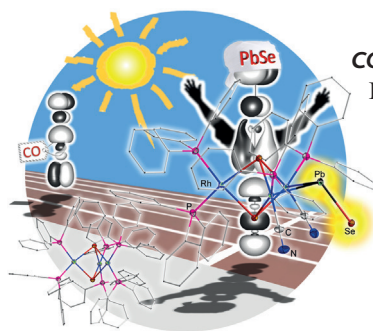
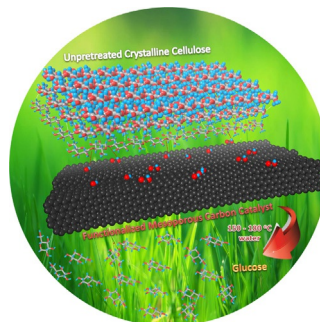




... to incubate their eggs and raise their young in a protective environment. In their Communication on page 11265 ff., J. Pérez-Ramírez, N. López et al. apply a nesting concept to anchor isolated palladium atoms within the cavities of graphitic carbon nitride. This leads to a stable single-site heterogeneous catalyst with outstanding performance in hydrogenation reactions (artwork concept: Amalia Gallardo, illustration: Marcel Reich).

Biofuels

A postsynthetically functionalized nanoporous carbon catalyst for the hydrolysis of crystalline cellulose to glucose without the need for pretreatment is described by A. Katz et al. in their Communication on page 11050 ff.

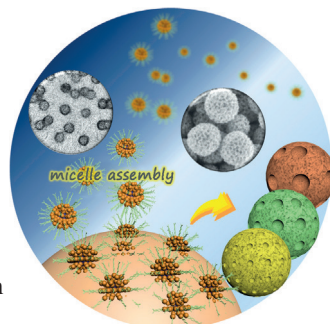


CO Homologues

In their Communication on page 11283 ff., S. Dehnen and co-workers report the coordination of $\{\mu\text{-PbSe}\}$, the heaviest CO-homologous ligand for transition metals, with a distinct bent coordination mode to an $\{\text{Rh}_3\text{Se}_2\}$ -based cluster.

Mesoporous Metals

A polymeric micelle assembly with a core-shell-corona triblock copolymer as the pore-directing agent for the fabrication of mesoporous platinum nanospheres is described by Y. Yamauchi, B. P. Bastakoti et al. in their Communication on page 11073 ff.



How to contact us:

Editorial Office:

E-mail: angewandte@wiley-vch.de

Fax: (+49) 62 01-606-331

Telephone: (+49) 62 01-606-315

Reprints, E-Prints, Posters, Calendars:

Carmen Leitner

E-mail: chem-reprints@wiley-vch.de

Fax: (+49) 62 01-606-331

Telephone: (+49) 62 01-606-327

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Bettina Loycke

E-mail: rights-and-licences@wiley-vch.de

Fax: (+49) 62 01-606-332

Telephone: (+49) 62 01-606-280

Online Open:

Margitta Schmitt

E-mail: angewandte@wiley-vch.de

Fax: (+49) 62 01-606-331

Telephone: (+49) 62 01-606-315

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Telephone: (+49) 62 01-606-565

Courier Services:

Boschstrasse 12, 69469 Weinheim

Regular Mail:

Postfach 101161, 69451 Weinheim

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11008–11011

Author Profile

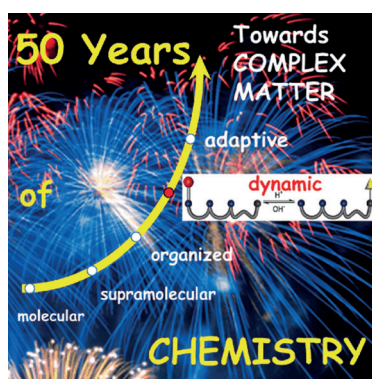


"If I could be anyone for a day, I would be James Bond ... because ...

If I were a car I would be an Aston Martin DB5 ..."

This and more about Ryan Gilmour can be found on page 11012.

Ryan Gilmour _____ 11012



The research group of Jean-Marie Lehn recently celebrated its 50th anniversary. Lehn, who shared the Nobel Prize in Chemistry 1987 with Donald J. Cram and Charles J. Pedersen, has been active in many initiatives in the European chemical community, and was instrumental in the founding of *Chemistry—A European Journal* and *ChemBioChem*. This Meeting Report summarizes the symposium that was recently held to commemorate the achievements of the Lehn group.

Meeting Reviews

Symposium Report

A. K. H. Hirsch* _____ 11013–11014

Supramolecular Chemistry ... and Beyond

Correspondence

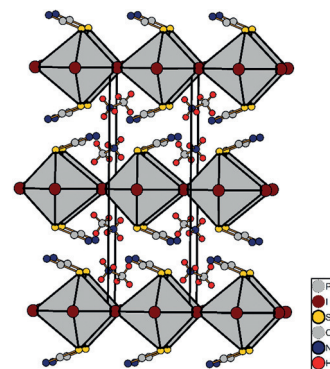
Perovskite Phases

M. Daub, H. Hillebrecht* 11016–11017



Synthesis, Single-Crystal Structure and Characterization of $(\text{CH}_3\text{NH}_3)_2\text{Pb}(\text{SCN})_2\text{I}_2$

The perovskite phase $(\text{CH}_3\text{NH}_3)_2\text{Pb}(\text{SCN})_2\text{I}_2$ with a structure closely related to the K_2NiF_4 -type was identified as the product of the reaction of $\text{CH}_3\text{NH}_3\text{I}$ and $\text{Pb}(\text{SCN})_2$ by single-crystal X-ray analysis. This extends the range of suitable dyes for solar cell applications to a class of perovskite-related structures of the general composition $(\text{AMX}_3)_n(\text{AX})_m$.

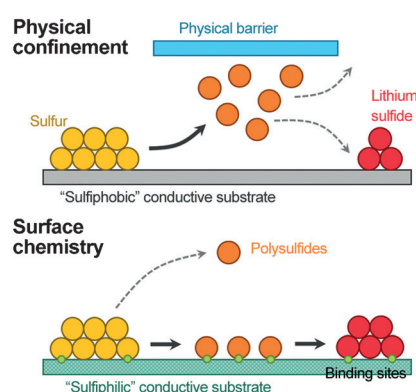


Highlights

Lithium–Sulfur Batteries

H. J. Peng, Q. Zhang* 11018–11020

Designing Host Materials for Sulfur Cathodes: From Physical Confinement to Surface Chemistry



Sulfiphilic surfaces: The design of novel host materials for sulfur cathodes in lithium–sulfur batteries has been achieved through modification of the surface chemistry, by employing sulfiphilic surfaces with high electrical conductivity to develop stable, high-energy batteries. Compared to the physical-confinement technique (see picture), systems prepared by this method exhibited remarkable enhancements of both capacity and cycling stability.

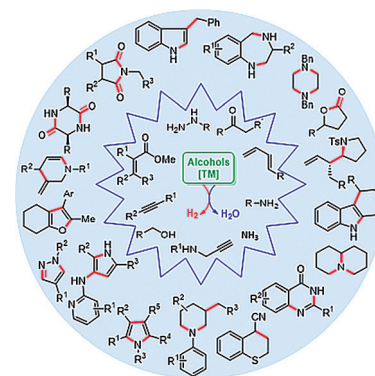
Minireviews

Synthetic Methods

A. Nandakumar,* S. P. Midya,
V. G. Landge,
E. Balaraman* 11022–11034

Transition-Metal-Catalyzed Hydrogen-Transfer Annulations: Access to Heterocyclic Scaffolds

Pass it along: Transition-metal-catalyzed hydrogen-transfer annulation strategies have received significant attention for the construction of a variety of heterocyclic scaffolds. They are environmentally benign and highly atom-economical as they utilize renewable feedstock alcohols as the starting materials and generate hydrogen gas and water as the by-products. Described are recent advances in the development of such annulations.



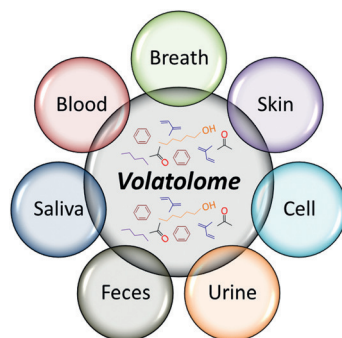
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electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Ill-gotten gains: Volatolomes enable identification of the collection of volatile organic compounds in a biological cell, tissue, or organism that are the by-/end products of cellular processes in the living organism. The new analytical approach of volatolomics allows the large-scale scientific study of chemical processes involving volatile organic compounds.



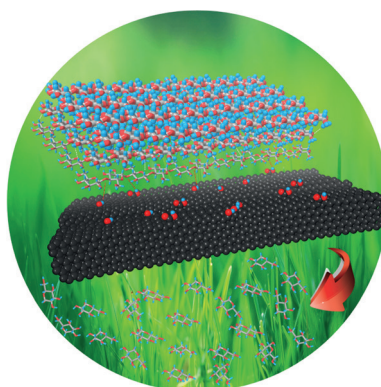
Reviews

Volatolomics

Y. Y. Broza, P. Mochalski, V. Ruzsanyi, A. Amann, H. Haick* — 11036–11048

Hybrid Volatolomics and Disease Detection

Somewhat acidic: The post-synthetic functionalization of a nanoporous carbon catalyst by oxidation leads to a high density of functional weak-acid sites on the surface. These sites catalyze the hydrolysis of crystalline cellulose to glucose in high yield (70%) and selectivity (96%) without the need for any pretreatment.



Communications

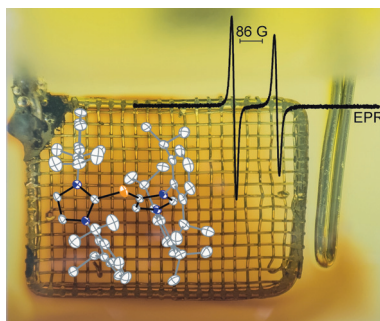
Biofuels

A. T. To, P. W. Chung, A. Katz* — 11050–11053

Weak-Acid Sites Catalyze the Hydrolysis of Crystalline Cellulose to Glucose in Water: Importance of Post-Synthetic Functionalization of the Carbon Surface

Frontispiece

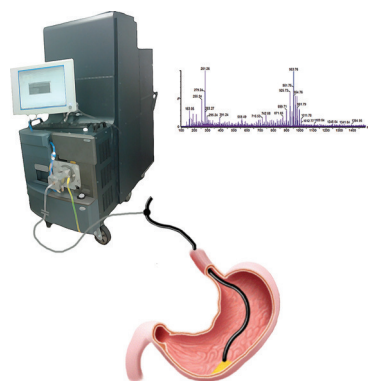
Stable phosphorous radical: The reaction of a bis(imidazoliumyl)-substituted, two-coordinate P^I cation with trifluoromethanesulfonic acid or methyl trifluoromethylsulfonate gives the corresponding protonated or methylated dications. In-depth EPR/UV/Vis-NIR spectroelectrochemical investigation of this P^I cation predicted the formation of a stable radical species (see picture).



Phosphorus Radicals

K. Schwedtmann, S. Schulz, F. Hennersdorf, T. Strassner, E. Dmitrieva, J. J. Weigand* — 11054–11058

Synthesis and EPR/UV/Vis-NIR Spectroelectrochemical Investigation of a Persistent Phosphanyl Radical Dication



Inside story: Rapid evaporative ionization mass spectrometry (REIMS) was integrated with an endoscopic polypectomy snare to enable in vivo analysis of the gastrointestinal tract. This novel endoscopy method was shown to be capable of differentiating between healthy layers of the intestinal wall, cancer, and adenomatous polyps based on the REIMS fingerprint of each tissue type in vivo.

Tumor Detection

J. Balog, S. Kumar, J. Alexander, O. Golf, F. J. Huang, T. Wiggins, N. Abbassi-Ghadi, A. Enyedi, S. Kacska, J. Kinross, G. B. Hanna, J. K. Nicholson, Z. Takats* — 11059–11062

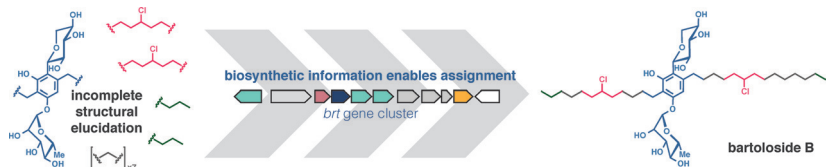
In Vivo Endoscopic Tissue Identification by Rapid Evaporative Ionization Mass Spectrometry (REIMS)

Structure Elucidation

P. N. Leão, H. Nakamura, M. Costa,
A. R. Pereira, R. Martins, V. Vasconcelos,*
W. H. Gerwick,*
E. P. Balskus* 11063–11067



Biosynthesis-Assisted Structural
Elucidation of the Bartolosides,
Chlorinated Aromatic Glycolipids from
Cyanobacteria



Biosynthesis lends a helping hand: A family of unprecedented dialkylresorcinol glycolipids was isolated from two marine cyanobacteria. These feature two very similar chlorinated alkyl chains, which are

indistinguishable by NMR and MS methods alone. Investigations into the biosynthesis of these compounds provided crucial information that enabled the elucidation of their complete structures.

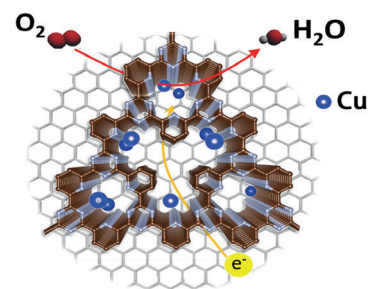
Electrocatalysis

K. Iwase, T. Yoshioka, S. Nakanishi,
K. Hashimoto,*
K. Kamiya* 11068–11072



Copper-Modified Covalent Triazine
Frameworks as Non-Noble-Metal
Electrocatalysts for Oxygen Reduction

Stable and efficient: The pores of covalent triazine frameworks hybridized with carbon nanoparticles were functionalized with Cu atoms by coordination to N atoms. The material functions as an efficient electrocatalyst for oxygen reduction reactions (ORR) in neutral solutions. The catalyst exhibited higher stability compared to other Cu-based organometallic catalysts as a result of the rigid network of covalent bonds in the framework.

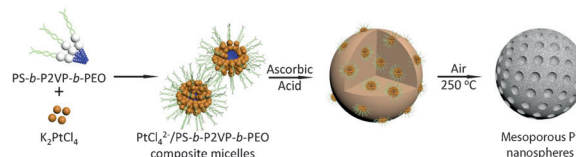


Mesoporous Metals

Y. Li, B. P. Bastakoti,* V. Malgras, C. Li,
J. Tang, J. H. Kim,
Y. Yamauchi* 11073–11077



Polymeric Micelle Assembly for the Smart
Synthesis of Mesoporous Platinum
Nanospheres with Tunable Pore Sizes



A polymeric micelle assembly is used for the fabrication of well-dispersed mesoporous Pt nanospheres. A core-shell-corona triblock copolymer [poly(styrene-*b*-2-vinylpyridine-*b*-ethylene oxide), PS-*b*-P2VP-*b*-PEO], is employed as the pore-directing

agent. The negatively charged PtCl_4^{2-} ions preferably interact with the protonated P2VP⁺ blocks while the free PEO chains prevent the aggregation of the Pt nanospheres.

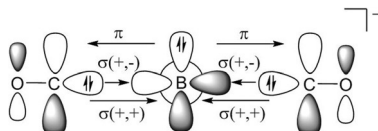
Back Cover

Bonding Analysis

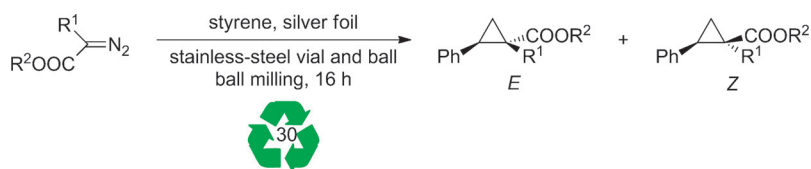
Q. Zhang, W.-L. Li, C.-Q. Xu, M. Chen,
M. Zhou,* J. Li,* D. M. Andrada,
G. Frenking* 11078–11083



Formation and Characterization of the
Boron Dicarboxyl Complex $[\text{B}(\text{CO})_2]^-$



The synthesis and spectroscopic characterization of the boron dicarboxyl complex $[\text{B}(\text{CO})_2]^-$ is reported. The bonding situation is analyzed and compared with the aluminum homologue $[\text{Al}(\text{CO})_2]^-$ using state-of-the-art quantum chemical methods.



Silver and steel: The diastereoselective cyclopropanation of various alkenes with diazoacetate derivatives can be achieved under mechanochemical conditions using silver-metal foil and a stainless-steel vial

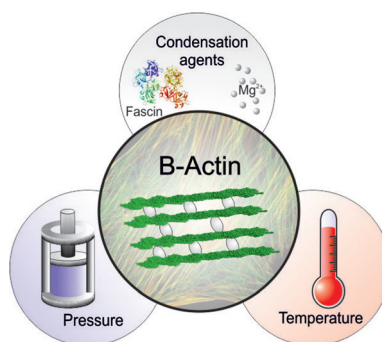
and ball system. The cyclopropanation products were obtained with excellent diastereoselectivities (up to 98:2 d.r.) and in high yields (up to 96%).

Solid-Phase Synthesis

L. Chen, M. O. Bovee, B. E. Lemma, K. S. M. Keithley, S. L. Pilson, M. G. Coleman,*
J. Mack* — 11084–11087

An Inexpensive and Recyclable Silver-Foil Catalyst for the Cyclopropanation of Alkenes with Diazoacetates under Mechanochemical Conditions

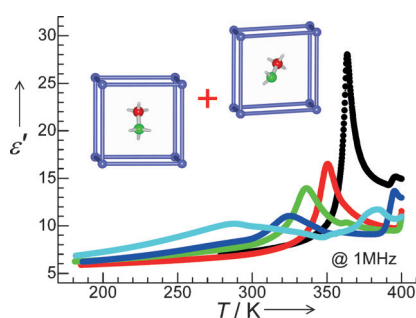
Under pressure: Unravelling temperature and pressure stabilities of actin bundles as a function of condensation agents helps to explain why cells actively use proteins to ensure sufficient stability and mechanical resistance of the cytoskeleton. This understanding is important, in particular, for organisms living under extreme environmental conditions.



Biophysics

M. Gao, M. Berghaus, J. von der Ecken, S. Raunser, R. Winter* — 11088–11092

Condensation Agents Determine the Temperature–Pressure Stability of F-Actin Bundles

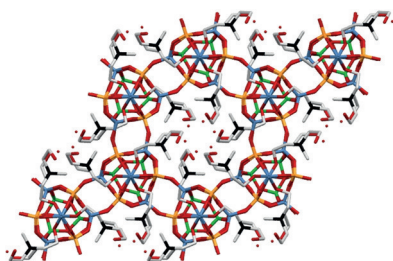


Mix and match: $[(NH_2NH_3)_x(CH_3NH_3)_{1-x}][Mn(HCOO)_3]$ ($x = 1.00$ – 0.67), an A-site solid solution series of metal–organic perovskites, shows para-to ferroelectric transitions, with the critical temperature and phase-transition character modulated by the ammonium composition. Phase transitions are studied by variable-temperature X-ray crystallography and dielectric permittivity (ϵ') measurements (plots shown are for different ammonium compositions).

Perovskite Phases

S. Chen, R. Shang, B.-W. Wang, Z.-M. Wang,* S. Gao* — 11093–11096

An A-Site Mixed-Ammonium Solid Solution Perovskite Series of $[(NH_2NH_3)_x(CH_3NH_3)_{1-x}][Mn(HCOO)_3]$ ($x = 1.00$ – 0.67)



Crystal clear: The discovery of molecular sieves containing framework-bound organic structure-directing agents is described. A plausible formation pathway for this novel class of inorganic–organic hybrid crystals is presented.

Crystal Growth

J. K. Lee, J. Shin, N. H. Ahn, A. Turrina, M. B. Park, Y. Byun, S. J. Cho, P. A. Wright, S. B. Hong* — 11097–11101

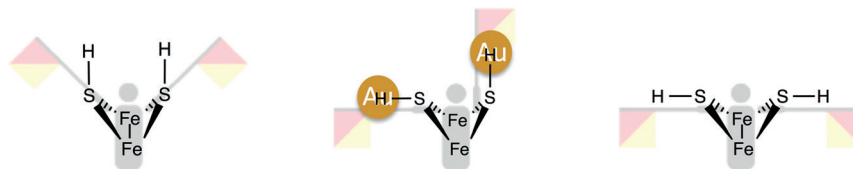
A Family of Molecular Sieves Containing Framework-Bound Organic Structure-Directing Agents

Iron–Sulfur–Gold Clusters

D. J. Crouthers, S. Ding, J. A. Denny,
R. D. Bethel, C.-H. Hsieh, M. B. Hall,
M. Y. Darensbourg* — 11102–11106



A Reduced 2Fe2S Cluster Probe of
Sulfur–Hydrogen versus Sulfur–Gold
Interactions



A placid, rich relative: The Ph_3PAu^+ cation was found to serve as a proton surrogate and form a stable Au_2Fe_2 complex, $[(\mu\text{-SAuPPh}_3)_2\{\text{Fe}(\text{CO})_3\}_2]$, analogous to the highly reactive dihydrosulfide $[(\mu\text{-SH})_2\{\text{Fe}(\text{CO})_3\}_2]$ (see picture). Deprotection of

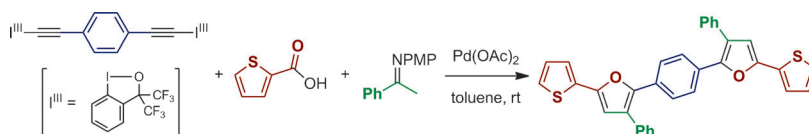
the S atoms of $[(\mu\text{-SAuPPh}_3)_2\{\text{Fe}(\text{CO})_3\}_2]$ by treatment with a strong acid generated the precursor $[(\mu\text{-SH})_2\{\text{Fe}(\text{CO})_3\}_2]$ to the active-site biomimetic $[(\mu_2\text{-SCH}_2(\text{NR})\text{-CH}_2\text{S})\{\text{Fe}(\text{CO})_3\}_2]$ of diiron hydrogenase.

Multicomponent Reactions

J. Wu, N. Yoshikai* — 11107–11111



Modular Synthesis of Multisubstituted
Furans through Palladium-Catalyzed
Three-Component Condensation of
Alkynylbenziodoxoles, Carboxylic Acids,
and Imines



The regiocontrolled synthesis of a multisubstituted furan through palladium-catalyzed condensation of an alkynylbenziodoxole, a carboxylic acid, and an enolizable ketimine is reported. The three-

component reaction allows highly modular, flexible, and mild synthesis of diversely substituted furans including furan-containing oligoarylenes.

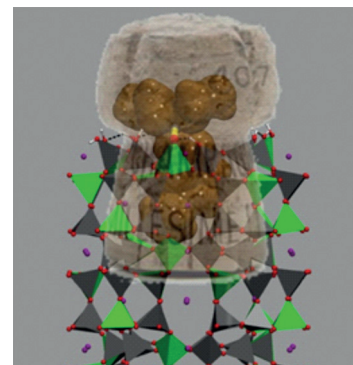
Zeolites

G. Tabacchi, E. Fois,*
G. Calzaferri* — 11112–11116



Structure of Nanochannel Entrances in
Stopcock-Functionalized Zeolite L
Composites

Message in a bottle: To address the lack of available microscale structural information on the site-specific functionalization of zeolite L (ZL), first-principles calculations are used to investigate how stopper molecules irreversibly modify ZL by condensing with OH groups at the channel entrances. The nature of the interactions of the tail group with the inner surface of the channels and the head group with the channel entrances are elucidated.

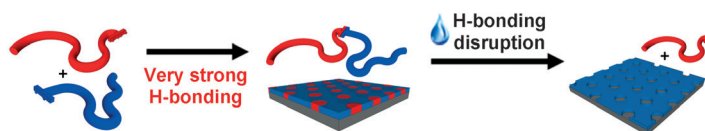


Nanoporous Membranes

D. Montarnal, N. Delbosc, C. Chamignon,
M. A. Virolleaud, Y. Luo, C. J. Hawker,
E. Drockenmüller,
J. Bernard* — 11117–11121

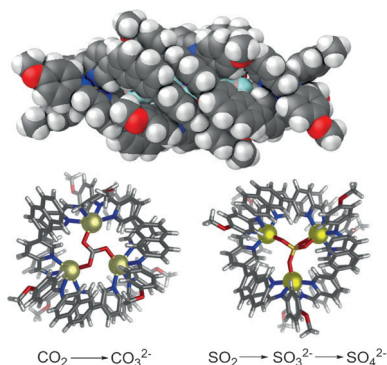


Highly Ordered Nanoporous Films from
Supramolecular Diblock Copolymers with
Hydrogen-Bonding Junctions



Link for a minute: Supramolecular diblock copolymers self-assemble from high molecular weight polymers bearing complementary strong hydrogen-bonding groups. Hierarchical organization affords

thin films with excellent lateral order that can be readily transformed into porous membranes, without any degradation, by disruption of the supramolecular links with water/alcohol solutions.



It's a trap! A dialdehyde with acute coordination vectors self-assembles to form uncommon supramolecular structures, including a molecular rectangle and a trigonal bipyramid, by metal and anion templation. The tight arrangement of the equatorial metals of the trigonal bipyramid was exploited to fix carbon dioxide as carbonate and capture sulfate from oxidized sulfite.

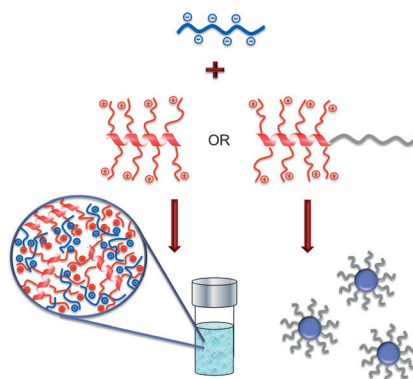
Supramolecular Chemistry

C. Browne, W. J. Ramsay, T. K. Ronson, J. Medley-Hallam, J. R. Nitschke* — 11122–11127

Carbon Dioxide Fixation and Sulfate Sequestration by a Supramolecular Trigonal Bipyramid



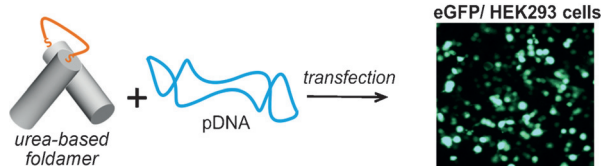
Twisted liquids: Stable α -helical polypeptides self-assemble with oppositely charged, random-coil polypeptides to form dense, polymer-rich, liquid polyelectrolyte complexes (complex coacervates) while maintaining their α -helical secondary structure. The assemblies have potential applications for either drug or gene delivery.



Micelles

D. Priftis, L. Leon, Z. Song, S. L. Perry, K. O. Margossian, A. Tropnikova, J. Cheng, M. Tirrell* — 11128–11132

Self-Assembly of α -Helical Polypeptides Driven by Complex Coacervation



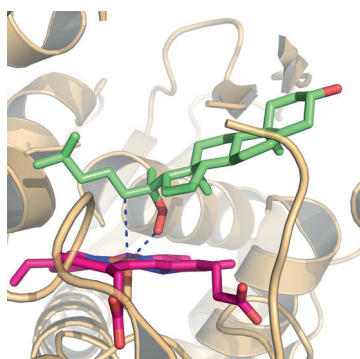
Foldaplex: A pH-responsive cell-penetrating foldamer (CPF) was designed for nucleic acid delivery. Histidine-type residues were introduced along the oligoureia sequence to facilitate the release of the cargo into the cytoplasm. Dimerization of

the urea-based foldamer sequence through a disulfide bridge enhanced cellular uptake and led to transfection efficiency comparable to that of commercially available transfection agents, as well as negligible cytotoxicity.

Gene Delivery

C. Douat, C. Aisenbrey, S. Antunes, M. Decossas, O. Lambert, B. Bechinger, A. Kichler,* G. Guichard* — 11133–11137

A Cell-Penetrating Foldamer with a Bio-reducible Linkage for Intracellular Delivery of DNA



The interaction of the cholesterol auto-oxidation products 25- and 20 ξ -hydroperoxides with cytochrome P450 (CYP) enzymes is reported. The addition of the hydroperoxides to CYP11A1 (structure with 20 α -hydroperoxide shown) and CYP27A1 induced well-defined spectral changes while the 25-hydroperoxide generated 25-hydroxycholesterol as the major product. A P450 hydroperoxide-shunt reaction is proposed, where the hydroperoxides serve as both the donor for reduced oxygen and substrate.

Cholesterol

J. E. van Lier,* N. Mast, I. A. Pikuleva* — 11138–11142

Cholesterol Hydroperoxides as Substrates for Cholesterol-Metabolizing Cytochrome P450 Enzymes and Alternative Sources of 25-Hydroxycholesterol and other Oxysterols

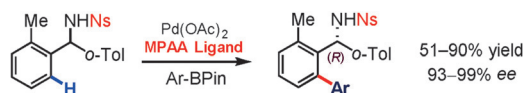


C–H Activation

B. N. Laforteza, K. S. L. Chan,
J.-Q. Yu* 11143–11146



Enantioselective *ortho*-C–H
Cross-Coupling of Diarylmethylamines
with Organoborons



Amine-directed: A new enantioselective *ortho*-C–H cross-coupling reaction between nosyl-protected diarylmethylamines and arylboronic acid pinacol esters has been achieved with chiral

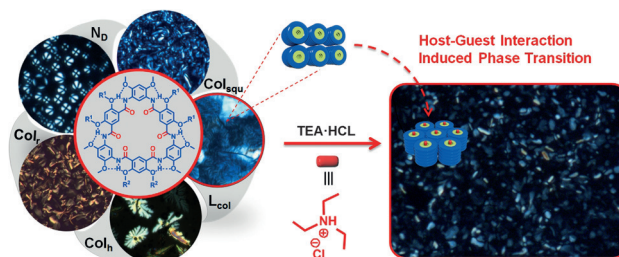
mono-*N*-protected amino acids (MPAA) as chiral ligands. This reaction also demonstrates the feasibility of using a common protecting group to direct C–H activation of amines for the first time.

Liquid Crystals

X. W. Li, B. Li, L. Chen, J. C. Hu,
C. D. Y. Wen, Q. D. Zheng, L. X. Wu,
H. Q. Zeng, B. Gong,*
L. H. Yuan* 11147–11152



Liquid-Crystalline Mesogens Based on
Cyclo[6]aramides: Distinctive Phase
Transitions in Response to Macrocyclic
Host–Guest Interactions



Stack the deck: Cyclo[6]aramides, having a hydrogen-bond-constrained backbone and a well-defined inner cavity, exhibit rich liquid-crystalline mesomorphic properties. Exploitation of host–guest interactions between the cavity (blue/green

discs) and alkylammonium salts (red) leads to distinct mesophase transitions from a lamellar to a hexagonal columnar phase, as shown by polarized optical microscopy.

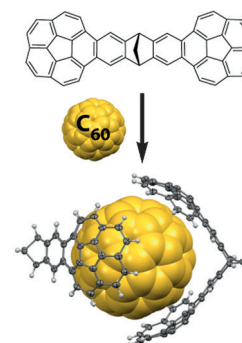
Supramolecular Chemistry

M. Yanney,* F. R. Fronczek,
A. Sygula* 11153–11156



A 2:1 Receptor/C₆₀ Complex as
a Nanosized Universal Joint

It's a wrap: Tuning the topology of the tether led to buckycatcher II (C₅₁H₂₄, gray), which exhibits dramatically higher affinity toward C₆₀ (yellow) than the original buckycatcher C₆₀H₂₈ or other similar molecular receptors for fullerenes. X-ray structure determination of a trimeric C₆₀@(catcher)₂ complex revealed a remarkable solvent-free crystal arrangement with the fullerene cage wrapped by four corannulene subunits of two cooperating receptors.

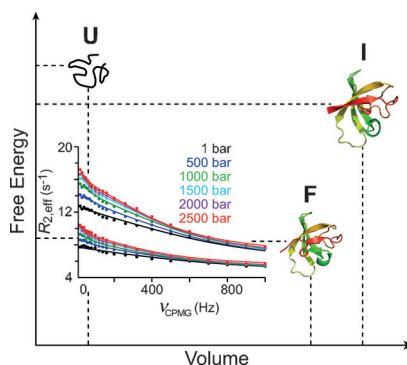


High-Pressure NMR Spectroscopy

V. Tugarinov,* D. S. Libich, V. Meyer,
J. Roche, G. M. Clore* 11157–11161

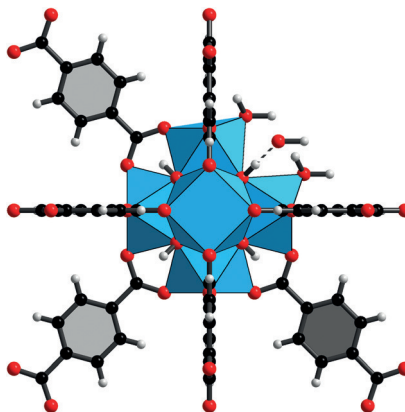


The Energetics of a Three-State Protein
Folding System Probed by High-Pressure
Relaxation Dispersion NMR Spectroscopy



Under pressure: The energetic and volumetric properties of a three-state protein folding system (states U, I, and F; see picture), comprising a triple metastable mutant of the Fyn SH3 domain, have been investigated using pressure-dependent relaxation dispersion NMR spectroscopy. While the intermediate is energetically close to the unfolded state, its volumetric properties are similar to those of the folded protein.

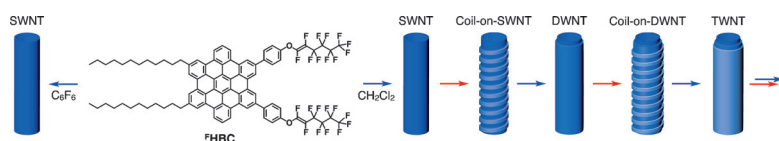
The missing link: The defects in the zirconium-based metal-organic framework UiO-66 have been characterized at a molecular level by single-crystal X-ray diffraction (see structure). Water molecules have been identified as replacing the missing linkers, with charge-balancing achieved by hydroxide ions hydrogen bonding to the hydroxy groups of the $\text{Zr}_6\text{O}_4(\text{OH})_4$ cluster.



Metal-Organic Frameworks

C. A. Trickett, K. J. Gagnon, S. Lee, F. Gándara, H.-B. Bürgi, O. M. Yaghi* — 11162–11167

Definitive Molecular Level Characterization of Defects in UiO-66 Crystals



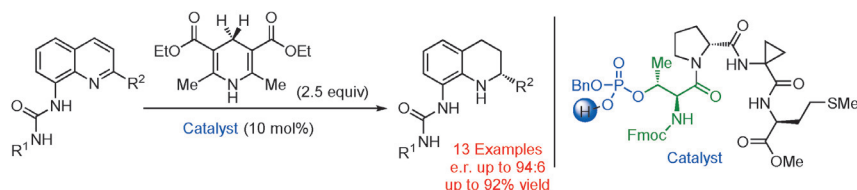
Coiled for action: The hierarchical assembly of hexabenzocoronene derivatives with perfluoroalkyl segments can be controlled by solvophobic and solvophilic effects. This control enables the selective

synthesis of single- and multiwalled nanotubes. Increasing the number of walls occurs via coil-on-tube intermediates.

Nanotubes

S. Prasanthkumar, W. Zhang, W. Jin,* T. Fukushima,* T. Aida* — 11168–11172

Selective Synthesis of Single- and Multi-Walled Supramolecular Nanotubes by Using Solvophobic/Solvophilic Controls: Stepwise Radial Growth via “Coil-on-Tube” Intermediates



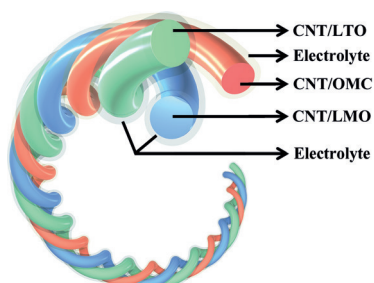
Very one-sided: Phosphothreonine (pThr) was found to act as a chiral phosphoric acid (CPA) catalyst upon insertion into peptides. To demonstrate the potential of these phosphopeptides as asymmetric catalysts, enantioselective transfer hydro-

genations of a previously underexplored substrate class for CPA-catalyzed reductions were carried out. The pThr-containing peptides lead to up to 94:6 e.r. with 2-substituted quinolines containing a C8-amino functionality.

Asymmetric Catalysis

C. R. Shugrue, S. J. Miller* — 11173–11176

Phosphothreonine as a Catalytic Residue in Peptide-Mediated Asymmetric Transfer Hydrogenations of 8-Aminoquinolines



Strand and deliver: A fiber-shaped hybrid energy-storage device is created by twisting three different carbon nanotube hybrid fibers together to integrate the properties of a lithium-ion battery and a supercapacitor. The twisted strands give rise to both high energy and power densities. The hybrid device is three-dimensionally flexible, weaveable, and wearable, which offers promising advantages in modern electronics.

Wearable Electronics

Y. Zhang, Y. Zhao, X. Cheng, W. Weng, J. Ren, X. Fang, Y. Jiang, P. Chen, Z. Zhang, Y. Wang, H. Peng* — 11177–11182

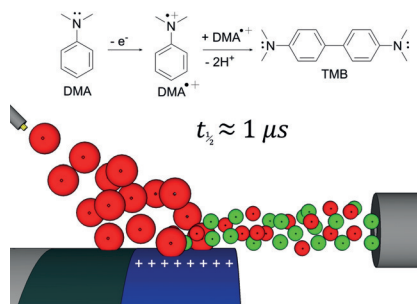
Realizing both High Energy and High Power Densities by Twisting Three Carbon-Nanotube-Based Hybrid Fibers



VIP **Electrochemistry**

T. A. Brown, H. Chen,*
R. N. Zare* 11183–11185

Detection of the Short-Lived Radical Cation Intermediate in the Electrooxidation of *N,N*-Dimethylaniline by Mass Spectrometry

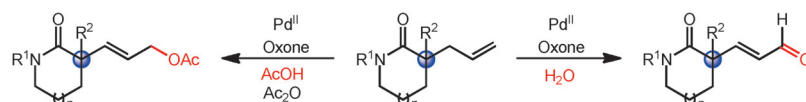


Now you see it: The *N,N*-dimethylaniline radical cation DMA•+, a transient intermediate with a half-life shorter than 1 μs, was detected by mass spectrometry (MS) during the electrochemical oxidation of DMA by coupling desorption electrospray ionization (DESI)-MS with a waterwheel working electrode system.

Allylic Compounds

X. Xing, N. R. O'Connor,
B. M. Stoltz* 11186–11190

Palladium(II)-Catalyzed Allylic C–H Oxidation of Hindered Substrates Featuring Tunable Selectivity Over Extent of Oxidation



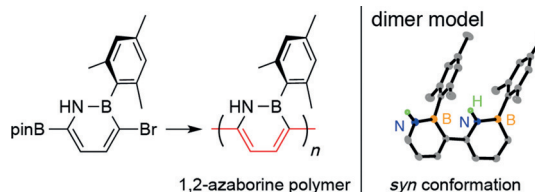
SwitcherR-O-O-H: The use of potassium peroxymonosulfate (KOSO₂-O-O-H, Oxone) and a Pd^{II} catalyst enables the efficient allylic C–H oxidation of sterically hindered α-quaternary lactams. This simple and environmentally safe protocol

allows unusual tunable selectivity between a two-electron oxidation to the allylic acetates and a four-electron oxidation to the corresponding enals, with the dominant product depending on the presence or absence of water.

Polymerization

A. W. Baggett, F. Guo, B. Li, S.-Y. Liu,*
F. Jäkle* 11191–11195

Regioregular Synthesis of Azaborine Oligomers and a Polymer with a *syn* Conformation Stabilized by N–H⋯π Interactions



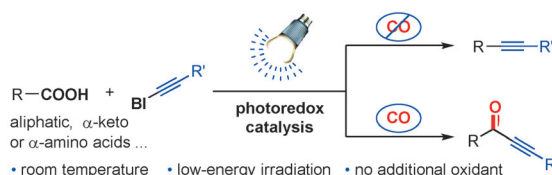
A BN serial: A regioregular conjugated polymer and short model oligomers constructed solely from 1,2-azaborine units by Suzuki–Miyaura cross-coupling have been synthesized and found to adopt an unusual *syn* conformation stabilized by

N–H⋯π interactions. The optoelectronic properties of the polymer more closely resemble the computationally predicted properties of poly(cyclohexadiene) rather than those of poly(*p*-phenylene). pin = pinacol.

Cross-Coupling Reaction

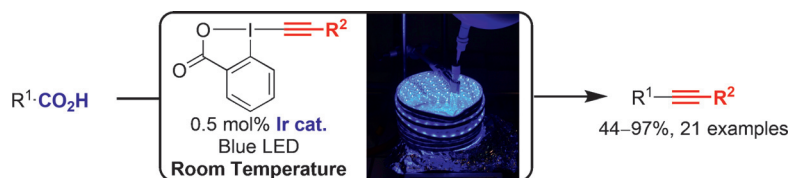
Q.-Q. Zhou, W. Guo, W. Ding, X. Wu,
X. Chen, L.-Q. Lu,*
W.-J. Xiao* 11196–11199

Decarboxylative Alkynylation and Carbonylative Alkynylation of Carboxylic Acids Enabled by Visible-Light Photoredox Catalysis



Readily available carboxylic acids can easily undergo decarboxylative alkynylation/carbonylative alkynylation under visible-light photoredox catalysis to afford

a variety of versatile alkynes and ynones in good to excellent yields. These transformations feature mild conditions and a broad substrate scope.



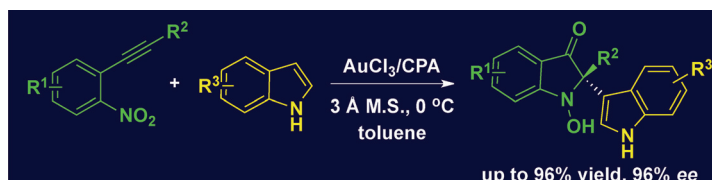
EBX-cellent: A range of alkynes can be synthesized in good yields by the direct reaction of readily available carboxylic acids with ethynylbenziodoxolone (EBX) reagents in the presence of an iridium

photocatalyst (see figure). This decarboxylative alkynylation reaction proceeds at room temperature under visible light irradiation, and could be applied to silyl-, aryl-, and alkyl-substituted alkynes.

Photocatalysis

F. Le Vaillant, T. Courant, J. Waser* — 11200–11204

Room-Temperature Decarboxylative Alkynylation of Carboxylic Acids Using Photoredox Catalysis and EBX Reagents



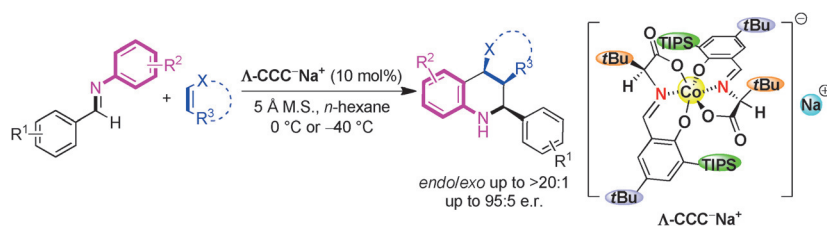
Two are better than one: An enantioselective redox annulation of nitroalkynes with indoles is enabled by gold/chiral phosphoric acid (CPA) dual catalysis. A range of indolin-3-one derivatives bearing

quaternary stereocenters at the C2 positions were thus obtained in good yields and excellent enantioselectivities (up to 96% ee).

Asymmetric Catalysis

R.-R. Liu, S.-C. Ye, C.-J. Lu, G.-L. Zhuang, J.-R. Gao, Y.-X. Jia* — 11205–11208

Dual Catalysis for the Redox Annulation of Nitroalkynes with Indoles: Enantioselective Construction of Indolin-3-ones Bearing Quaternary Stereocenters



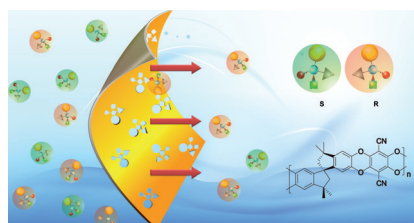
A salty catalyst: The sodium salts of anionic chiral cobalt(III) complexes (CCC[−]Na⁺) have been found to be efficient catalysts of the asymmetric Povarov reaction of easily accessible dienophiles with 2-azadienes. Ring-fused tetrahydro-

quinolines with up to three contiguous stereogenic centers were thus obtained in high yields, excellent diastereoselectivities, and high enantioselectivities (TIPS = triisopropylsilyl).

Chiral Anion Catalysis

J. Yu, H.-J. Jiang, Y. Zhou, S.-W. Luo, L.-Z. Gong* — 11209–11213

Sodium Salts of Anionic Chiral Cobalt(III) Complexes as Catalysts of the Enantioselective Povarov Reaction



Born to sort: Solvent-cast membranes of chiral ladder polymers of intrinsic microporosity (see example structure) showed high enantioselectivity towards the permeation of racemic compounds ranging from amino acid derivatives to chiral auxiliaries. The high permeability, high processability, and ease of chemical modification of the materials offer potential for liquid-phase membrane separation and related applications in chiral resolution.

Enantioselective Membranes

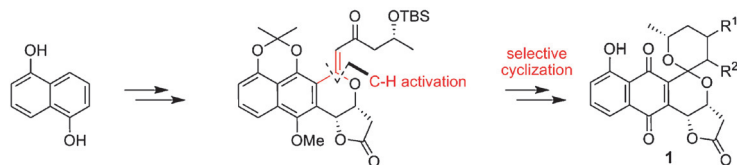
X. Weng, J. E. Baez, M. Khiterer, M. Y. Hoe, Z. Bao, K. J. Shea* — 11214–11218

Chiral Polymers of Intrinsic Microporosity: Selective Membrane Permeation of Enantiomers



Total Synthesis

Y. Zhang, Q. Ye, X. Wang, Q.-B. She,
J. S. Thorson* 11219–11222



The total synthesis of three naturally occurring and two non-natural griseusins **1** is achieved by a strategy including a key hydroxy-directed C–H olefination of 1-methylene isochroman with an α,β -unsaturated ketone followed by subsequent

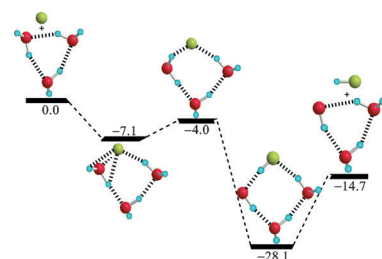
stereoselective epoxidation and regioselective cyclization to afford the signature tetrahydro-spiropyran ring. It was found that the stereochemistry and functionalization of the tetrahydro-spiropyran ring has a high impact on bioactivity.

Atom–Molecule Reactions

G. Li,* Q.-S. Li, Y. Xie,
H. F. Schaefer, III* 11223–11226

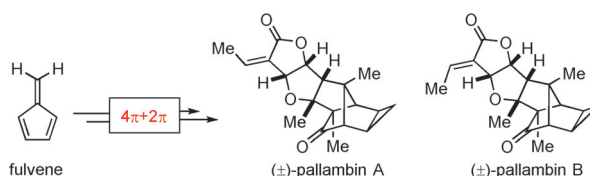
From Gas-Phase to Liquid-Water
Chemical Reactions: The Fluorine Atom
Plus Water Trimer System

The potential energy profile for the $F + (H_2O)_3 \rightarrow HF + (H_2O)_2OH$ reaction has been investigated using the “gold standard” CCSD(T) method with correlation-consistent basis sets up to cc-pVQZ. Four different reaction pathways have been found and these are related, both geometrically and energetically.



Cycloaddition

C. Ebner, E. M. Carreira* 11227–11230



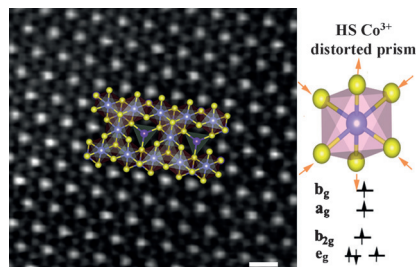
Pentafulvene for the Synthesis of Complex
Natural Products: Total Syntheses of
(±)-Pallambins A and B

Core congestion: The first total syntheses of the diterpenoids (±)-pallambins A and B are reported. The use of fulvene in a Diels–Alder cycloaddition is without

precedence in complex synthesis and enables, in combination with a strategic C–H insertion, rapid assembly of the tetracyclo[4.4.0^{3,5}.0^{2,8}]decane core.

Oxygen Evolution Reaction

Y. W. Liu, C. Xiao,* M.-J. Lyu, Y. Lin,
W. Z. Cai, P. C. Huang, W. Tong, Y. M. Zou,
Y. Xie* 11231–11235



Ultrathin Co_3S_4 Nanosheets that
Synergistically Engineer Spin States and
Exposed Polyhedra that Promote Water
Oxidation under Neutral Conditions

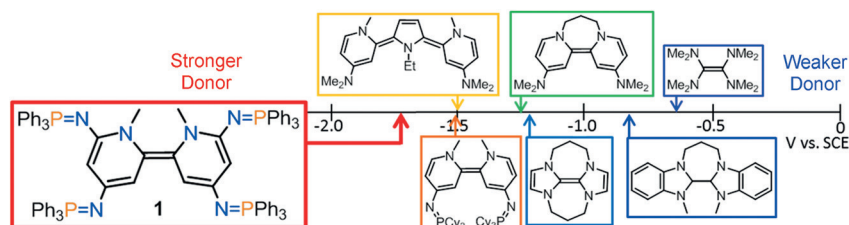
The OER performance of Co_3S_4 under neutral conditions can be enhanced by exposed octahedral planes and self-adapted spin states in atomically thin nanosheets. The Co_3S_4 nanosheets possess superior oxygen evolution reaction performance with exceptional low onset overpotentials of about 0.31 V in neutral solutions.



Organic Reductants

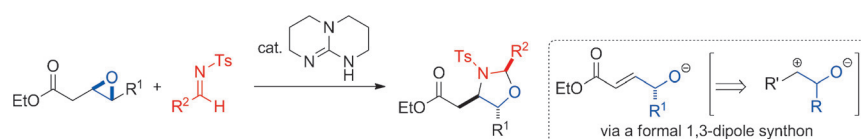
S. S. Hanson, E. Doni, K. T. Traboulsee,
G. Coulthard, J. A. Murphy,*
C. A. Dyker* — 11236–11239

Pushing the Limits of Neutral Organic
Electron Donors: A Tetra(iminophos-
phorano)-Substituted Bispyridinylidene



Unlocking max potential: The four strongly π -donating iminophosphorano substituents of compound **1** impart an impressive redox potential of -1.70 V versus the saturated calomel electrode

(SCE) for the $1^{2+}/1$ redox couple, and make **1** the first organic donor able to reduce malononitriles and dialkylarene-sulfonamides without photoexcitation.



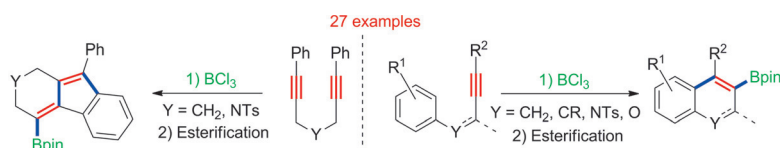
A novel ring expansion reaction of epoxides under Brønsted base catalysis was developed. The formal [3+2] cycloaddition reaction of β,γ -epoxy esters with imines proceeded in the presence of triazabicyclodecene as a Brønsted base

catalyst to afford 2,4,5-trisubstituted 1,3-oxazolidines in a highly diastereoselective manner. This methodology enables facile synthesis of enantioenriched 1,3-oxazolidines from easily accessible enantio-enriched epoxides.

Asymmetric Synthesis

A. Kondoh, K. Odaira,
M. Terada* — 11240–11244

Ring Expansion of Epoxides under
Brønsted Base Catalysis: Formal [3+2]
Cycloaddition of β,γ -Epoxy Esters with
Imines Providing 2,4,5-Trisubstituted
1,3-Oxazolidines



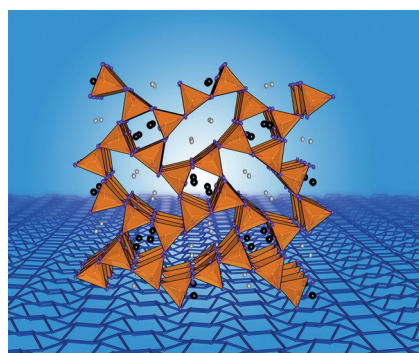
Alkyne + $\text{BCl}_3 \rightarrow \text{Cyclization (A + B = C)}$:
 BCl_3 is a simple and inexpensive electrophile which induces a functional-group-tolerant borylative cyclization of aryl-sub-

stituted alkynes and dialkynes. The reaction affords useful and regioselectively borylated polycycles.

Isomerization

A. J. Warner, J. R. Lawson, V. Fasano,
M. J. Ingleson* — 11245–11249

Formation of $\text{C}(\text{sp}^2)$ -Boronate Esters by
Borylative Cyclization of Alkynes Using
 BCl_3



In rare form: Trivalent rare-earth-metal nitridophosphates are a completely uncharted family of materials and can feature intriguing properties. The first member of this family, LiNdP_4N_8 , was prepared through high-pressure metathesis starting from NdF_3 and LiPN_2 . LiNdP_4N_8 was studied as a model system to demonstrate the potential of high-pressure metathesis in the synthesis of such nitridophosphates.

High-Pressure Chemistry

S. D. Klotz, W. Schnick* — 11250–11253

Rare-Earth-Metal Nitridophosphates
through High-Pressure Metathesis

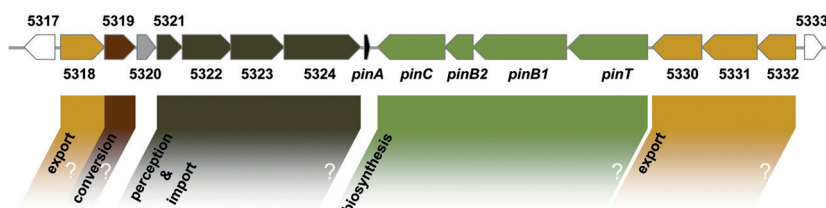


Lantibiotics

K. I. Mohr, C. Volz, R. Jansen, V. Wray,
J. Hoffmann, S. Bernecker, J. Wink,
K. Gerth, M. Stadler,
R. Müller* 11254–11258



Pinensins: The First Antifungal
Lantibiotics



(L)antifungals: Decades of research in the field of lantibiotics have led to the discovery of numerous compounds with antibacterial activity. Herein, the first antifungal lantibiotics are presented. Pinensins originate from a Gram-negative

producer, *Chitinophaga pinensis*. Antifungal activity, structure elucidation, and an in-depth bioinformatic analysis of the biosynthetic gene cluster establish the basis for promising future research with the aim of fighting fungal infections.

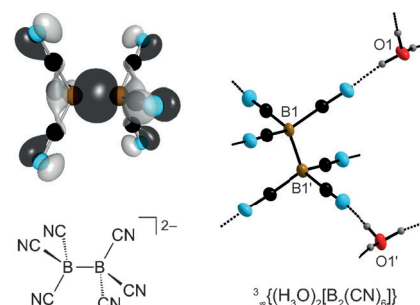
Diborane(6)

J. Landmann, J. A. P. Sprenger,
M. Hailmann, V. Bernhardt-Pitchougina,
H. Willner, N. Ignat'ev, E. Bernhardt,*
M. Finze* 11259–11264



The Hexacyanodiborane(6) Dianion
[B₂(CN)₆]²⁻

Highly stable B–B σ-bond: The homoleptic hexacyanodiborane(6) dianion [B₂(CN)₆]²⁻ (see picture) is chemically very robust and its salts are thermally highly stable. Salts of the diborane(6) dianion are readily accessible in high yields from salts of the anions B(CN)₃²⁻ and [BHal(CN)₃]⁻ (Hal = F, Br). Mechanistic studies show that the [B₂(CN)₆]²⁻ dianion is formed by an unprecedented S_N2-type reaction.



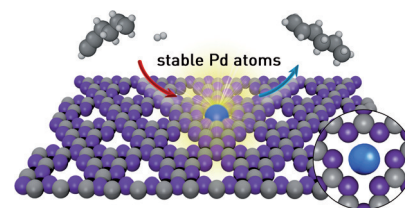
Heterogeneous Catalysis

G. Vilé, D. Albani, M. Nachtegaal, Z. Chen,
D. Dontsova, M. Antonietti, N. López,*
J. Pérez-Ramírez* 11265–11269



A Stable Single-Site Palladium Catalyst for
Hydrogenations

One (sheltered) atom is enough: The unique porous structure of carbon nitride enables the incorporation of isolated palladium atoms in a stable manner. This heterogeneous single-site catalyst outperforms state-of-the-art catalysts that are based on modified palladium nanoparticles in selective hydrogenation reactions.



Front Cover

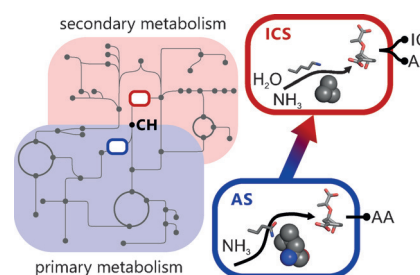
Enzymes

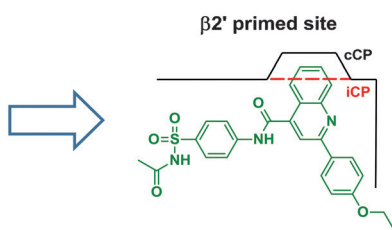
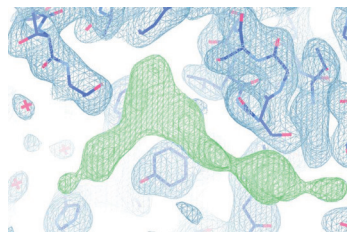
M. G. Plach, P. Löffler, R. Merkl,
R. Sterner* 11270–11274



Conversion of Anthranilate Synthase into Isochorismate Synthase: Implications for the Evolution of Chorismate-Utilizing Enzymes

It works both ways: The nucleophile specificity of the chorismate (CH) utilizing enzyme anthranilate synthase (AS) can be extended from ammonia to water by just two mutations in the active-site access channel. The resulting bifunctional isochorismate synthase (ICS)/AS suggests that a similar process may have led to the emergence of secondary from primary metabolic enzymes in CH-related pathways.





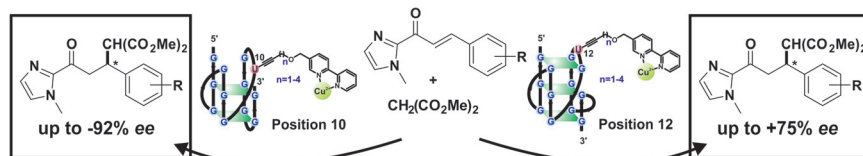
Crystal clear: A non-peptidic sulfonamide was identified as a proteasome ligand in a crystallographic screening approach for inhibitors with a novel mode of action.

The newly discovered binding site displays significant differences in size and polarity between the immuno- and constitutive proteasome.

Proteasome Inhibition

P. Beck, M. Reboud-Ravaux,
M. Groll* 11275 – 11278

Identification of a $\beta 1/\beta 2$ -Specific Sulfonamide Proteasome Ligand by Crystallographic Screening



Location matters: G-quadruplex DNA covalently modified with bpy-Cu^{II} complexes was used as a catalyst in asymmetric aqueous Michael additions. Modifying the position of attachment to the G-quadruplex was found to play a crucial

role in the stereoselectivity of the reaction. While DNA sequences modified at position 10 led to preferential formation of the (–)-enantiomer, those derivatized at position 12 preferentially produced the (+)-enantiomer.

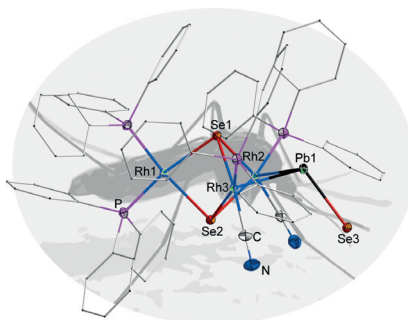
G-Quadruplexes

S. Dey, A. Jäschke* 11279 – 11282

Tuning the Stereoselectivity of a DNA-Catalyzed Michael Addition through Covalent Modification



Like a mosquito's stinger, the second heaviest CO homologue, μ -PbSe, is attached with a distinct bent coordination mode to an Rh₃Se₂ cluster moiety. The ionic compound comprising the [Rh₃(CN)₂(PPh₃)₄(μ_3 -Se)₂(μ -PbSe)]^{3–} anion (shown) was obtained as a side product along with a larger Rh/Se cluster, and apparently arises from an unbridged species that crystallizes under slightly different reaction conditions. Experimental and quantum chemical analyses explain the nature of this uncommon ligand.



CO Homologues

G. Thiele, Y. Franzke, F. Weigend,
S. Dehnen* 11283 – 11288

{ μ -PbSe}: A Heavy CO Homologue as an Unexpected Ligand



Inside Back Cover



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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VIP 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.

Angewandte Corrigendum

Pseudohalide-Induced Moisture-
Tolerance in Perovskite
 $\text{CH}_3\text{NH}_3\text{Pb}(\text{SCN})_2\text{I}$ Thin Films

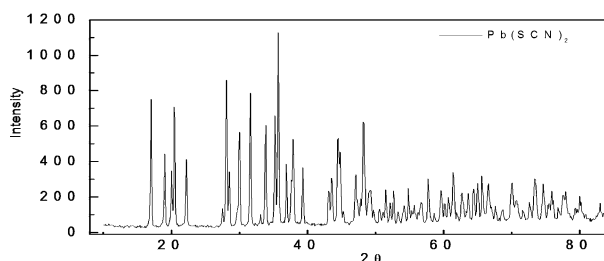
Q. Jiang, D. Rebollar, J. Gong,
E. L. Piacentino, C. Zheng,
T. Xu* **7617–7620**

Angew. Chem. Int. Ed. **2015**, 54

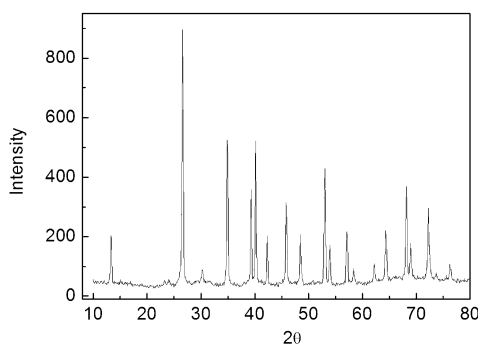
DOI: 10.1002/anie.201503038

Upon further examination of the XRD data of $\text{Pb}(\text{SCN})_2$ powder and PbI_2 powder reported in this Communication, the authors are prompted to make two corrections as follows:

1) The corrected powder XRD of $\text{Pb}(\text{SCN})_2$ is shown as below, which should replace the corresponding XRD pattern of $\text{Pb}(\text{SCN})_2$ in Figure 2 of the original Communication.



2) The corrected powder XRD of PbI_2 is shown as below, which should replace the corresponding XRD pattern of “Pure PbI_2 ” (the blue curve) in Figure S2a in the Supporting Information of the original Communication.



2016 International Symposium on

CHEMICAL BIOLOGY

January 13 - 15, 2016

Campus Biotech, Geneva

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<http://symposium.nccr-chembio.ch>