the functionalization of carboxylic anhydrides. The β carbon acts as a nucleophilic carbon and undergoes asymmetric reactions with electrophiles. Anhydrides with challenging β-alkyl substituents work effectively.

Self-Assembly

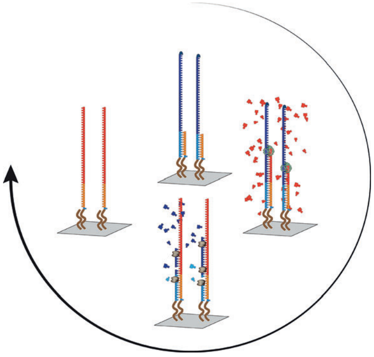
Q.-F. Sun, S. Sato,
M. Fujita* ________ **13510 – 13513**

An $M_{12}(L^1)_{12}(L^2)_{12}$ Cantellated Tetrahedron: A Case Study on Mixed-Ligand Self-Assembly



Intramolecular self-sorting: The complexation of Pd^{II} ions with two similarly shaped ligands with distinctly different bridging lengths has generated a $Pd_{12}(L^1)_{12}(L^2)_{12}$ cantellated tetrahedron and its pseudoisomer in which the two ligands are mixed but are regularly mapped onto the polyhedral framework. A study showed that a homothetic ratio of >2 is necessary to observe cantellated tetrahedra.

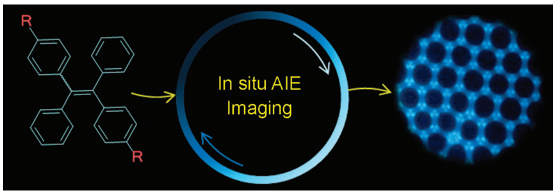
Molecular duplicating: A new technique converts DNA arrays to high-density arrays of RNA. The process functions by synthesizing a DNA array containing short RNA primers, followed by steps of transcription and DNase digestion to produce only the desired RNA sequences bound to the surface.



RNA Arrays

C. Wu, M. T. Holden,
L. M. Smith* ———— 13514 – 13517

Enzymatic Fabrication of High-Density RNA Arrays



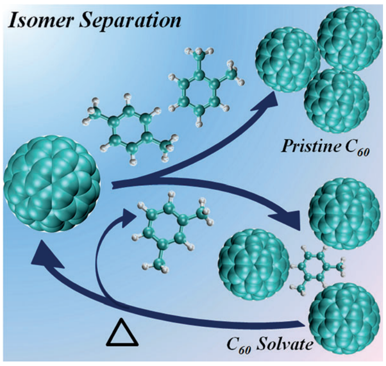
Interfacial Self-Assembly

J. W. Li, Y. Li, C. Y. K. Chan, R. T. K. Kwok,
H. K. Li, P. Zrazhevskiy, X. H. Gao,
J. Z. Sun, A. J. Qin,*
B. Z. Tang* ———— 13518 – 13522

Monitoring the interfacial world: A new in situ imaging technology capable of selectively highlighting interfacial self-assembly in real time was developed by employing the unique photophysical properties of aggregation-induced emission (AIE). Application of this technology enabled direct high-contrast visualization of microemulsion evolution, "coffee-ring" formation, and breath-figure dynamics by fluorescence microscopy.

An Aggregation-Induced-Emission Platform for Direct Visualization of Interfacial Dynamic Self-Assembly

Pick and choose: The ability of C_{60} to form crystals with molecules of a suitable geometry under ambient conditions was used to develop a method to separate geometrical isomers of molecules such as xylene and trimethylbenzene. The versatility of this approach is demonstrated by preparing a C_{60}–trimethylbenzene solvate crystal, where the purity of the separated isomers is much higher than the commercially available products.

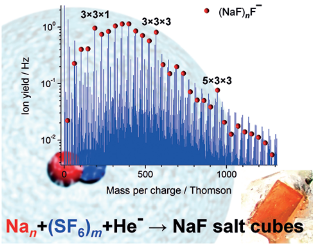


Isomer Separation

M. Rana, R. B. Reddy, B. B. Rath,
U. K. Gautam* ———— 13523 – 13527

C_{60}-Mediated Molecular Shape Sorting: Separation and Purification of Geometrical Isomers

Salting droplets: Electrons are used to initiate reaction between SF_6 and sodium clusters inside helium nanodroplets. The resulting NaF products self-assemble into crystalline salt structures.



Salt Nanocrystals

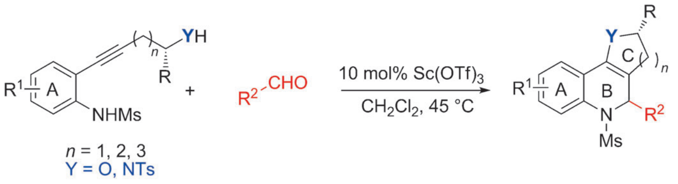
M. Daxner, S. Denifl, P. Scheier,*
A. M. Ellis* ———— 13528 – 13531

Electron-Driven Self-Assembly of Salt Nanocrystals in Liquid Helium

Heterocycles

C. Zhu, S. Ma* ______ **13532–13535**

Sc(OTf)$_3$-Catalyzed Bicyclization of *o*-Alkynylanilines with Aldehydes: Ring-Fused 1,2-Dihydroquinolines



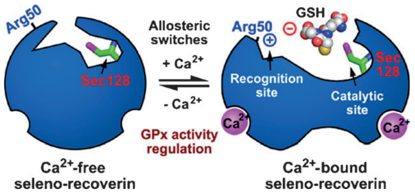
Reversed selectivity in the Sc(OTf)$_3$-catalyzed cascade Prins-type cyclization reaction of *o*-alkynylanilines, bearing a hydroxy or amine functionality, with aldehydes has been observed to afford 1,2-dihydroquinoline derivatives. The reaction proceeds through a bicyclization pathway to construct tricycles in a one-pot process under mild reaction conditions.

Enzyme Engineering

C. Zhang, T. Pan, C. Salesse, D. Zhang, L. Miao, L. Wang, Y. Gao, J. Xu, Z. Dong, Q. Luo,* J. Liu* ______ **13536–13539**

Reversible Ca^{2+} Switch of An Engineered Allosteric Antioxidant Selenoenzyme

A smart artificial enzyme with tunable glutathione peroxidase (GPx) activity was constructed by incorporating the catalytic selenium active site of GPx into recoverin, a calcium-binding protein. The biomimetic model exhibits excellent Ca^{2+}-switching characteristics allowing the modulation of the catalytic behavior and biological effects of GPx.

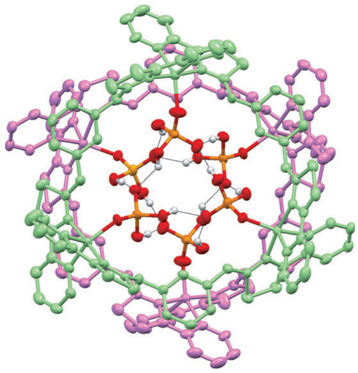


Circular Helicates

R. A. Faulkner, L. P. Harding, J. Higginson, C. R. Rice,* C. Slater ______ **13540–13543**

Formation of a Dimer of Trinuclear Helicates which Encapsulates an Array of Six Hydrogen-Bonded Anions

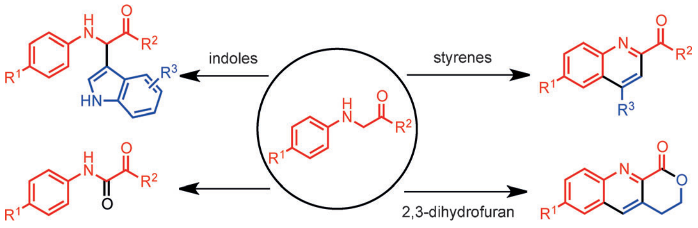
Cu does the twist: Cu^{2+} ions react with ligand L, containing two bidentate pyridylthiazole units linked by 1,3-diaminophenylene, to form a dinuclear double helicate $[Cu_2L_2]^{4+}$. $[Cu_2L_2]^{4+}$ reacts with $OPO_3H_2^-$ ions (0.5 equiv) to give the unsaturated double helicate $[Cu_2L_2(OPO_3H_2)]^{3+}$. Further reaction of $[Cu_2L_2(OPO_3H_2)]^{3+}$ with $OPO_3H_2^-$ yields a trinuclear circular helicate which self-assembles into a hexameric cluster $[\{Cu_3L_3(OPO_3H_2)_3\}_2]^{6+}$ (see structure).



Synthetic Methods

C. Huo,* Y. Yuan, M. Wu, X. Jia, X. Wang, F. Chen, J. Tang ______ **13544–13547**

Auto-Oxidative Coupling of Glycine Derivatives

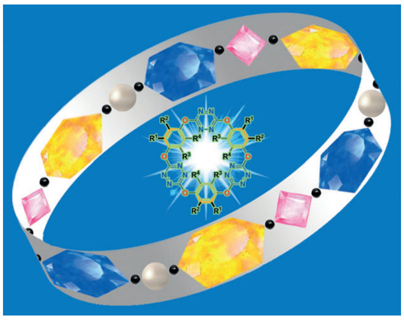


Aired out: The unprecedented title reaction between glycine derivatives and indoles, as well as the auto-oxidative Povarov/aromatization tandem reaction of glycine derivatives with olefins are described. The reactions were performed in the absence of redox-active catalysts and chemical oxidants under mild reaction conditions. Only simple organic solvents and air (or O$_2$) were required.

Macrocycles

Q.-H. Guo, Z.-D. Fu, L. Zhao, M.-X. Wang* ________ **13548 – 13552**

Synthesis, Structure, and Properties of O_6-Corona[3]arene[3]tetrazines

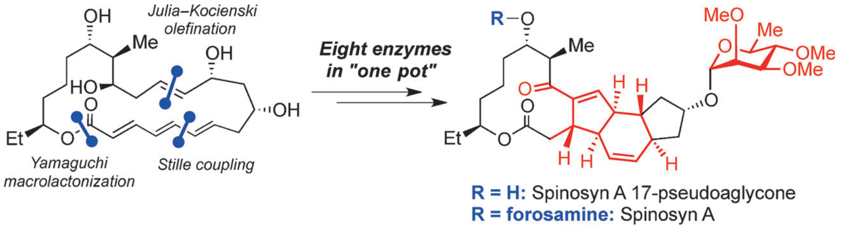


To crown it all: A novel class of functionalized macrocycles consisting of oxygen-bridged 1,4-arylene and 3,6-tetrazinylene units was synthesized efficiently in a one-pot reaction, and they adopted unique corona-like structures with large hexagonal cavities. The macrocycles have tunable electronic properties and provide powerful molecular hosts which could find many applications in supramolecular chemistry.

Macrolide Total Synthesis

H. J. Kim, S.-h. Choi, B.-s. Jeon, N. Kim, R. Pongdee, Q. Wu, H.-w. Liu* ________ **13553 – 13557**

Chemoenzymatic Synthesis of Spinosyn A

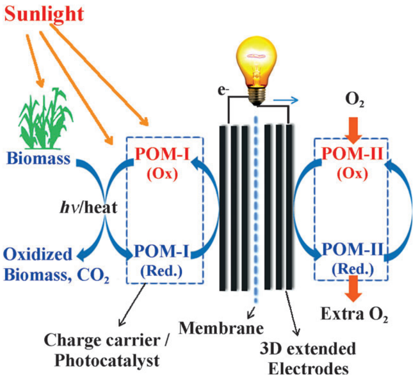


First chemistry, then biology: For the total synthesis of spinosyn A, the monocyclic macrolide precursor was constructed by conventional chemical methods. The synthetically challenging structural elements were introduced by the use of eight enzymes in a “one-pot” reaction system. Final chemical forosamylation of 17-pseudoglycone completed the total synthesis.

Biomass Conversion

W. Liu, W. Mu, Y. Deng* **13558 – 13562**

High-Performance Liquid-Catalyst Fuel Cell for Direct Biomass-into-Electricity Conversion

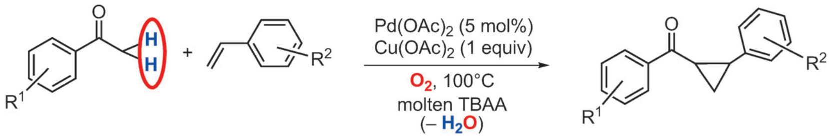


Plant light: The liquid-catalyst fuel cell is catalyzed solely by a polyoxometalate (POM) solution without any noble-metal components. Raw biomass, such as cellulose, starch, and even grass or wood powders, can be directly converted into electricity. High performance and a robust catalyst hold the key to achieving a breakthrough in direct biomass fuel-cell technology.

C–H Activation

P. Cotugno, A. Monopoli,* F. Ciminale, A. Milella, A. Nacci* ____ **13563 – 13567**

Palladium-Catalyzed Cross-Coupling of Styrenes with Aryl Methyl Ketones in Ionic Liquids: Direct Access to Cyclopropanes

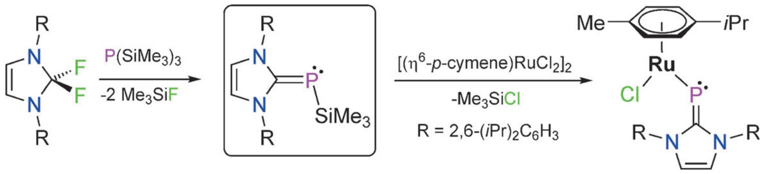


Double activation: The combined use of $Pd(OAc)_2$, $Cu(OAc)_2$, and dioxygen in molten tetrabutylammonium acetate (TBAA) promotes an unusual cyclopropanation reaction between aryl methyl ketones and styrenes. The process is a dehydrogenative cyclizing coupling that involves a twofold C–H activation at the α-position of the ketone.

NHC–Phosphinidyne Complexes

A. Doddi, D. Bockfeld, T. Bannenberg, P. G. Jones, M. Tamm* **13568 – 13572**

N-Heterocyclic Carbene–Phosphinidyne Transition Metal Complexes

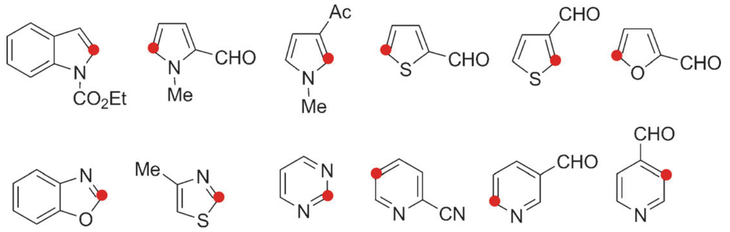


IPr=PSiMe$_3$, an N-heterocyclic carbene–phosphinidene adduct, is used as a synthon for the preparation of terminal carbene–phosphinidyne transition metal complexes of the type [(IPr=P)ML$_n$]. These complexes exhibit spectroscopic and structural characteristics similar to those of arylphosphinidene complexes. The IPr=P ligand is also capable of bridging two or three metal atoms, for example in bi- and trimetallic RuAu, RhAu, Rh$_2$, and Rh$_2$Au complexes.

Heterocycles

X. Wu, J. W. T. See, K. Xu, H. Hirao, J. Roger, J.-C. Hierso, J. Zhou* **13573 – 13577**

A General Palladium-Catalyzed Method for Alkylation of Heteroarenes Using Secondary and Tertiary Alkyl Halides



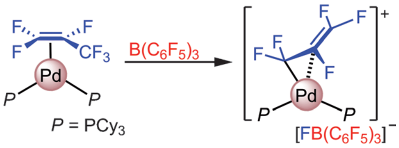
A radical way: The title reaction has been realized for many unactivated alkyl halides and a variety of heteroarenes (see picture; red dots denote the point of alkylation with secondary and tertiary alkyl halides). Preliminary mechanistic studies indicate that the palladium catalyst initiates an alkyl radical addition to heterocycles.

Ligand Effects

M. Ohashi,* M. Shibata, S. Ogoshi* **13578 – 13582**

Regioselective C−F Bond Activation of Hexafluoropropylene on Palladium(0): Formation of a Cationic η^2-Perfluoroallylpalladium Complex

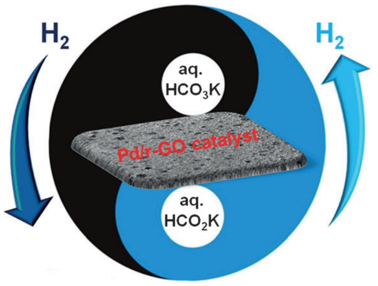
À la mode: A chemoselective C(sp^2)−F or C(sp^3)−F bond activation of hexafluoropropylene (HFP) was achieved by adopting the proper combination of a Lewis acid co-additive with a ligand which would coordinate Pd^0. The treatment of [(η^2-HFP)Pd(PCy$_3$)$_2$] with B(C$_6$F$_5$)$_3$ allowed a C(sp^3)−F bond cleavage of HFP to give a cationic perfluoroallylpalladium complex. The η^2-type coordination mode of the perfluoroallyl ligand is unique.



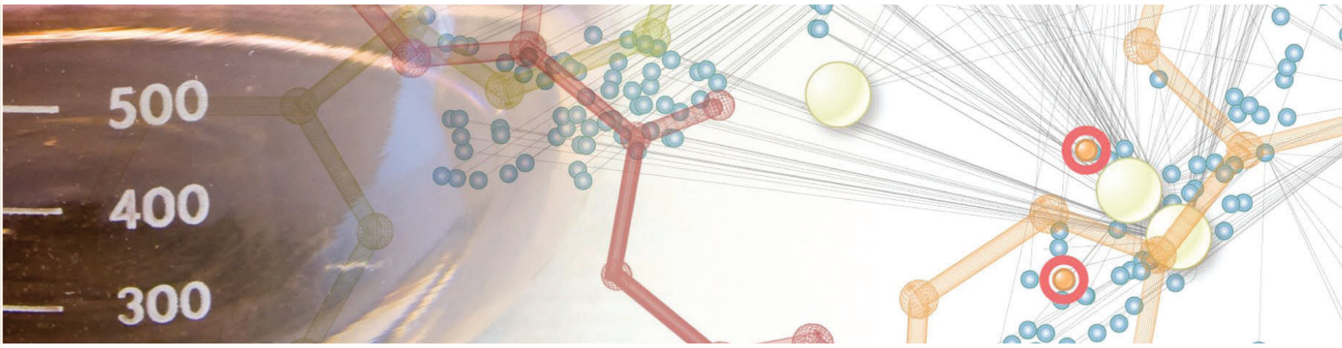
Hydrogen Storage

Q. Y. Bi, J. D. Lin, Y. M. Liu, X. L. Du, J. Q. Wang, H. Y. He, Y. Cao* **13583 – 13587**

An Aqueous Rechargeable Formate-Based Hydrogen Battery Driven by Heterogeneous Pd Catalysis



The formate/bicarbonate pair: A rechargeable hydrogen battery based on repetitive formate/bicarbonate interconversion in aqueous solution was developed. A hybrid material of Pd nanoparticles and reduced graphite oxide serves as the robust and efficient catalyst for both steps. Multiple charging and discharging cycles were performed with comparable storage/release efficiency and the resulting H$_2$ gas is free of CO and CO$_2$.

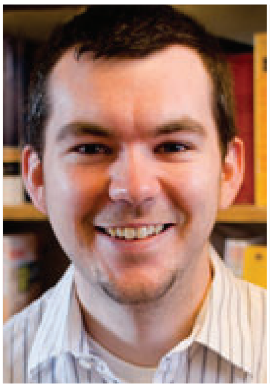


Novartis is pleased to announce the 2014 recipients of the

Novartis Early Career Award in Organic Chemistry

Professor Ryan A. Shenvi, *The Scripps Research Institute, La Jolla, CA, USA*

Ryan Shenvi earned his Ph.D. in 2008 in the group of Phil Baran at The Scripps Research Institute, La Jolla. He then joined the group of E. J. Corey at Harvard University as a NIH postdoctoral fellow. In 2010, Ryan began his independent career at The Scripps Research Institute, La Jolla. His research focuses on creating new chemical reactions to access terpene and pseudoalkaloid complex molecules, as well as the synthesis of natural product scaffolds with biological activity toward neglected tropical diseases.



Professor Daniel J. Weix, *University of Rochester, Rochester, NY, USA*

Dan Weix earned his Ph.D. in 2005 from the University of California, Berkeley, working with Professor Jonathan Ellman. He went on to postdoctoral studies with Professor John Hartwig as a NIH fellow at Yale University and the University of Illinois, Urbana. In 2008 Dan joined the Department of Chemistry at the University of Rochester. His research interests include methods development and concurrent tandem catalysis, with a focus on developing coupling reactions that will find immediate use in academia and industry, using stable and readily available starting materials.

The Novartis Early Career Award in Organic Chemistry is given annually to outstanding scientists within 10 years of having established an independent academic research career in the areas of organic or bioorganic chemistry in the broadest sense. Two awardees are identified each year from the global research community, each of whom receives an unrestricted research grant.

Past Awardees:

2013	Nicolai Cramer and Daniel Rauh
2012	Sarah E. Reisman and Corey R.J. Stephenson
2011	David Chen and David Spiegel
2010	Karl Gademann and Jin-Quan Yu
2009	Christopher J. Chang and Magnus Rueping
2008	Matthew J. Gaunt and Jeffrey S. Johnson
2007	Lukas J. Goossen and Anna K. Mapp
2006	Armido Studer and F. Dean Toste
2005	Benjamin List and Dirk Trauner
2004	J. Stephen Clark and Jonathan P. Clayden
2003	Thorsten Bach
2002	Bernhard Breit and Thomas Carell
2001	Tim Donohoe
2000	Andrew Miller
1999	Alan Armstrong
1998	Mark Bradley

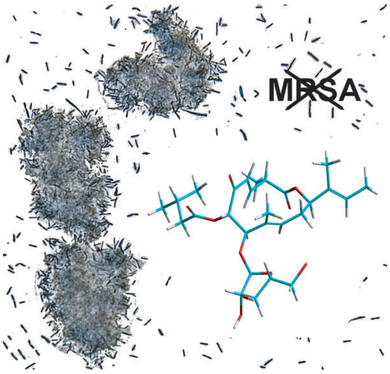
NOVARTIS

Antibiotics

F. Surup, K. Viehrig, K. I. Mohr,
J. Herrmann, R. Jansen,
R. Müller* ——— **13588 – 13591**

Disciformycins A and B: 12-Membered Macrolide Glycoside Antibiotics from the Myxobacterium *Pyxidicoccus fallax* Active against Multiresistant Staphylococci

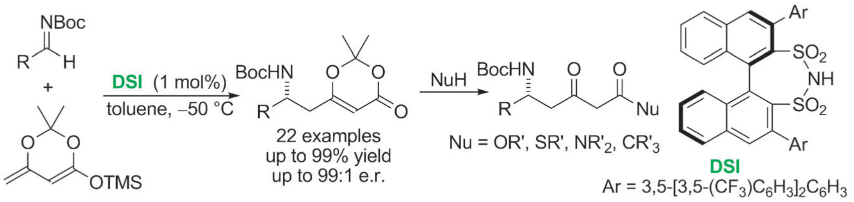
The myxobacterium *Pyxidicoccus fallax* was the source of two natural products with a unique scaffold, disciformycins, which exhibit promising and almost selective activity against multiresistant staphylococci. The more active compound, disciformycin B, shows strong inhibition even of methicillin- and vancomycin-resistant isolates (see picture).



Organocatalysis

Q. Wang, M. van Gemmeren,
B. List* ——— **13592 – 13595**

Asymmetric Disulfonimide-Catalyzed Synthesis of δ-Amino-β-Ketoester Derivatives by Vinylogous Mukaiyama–Mannich Reactions



Lewis acid catalysis: A chiral disulfonimide (DSI) serves as a highly efficient precatalyst for vinylogous Mukaiyama–Mannich reactions of a readily available silyloxydiene with protected imines, delivering δ-amino-β-ketoesters. The synthetic utility of the reaction is illustrated by the preparation of valuable enantiomerically enriched building blocks and the formal synthesis of (−)-lasubin.

Anti-Corrosion Coatings

S. Herrmann, M. Kostrzewa,
A. Wierschem, C. Streb* **13596 – 13599**

Polyoxometalate Ionic Liquids as Self-Repairing Acid-Resistant Corrosion Protection

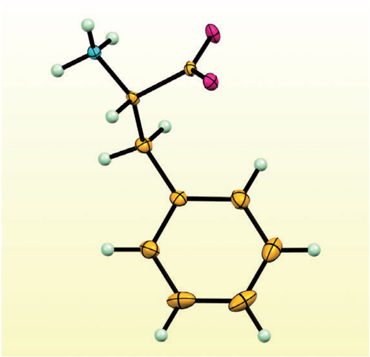
Inside Cover

This corrosion: Hydrophobic polyoxometalate-based ionic liquids (POM-ILs) are used as temporary acid-resistant coatings for copper metal. Complete protection against acid vapors and liquid acids is observed and the POM-IL coating can withstand mechanical damage by a self-repairing mechanism. The compounds are easily removed and recovered for subsequent usage.

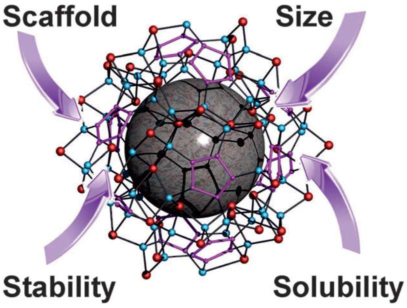
Crystal Structures

F. S. Ihlefeldt, F. B. Pettersen,
A. von Bonin, M. Zawadzka,
C. H. Görbitz* ——— **13600 – 13604**

The Polymorphs of L-Phenylalanine



It was long considered impossible to prepare crystals of L-phenylalanine, the prototypical aromatic amino acid. High-quality crystals have now been obtained that provide solid-state data for two polymorphs. For one of these polymorphs the C2 space group previously assigned was revised to $P2_1$ (with $Z'=4$). Good-quality crystals can also be grown from solutions of DL-phenylalanine, but these are not proper racemic crystals.

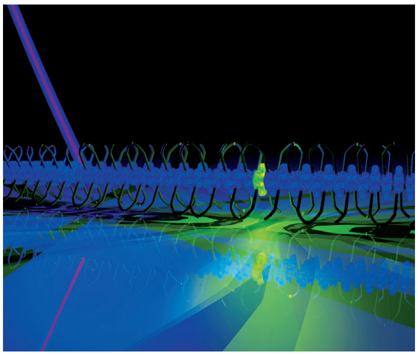


The four S: Novel scaffold, large size, remarkable solubility and high stability are the unique features of the supramolecule based on $[Cp^{Bn}Fe(\eta^5\text{-}P_5)]$ ($Cp^{Bn} = C_5(CH_2Ph)_5$) and CuI. A scaffold beyond the fullerene topology is formed by an extended CuI framework. Its solubility is provided by the Cp^{Bn} ligands, and the nano-sized sphere remains intact in solution demonstrating its stability.

Spherical Supramolecules

F. Dielmann, C. Heindl, F. Hastreiter,
E. V. Peresypkina, A. V. Virovets,
R. M. Gschwind,
M. Scheer* ———— **13605 – 13608**

A Nano-sized Supramolecule Beyond the Fullerene Topology



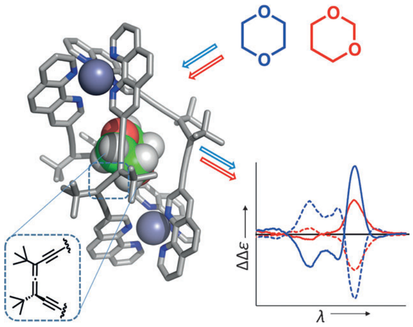
Collect and deliver: Pyrene-doped supramolecular polymers assembled from short amphiphilic phenanthrene oligomers exhibit light-harvesting properties. Energy transfer from the light absorbing phenanthrenes to the pyrene acceptor molecules proceeds in a highly efficient way over distances well beyond 100 nm, suggesting a quantum coherent mechanism.

Light-Harvesting Polymers

C. B. Winiger, S. Li, G. R. Kumar,
S. M. Langenegger,
R. Häner* ———— **13609 – 13613**

Long-Distance Electronic Energy Transfer in Light-Harvesting Supramolecular Polymers

Sensory perception: Enantiopure alleno-acetylenes can be assembled to form triple-stranded helicates having an internal cavity for the encapsulation of small cyclic guests. Guest-induced changes in the electronic circular dichroism (ECD) spectra of the helicate allowed the chiroptical detection of nonchromophoric, achiral solutes. Owing to the high affinity for 1,4-dioxane, this guest could be detected at low ppm levels.



Chemosensors

O. Gidron, M.-O. Ebert, N. Trapp,
F. Diederich* ———— **13614 – 13618**

Chiroptical Detection of Nonchromophoric, Achiral Guests by Enantiopure Alleno-Acetylenic Helicages

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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