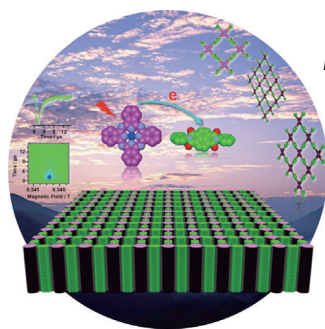
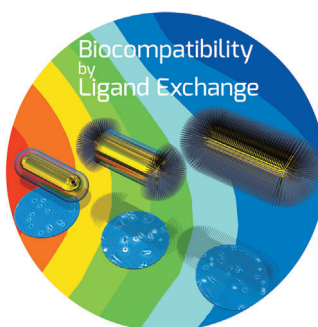


... occurs with perfection in nature (such as in trees) under laminar flows because these flows are symmetrical and continuous. In their Communication on page 1994 ff., A. Abou-Hassan and co-workers use laminar flow microreactors for the self-assembly of fluorescent, plasmonic, and magnetic nanoparticles for the preparation of different categories of assemblies with dual or triple functionalities.

## Nanochemistry

In their Communication on page 1934 ff., A. Petri-Fink et al. obtain complete control over the surface functionality of gold nanoparticles in both overall composition and spatial distribution.

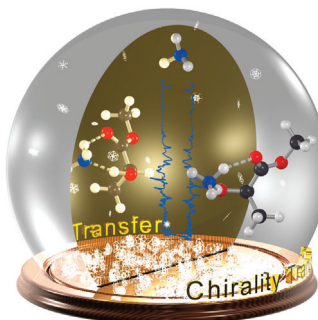


## Electron Transfer

D. Jiang et al. give mechanistic insights in their Communication on page 2017 ff. into the photochemical events and charge dynamics of a donor-acceptor covalent organic framework by using time-resolved spectroscopic methods.

## Chirality Transfer

In their Communication on page 2073 ff., Y. Xu and C. Merten use matrix-isolation vibrational circular dichroism spectroscopy to measure the spectral signatures of chirality transfer from methyl lactate to ammonia.



## How to contact us:

### Editorial Office:

E-mail: [angewandte@wiley-vch.de](mailto: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](mailto:chem-reprints@wiley-vch.de)

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

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

### Copyright Permission:

Bettina Loycke

E-mail: [rights-and-licences@wiley-vch.de](mailto:rights-and-licences@wiley-vch.de)

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

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

### Online Open:

Margitta Schmitt, Carmen Leitner

E-mail: [angewandte@wiley-vch.de](mailto:angewandte@wiley-vch.de)

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

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

### Subscriptions:

[www.wileycustomerhelp.com](http://www.wileycustomerhelp.com)

Fax: (+49) 62 01-606-184

Telephone: 0800 1800536 (Germany only)  
+44(0) 1865476721 (all other countries)

### Advertising:

Marion Schulz

E-mail: [mschulz@wiley-vch.de](mailto:mschulz@wiley-vch.de)

[jspiess@wiley-vch.de](mailto:jspiess@wiley-vch.de)

Fax: (+49) 62 01-606-550

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

### Courier Services:

Boschstrasse 12, 69469 Weinheim

### Regular Mail:

Postfach 101161, 69451 Weinheim

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

GDCh

GESELLSCHAFT  
DEUTSCHER CHEMIKER

Get the **Angewandte App**  
International Edition

Available on the  
**App Store**

## Enjoy Easy Browsing and a New Reading Experience on the iPad

- Keep up to date with the latest articles in Early View.
- Download new weekly issues automatically when they are published.
- Read new or favorite articles anytime, anywhere.



*"... From an international perspective, Sweden's research expenditure is high at 3.4% of the gross domestic product (GDP), compared to the average of 3.0% within the OECD countries. However, merely 24% of the funding in Sweden comes from the government ..."*

Read more in the Editorial by Christina Moberg.

## Editorial

C. Moberg\* \_\_\_\_\_ 1844–1845

Chemistry in Sweden—A Midsummer Night's Dream?

## Spotlight on Angewandte's Sister Journals

1864–1867



*"My favorite time of day is the night.  
My favorite book is anything by Helmut Krausser ..."*  
This and more about Günter Mayer can be found on page 1870.

## Service

## Author Profile

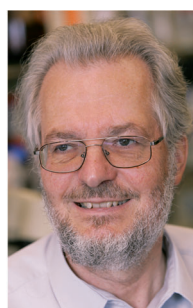
Günter Mayer \_\_\_\_\_ 1870



P. Mountford



N. Yabuuchi



H. Kessler

## News

Frankland Award:  
P. Mountford \_\_\_\_\_ 1871

Science Award Electrochemistry:  
N. Yabuuchi \_\_\_\_\_ 1871

Akabori Memorial Award:  
H. Kessler \_\_\_\_\_ 1871

## Books

Mass Spectrometry Handbook

Mike S. Lee

reviewed by F. De Angelis \_\_\_\_\_ 1872

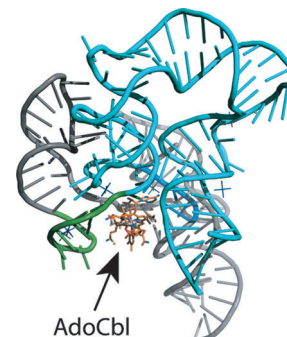
## Highlights

### Riboswitches

M. F. Soulière, A. Haller, T. Santner,  
R. Micura\* \_\_\_\_\_ 1874–1877

New Insights into Gene Regulation—  
High-Resolution Structures of Cobalamin  
Riboswitches

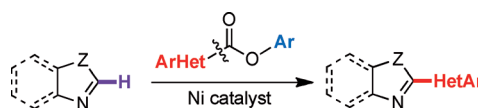
The complex class of cobalamin-sensitive riboswitches use a “kissing loop” to regulate gene expression. The molecular details of the recognition and folding mode of this riboswitch have been revealed by recent X-ray structures. These insights, together with the identification of RNA polymerase pause sites during transcription, have resulted in a more complete understanding of the response mechanism. AdoCbl = adenosylcobalamin.



### C–H Arylation

A. Correa, J. Cornella,  
R. Martin\* \_\_\_\_\_ 1878–1880

Nickel-Catalyzed Decarbonylative C–H  
Coupling Reactions: A Strategy for  
Preparing Bis(heteroaryl) Backbones



- No need for oxidants
- Wide substrate scope
- Unusual selectivity switch
- Natural product synthesis

**Activation à la carte:** The direct arylation of heteroarenes was accomplished by employing aromatic esters as effective coupling partners under nickel catalysis (see scheme; Z = O, S). The key process

implies an unconventional and unprecedented Ni-catalyzed decarbonylative coupling utilizing cost-efficient nickel catalysts.

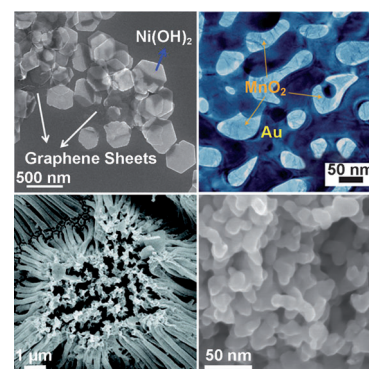
## Minireviews

### Energy Storage

Q. Lu, J. G. Chen,  
J. Q. Xiao\* \_\_\_\_\_ 1882–1889

Nanostructured Electrodes for High-  
Performance Pseudocapacitors

Three key parameters determine the performance of nanostructured electrodes for pseudocapacitor applications: pore structure, conductivity, and crystallinity. These parameters determine the utilization of electrode materials, especially at high power densities. Future progress can be seen in developing techniques that can simultaneously tailor those parameters and also be able to facilitate electrode production at large scales.



**For the USA and Canada:**  
ANGEWANDTE CHEMIE International  
Edition (ISSN 1433-7851) is published weekly  
by Wiley-VCH, PO Box 191161, 69451 Wein-  
heim, Germany. Air freight and mailing in the  
USA by Publications Expediting Inc., 200  
Meacham Ave., Elmont, NY 11003. Periodicals

postage paid at Jamaica, NY 11431. US POST-  
MASTER: send address changes to *Angewandte  
Chemie*, Journal Customer Services, John  
Wiley & Sons Inc., 350 Main St., Malden,  
MA 02148-5020. Annual subscription price for  
institutions: US\$ 11,738/10,206 (valid for print  
and electronic / print or electronic delivery); for

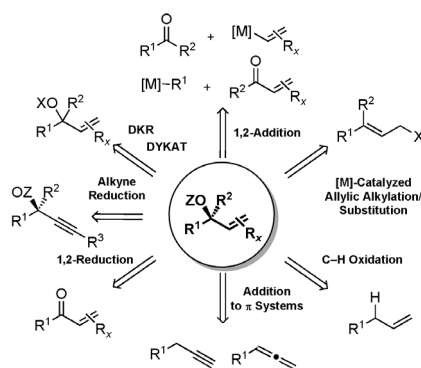
individuals who are personal members of  
a national chemical society prices are available  
on request. Postage and handling charges  
included. All prices are subject to local VAT/  
sales tax.

## Reviews

### Synthetic Methods

A. Lumbroso, M. L. Cooke,  
B. Breit\* 1890 – 1932

Catalytic Asymmetric Synthesis of Allylic Alcohols and Derivatives and their Applications in Organic Synthesis



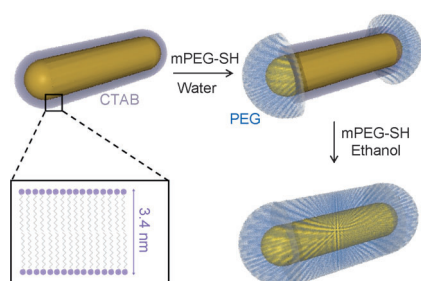
**Highly versatile:** Allylic alcohols represent an important class of chiral building blocks for organic synthesis. This Review addresses the plethora of methods developed for the catalytic asymmetric synthesis of enantioenriched allylic alcohols and their many applications in further synthesis, including of natural products.

## Communications

### Bio-Nanomaterials

C. Kinnear, H. Dietsch, M. J. D. Clift,  
C. Endes, B. Rothen-Rutishauser,  
A. Petri-Fink\* 1934 – 1938

Gold Nanorods: Controlling Their Surface Chemistry and Complete Detoxification by a Two-Step Place Exchange



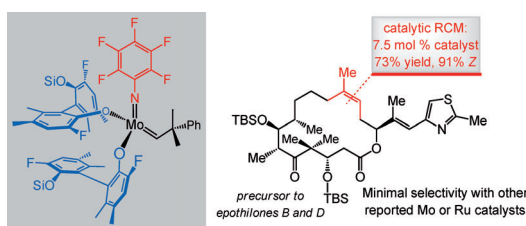
**Surface functionalization:** Complete detoxification of gold nanorods was achieved by manipulating the position in the stability map between surface-adsorbing polyethylene glycol (PEG) and destabilizing ethanol (see picture). This robust procedure complements studies related to the effects of shape when contemplating the nanoparticle–cell interaction.

Frontispiece

### Ring-Closing Metathesis

C. Wang, F. Haefner, R. R. Schrock,  
A. H. Hoveyda\* 1939 – 1943

Molybdenum-Based Complexes with Two Aryloxides and a Pentafluoroimido Ligand: Catalysts for Efficient Z-Selective Synthesis of a Macrocyclic Trisubstituted Alkene by Ring-Closing Metathesis



**Olefin metathesis catalysts** for controlling the formation of trisubstituted macrocyclic Z alkenes have been developed. The most effective complexes are Mo alkylidenes with a pentafluorophenylimido group and two large aryloxide ligands. The

macrocyclic lactone precursor to anti-cancer agents epothilones B and D is obtained in 73 % yield and 91 % Z selectivity in less than 6 hours at room temperature.



The German Chemical Society (GDCh) invites you to:



# Angewandte *Anniversary* Symposium

GDCh  
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

**Tuesday, March 12, 2013**

Henry Ford Building / FU Berlin

## Speakers



Carolyn R.  
Bertozzi



François  
Diederich



Alois  
Fürstner



Roald Hoffmann  
(Nobel Prize 1981)



Susumu  
Kitagawa



Jean-Marie Lehn  
(Nobel Prize 1987)



E.W. "Bert"  
Meijer



Frank  
Schirrmacher  
(Publisher, FAZ)



Robert  
Schlögl



George M.  
Whitesides



Ahmed Zewail  
(Nobel Prize 1999)



**Register  
now:**

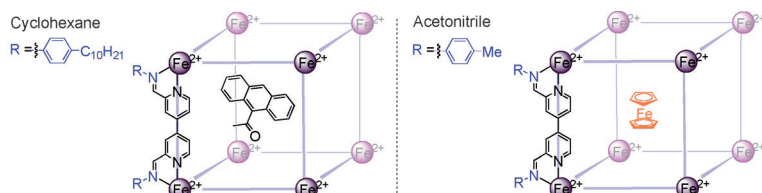
**[angewandte.org/symposium](http://angewandte.org/symposium)**



**WILEY-VCH**



GESELLSCHAFT  
DEUTSCHER CHEMIKER



**Cubes:** The rational design of a simple set of organic subcomponents led to the formation of a  $\text{M}_8\text{L}_{12}^{16+}$  cubic capsule upon their self-assembly with  $\text{Fe}^{\text{II}}$  ions. By altering the length of alkyl chains on these subcomponents, the solubility of the

assembled structures was greatly increased in apolar solvents, such as cyclohexane, and the structures displayed solvent-dependent host–guest interactions.

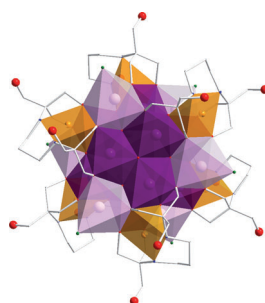
## Supramolecular Chemistry

C. Browne, S. Brenet, J. K. Clegg,  
J. R. Nitschke\* 1944 – 1948

Solvent-Dependent Host–Guest  
Chemistry of an  $\text{Fe}_8\text{L}_{12}$  Cubic Capsule



**A two-step method** for the directed synthesis of high-nuclearity  $\text{Mn}^{\text{III}}\text{--Mn}^{\text{II}}\text{--Cu}^{\text{II}}$  heterometallic transition metal complexes is described. The synthesis starts from a preformed copper(II) complex to trap an inner hexacapped cuboctahedral manganese oxide core.



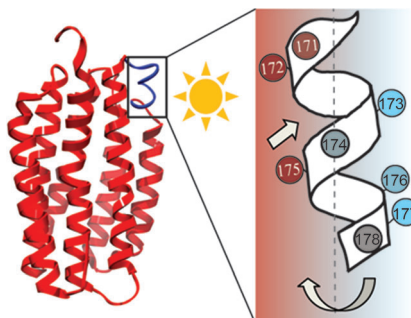
## Heterometallic Complexes

V. A. Milway, F. Tuna, A. R. Farrell,  
L. E. Sharp, S. Parsons,  
M. Murrie\* 1949 – 1952

Directed Synthesis of  $\{\text{Mn}_{18}\text{Cu}_6\}$   
Heterometallic Complexes



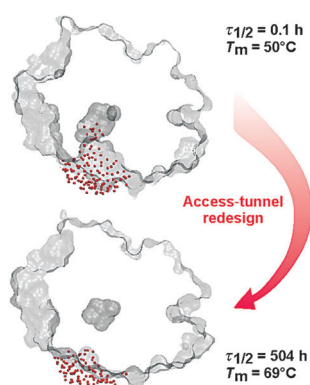
**Proteins on film:** The Overhauser dynamic nuclear polarization method resolves hydration dynamics to an unprecedented level of detail for a transmembrane protein surface. The heterogeneous hydration landscape of proteorhodopsin rearranges upon photoactivation (see picture), thus providing an insight into how water contributes to protein function even for biological systems embedded in a hydrophobic membrane.



## Membrane Protein Activation

S. Hussain, J. M. Franck,  
S. Han\* 1953 – 1958

Transmembrane Protein Activation  
Refined by Site-Specific Hydration  
Dynamics



**Mutations** targeting as few as four residues lining the access tunnel extended the half-life of an enzyme in 40% dimethyl sulfoxide from minutes to weeks and increased its melting temperature by  $19^\circ\text{C}$ . Protein crystallography and molecular dynamics revealed that the tunnel residue packing is a key determinant of protein stability and the active-site accessibility for cosolvent molecules (red dots).

## Protein Stability

T. Koudelakova, R. Chaloupkova,  
J. Brezovsky, Z. Prokop, E. Sebestova,  
M. Hesseler, M. Khabiri, M. Plevaka,  
D. Kulik, I. Kuta Smatanova, P. Rezacova,  
R. Ettrich, U. T. Bornscheuer,  
J. Damborsky\* 1959 – 1963

Engineering Enzyme Stability and  
Resistance to an Organic Cosolvent by  
Modification of Residues in the Access  
Tunnel

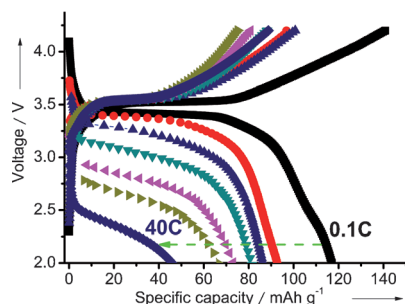


### Sodium-Ion Batteries

L. Wang, Y. H. Lu, J. Liu, M. W. Xu,  
J. G. Cheng, D. W. Zhang,  
J. B. Goodenough\* — 1964 – 1967



A Superior Low-Cost Cathode for a Na-Ion Battery



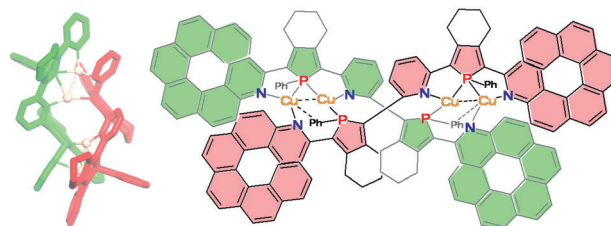
**Sodium manganese hexacyanoferrates (NMHFCs)** synthesized in aqueous solution at room temperature show high reversible capacity and outstanding rate capability as cathodes for a rechargeable sodium-ion battery (SIB). Earth-abundant elements and a low-cost synthesis route make these NMHFCs promising cathodes for SIBs, independent of natural lithium sources.

### Supramolecular Helices

V. Vreshch, M. El Sayed Moussa,  
B. Nohra, M. Srebro, N. Vanthuyne,  
C. Roussel, J. Autschbach,\* J. Crassous,\*  
C. Lescop,\* R. Réau\* — 1968 – 1972



Assembly of Helicene-Capped N,P,N,P,N-Helicands within Cu<sup>I</sup> Helicates: Impacting Chiroptical Properties by Ligand–Ligand Charge Transfer



**Combining helicate and helicene chemistry:** Pentadentate phosphole-pyridine helicands (see scheme) coordinated to Cu<sup>I</sup> or Ag<sup>I</sup> centers afford configurationally stable double-stranded helicates bearing multi-

ple bridging-phosphane coordination modes. Similarly enantiomerically pure helicene-grafted helicands afford enantiopure helicates.

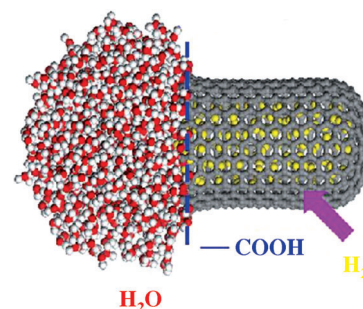
### Molecular Dynamics

H. Y. Chen, D. Y. Sun, X. G. Gong,  
Z.-F. Liu\* — 1973 – 1976



Self-Assembled Water Molecules as a Functional Valve for a High-Pressure Nanocontainer

**Carbon nanotubes:** The end section of a carbon nanotube, cut by acid treatment, contains hydrophilic oxygen groups, around which water molecules can assemble to block the entry of the tube. Hydrogen of pressures up to 10000 bar can be locked inside the tube by such an “aqueous valve” (see picture).

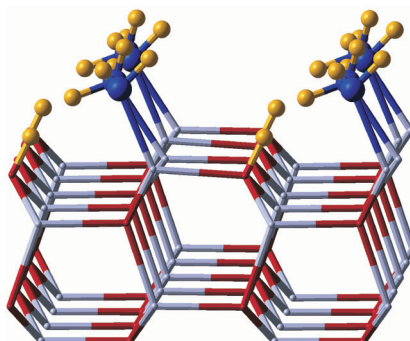


### Surface Chemistry

H. Noei, F. Gallino, L. Jin, J. Zhao,  
C. Di Valentin,\* Y. Wang\* — 1977 – 1981



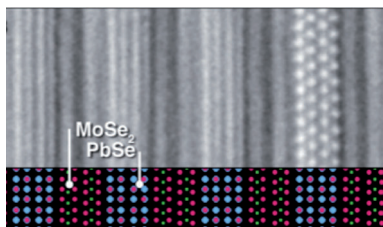
Coverage-Induced Hydrogen Transfer on ZnO Surfaces: From Ideal to Real Systems



**Deprotonating a base:** High-resolution electron energy loss spectroscopy and ultrahigh-vacuum infrared spectroscopy have been used to determine that high surface coverage can induce proton transfer from adsorbed ammonia to surface oxygen atoms on both single crystals and nanoparticles of ZnO (see picture; Zn blue sticks, O red, N blue spheres, H yellow). These observations are supported by DFT calculations.



**Inorganic nanocrystals:** The structures of the compounds  $[(\text{PbSe})_{1.00}]_m(\text{MoSe}_2)_n$  and  $[(\text{PbSe})_{0.99}]_m(\text{WSe}_2)_n$  ( $m \geq 1$  and  $n \leq 5$ ) were investigated using X-ray diffraction and scanning transmission electron microscopy, which revealed a pairing distortion of the PbSe component that is dependent on  $m$ , the thickness of the PbSe layers, but independent of  $n$ , the thickness of the dichalcogenide.



### Composite Materials

M. D. Anderson, C. L. Heideman, Q. Lin, M. Smeller, R. Kokenyesi, A. A. Herzing, I. M. Anderson, D. A. Keszler, P. Zschack, D. C. Johnson\* — 1982 – 1985

Size-Dependent Structural Distortions in One-Dimensional Nanostructures



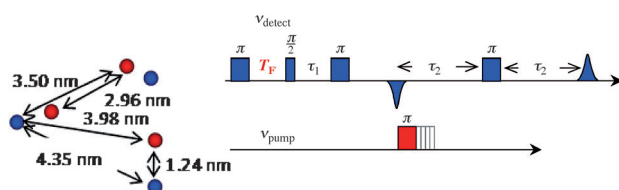
**Soaking up s'more:** Marshmallow-like flexible gels synthesized from organo-alkoxysilanes by a facile process show superior oil/water separation properties. The gels are superhydrophobic and can be used to remove organic compounds from water through absorption; they can then be recovered by squeezing them out of the gel, as if it were a sponge. The gel retains flexibility over a wide temperature range, even in liquid nitrogen (see photo).



### Hydrophobic Gels

G. Hayase, K. Kanamori,\* M. Fukuchi, H. Kaji, K. Nakanishi — 1986 – 1989

Facile Synthesis of Marshmallow-like Macroporous Gels Usable under Harsh Conditions for the Separation of Oil and Water



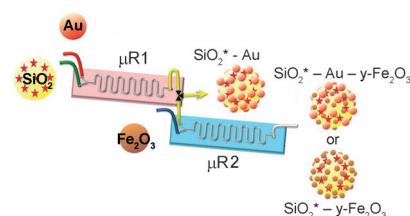
**A new pulse sequence:** The distances between copper sites of the homotrimeric Cu-containing nitrite reductase were determined by EPR spectroscopy (see picture). By exploiting the differences in the electron spin relaxation of the Cu ions,

a filtering technique allows the selective removal of distances from a complex distance distribution. This filter technique combined with the PELDOR experiment promises to be useful for distance mapping by EPR spectroscopy.

### Structure Elucidation

J. H. van Wonderen, D. N. Kostrz, C. Dennison, F. MacMillan\* — 1990 – 1993

Refined Distances Between Paramagnetic Centers of a Multi-Copper Nitrite Reductase Determined by Pulsed EPR (*i*DEER) Spectroscopy



**Lab-on-a-particle:** Fluorescent, plasmonic, and magnetic  $\text{SiO}_2^*-\text{Au}-\gamma\text{-Fe}_2\text{O}_3$  nanostructures were assembled under continuous flow using two microfluidic devices ( $\mu\text{R1}$  and  $\mu\text{R2}$ ) connected in series. After assembling the  $\text{SiO}_2^*-\text{Au}$  nanostructures by electrostatic interactions,  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles were attached to the structures (see picture).

### Microfluidic Assembly

N. Hassan, V. Cabuil, A. Abou-Hassan\* — 1994 – 1997

Continuous Multistep Microfluidic Assisted Assembly of Fluorescent, Plasmonic, and Magnetic Nanostructures



Front Cover



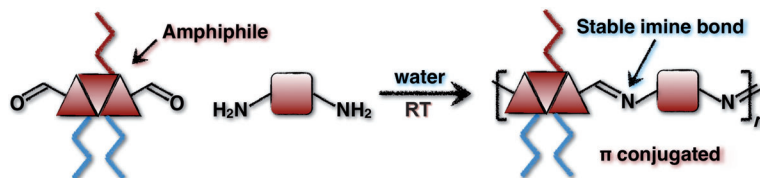


## Self-Assembly

D. Janeliunas, P. van Rijn, J. Boekhoven,  
C. B. Minkenberg, J. H. van Esch,\*  
R. Eelkema\* ————— 1998 – 2001



Aggregation-Driven Reversible Formation  
of Conjugated Polymers in Water



**Come together:** Self-assembly can drive the formation of conjugated imine polymers in water, and stabilization of otherwise unstable imine bonds is used to obtain fully  $\pi$ -conjugated, responsive

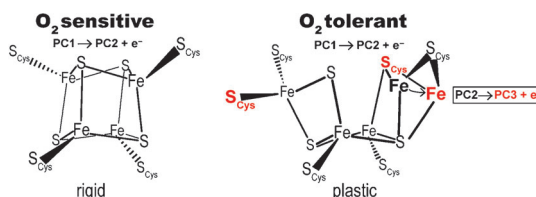
dynamic covalent polyimines in aqueous environments. Both the optical properties and the aggregate morphology can be tuned by varying the aromatic monomers.

## Hydrogenases

J.-M. Mouesca, J. C. Fontecilla-Camps,\*  
P. Amara\* ————— 2002 – 2006



The Structural Plasticity of the Proximal  
[4Fe3S] Cluster is Responsible for the O<sub>2</sub>  
Tolerance of Membrane-Bound [NiFe]  
Hydrogenases



**The main difference** between O<sub>2</sub>-sensitive and O<sub>2</sub>-tolerant [NiFe] hydrogenases is the plasticity of the proximal [4Fe3S] cluster in the latter hydrogenase (see scheme). Deprotonation of a conserved glutamate

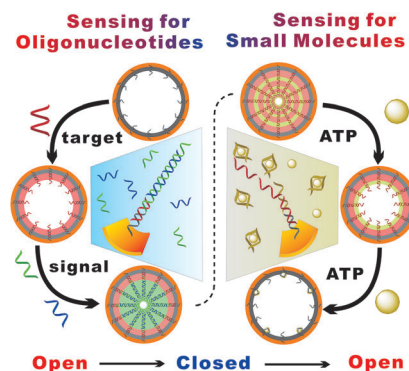
residue initiates the movement of the iron atom, resulting in its binding to the amide nitrogen atom of one of the two super-numerary cysteine ligands and superoxidation of the proximal cluster.

## Nanomaterials

N. Liu, Y. Jiang, Y. Zhou, F. Xia,\* W. Guo,\*  
L. Jiang ————— 2007 – 2011



Two-Way Nanopore Sensing of Sequence-  
Specific Oligonucleotides and Small-  
Molecule Targets in Complex Matrices  
Using Integrated DNA Supersandwich  
Structures



**Pore me another one:** Sub-nanomolar sequence-specific DNA detection and sub-micromolar small-molecule (ATP) detection was shown by way of self-assembly and disassembly of DNA superstructures within solid-state nanopores (see scheme). These DNA structures provide a built-in amplification mechanism to increase the signal strength and sensitivity. This sensor was also shown to work within complex mixtures, such as mammalian serum.

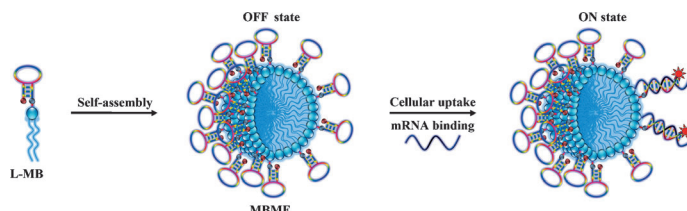
Inside Cover

## Molecular Beacons

T. Chen, C. S. Wu, E. Jimenez, Z. Zhu,  
J. G. Dajac, M. You, D. Han, X. Zhang,\*  
W. Tan\* ————— 2012 – 2016



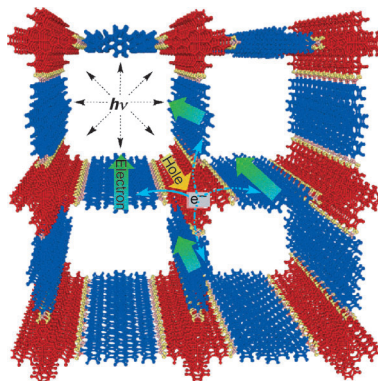
DNA Micelle Flares for Intracellular  
mRNA Imaging and Gene Therapy



**Lighting the way with DNA:** Molecular beacon micelle flares (MBMFs), based on self-assembly of diacylipid-molecular-beacon conjugates (L-MBs; see figure), have been developed for combined mRNA

detection and gene therapy. These MBMFs were shown to inhibit a model gene in vitro and decrease the viability of cancer cells in culture.

**Light works:** Mechanistic insights into the photochemical events and charge dynamics of a donor–acceptor covalent organic framework were given by time-resolved transient absorption spectroscopy and time-resolved electron spin resonance spectroscopy (see picture). The organic framework triggers ultrafast electron transfer and enables long-distance charge delocalization and exceptional long-term charge separation.



## Electron Transfer

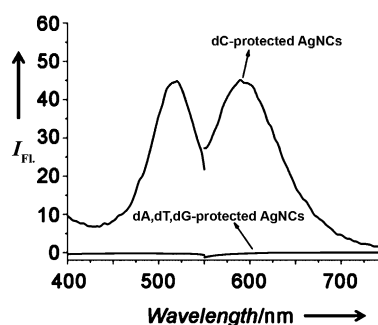
S. Jin, X. Ding, X. Feng, M. Supur, K. Furukawa, S. Takahashi, M. Addicoat, M. E. El-Khouly, T. Nakamura, S. Irle, S. Fukuzumi, A. Nagai, D. Jiang\* ————— 2017 – 2021

Charge Dynamics in A Donor–Acceptor Covalent Organic Framework with Periodically Ordered Bicontinuous Heterojunctions



Inside Back Cover

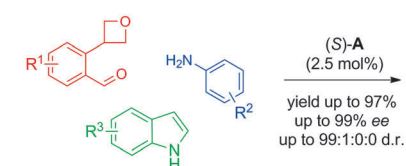
**Basic evidence** is provided for the benefits of using cytosine-rich DNA strands as scaffolds for fluorescent silver nanoclusters. The DFT-calculated fluorescence spectra of silver nanoclusters (AgNCs) protected by DNA monomers (dC, dA, dT, and dG) were in good agreement with the experimentally obtained spectra (see picture), showing that only the use of cytosine-rich DNA strands as scaffolds gives fluorescent nanoclusters.



## Nanotechnology

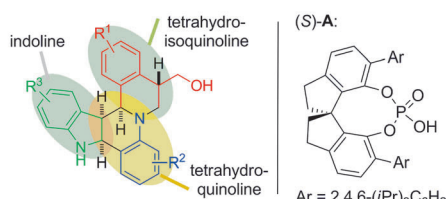
X. Yang, L. Gan, L. Han, E. Wang,\* J. Wang\* ————— 2022 – 2026

High-Yield Synthesis of Silver Nanoclusters Protected by DNA Monomers and DFT Prediction of their Photoluminescence Properties



**Starting from three achiral compounds**, the title reaction provides rapid access to a variety of molecules that contain indoline, tetrahydroquinoline, and tetrahydroisoquinoline moieties (see scheme). The

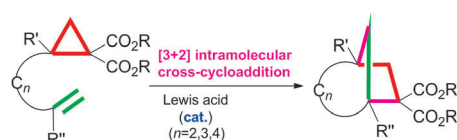
process features the efficient formation of multiple new bonds and chiral centers, excellent stereoselectivity, oxetane desymmetrization, and easy product purification through filtration.



## Synthetic Methods

Z. Chen, B. Wang, Z. Wang, G. Zhu,\* J. Sun\* ————— 2027 – 2031

Complex Bioactive Alkaloid-Type Polycycles through Efficient Catalytic Asymmetric Multicomponent Aza-Diels–Alder Reaction of Indoles with Oxetane as Directing Group



**Carbon bridges:** The title reaction has been successfully developed, and applied to the total synthesis of the tetracyclic diterpenoids phyllocladanol and phyllocladene. The method provides an effi-

cient, general, and conceptually new strategy for the construction of structurally complex and diverse  $[n.2.1]$  carbocyclic skeletons (see scheme).

## Synthetic Methodology

W. Zhu, J. Fang, Y. Liu, J. Ren, Z. Wang\* ————— 2032 – 2037

Lewis Acid Catalyzed Formal Intramolecular  $[3+2]$  Cross-Cycloaddition of Cyclopropane 1,1-Diesters with Alkenes: General and Efficient Strategy for Construction of Bridged  $[n.2.1]$  Carbocyclic Skeletons



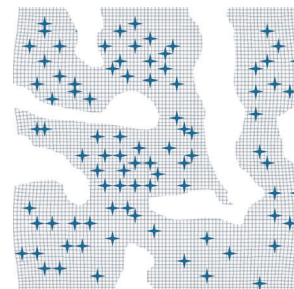
## Microporous Materials

P. Sazama,\* Z. Sobalik, J. Dedecek,  
I. Jakubec, V. Parvulescu, Z. Bastl,  
J. Rathousky, H. Jirglova — 2038–2041



Enhancement of Activity and Selectivity in  
Acid-Catalyzed Reactions by  
Dealuminated Hierarchical Zeolites

**Shape-selective reactions:** Highly selective catalysts are obtained by alkaline and subsequent acid leaching of conventionally prepared zeolites. Active sites that are located in the shape-selective environment of micropores and accessible through mesopores (see picture) provide high selectivity and activity in acid-catalyzed reactions.



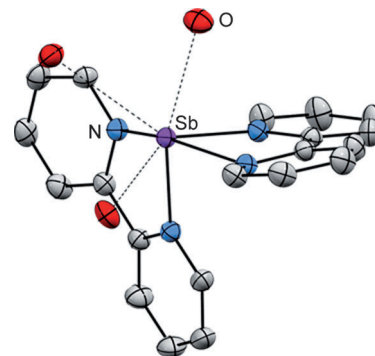
## Main-Group Elements

S. S. Chitnis, N. Burford,\*  
M. J. Ferguson — 2042–2045



2,2-Bipyridine Complexes of Antimony:  
Sequential Fluoride Ion Abstraction from  
SbF<sub>3</sub> by Exploiting the Fluoride Ion Affinity  
of Me<sub>3</sub>Si<sup>+</sup>

**Gas driven:** A high-yield approach to sequential fluoride ion abstraction from SbF<sub>3</sub> in the presence of 2,2'-bipyridine gives a series of complexes containing [SbF<sub>2</sub>]<sup>+</sup>, [SbF]<sup>2+</sup>, and [Sb]<sup>3+</sup> (see figure) acceptors. The thermodynamically favorable rapid elimination of gaseous Me<sub>3</sub>SiF provides a potentially general approach to enhance the Lewis acidity and coordination chemistry of p-block centers.

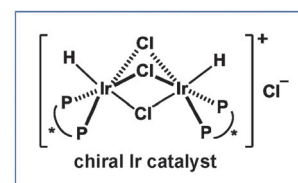
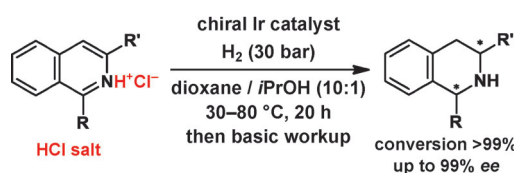


## Asymmetric Synthesis

A. Iimuro, K. Yamaji, S. Kandula,  
T. Nagano, Y. Kita,  
K. Mashima\* — 2046–2050



Asymmetric Hydrogenation of  
Isoquinolinium Salts Catalyzed by Chiral  
Iridium Complexes: Direct Synthesis for  
Optically Active 1,2,3,4-  
Tetrahydroisoquinolines



**The salt makes the difference:** In the presence of a chiral iridium catalyst, 1- and 3-substituted as well as 1,3-disubstituted isoquinolinium salts can be hydrogenated, giving the corresponding

1,2,3,4-tetrahydroisoquinolines in high enantiomeric excess after a basic workup (see scheme). This protocol is applicable to the synthesis of the prescription drug solifenacin.

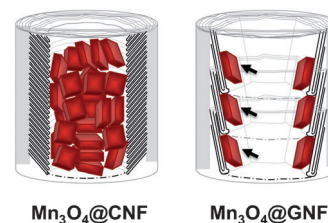
## Carbon Materials

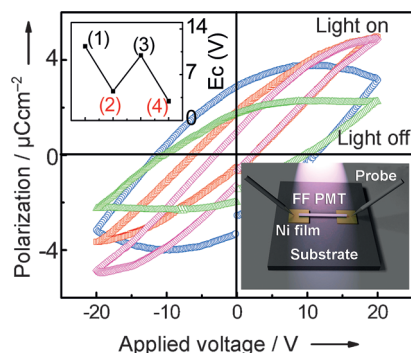
Dr. M. C. Gimenez-Lopez,\* A. La Torre,  
M. W. Fay, P. D. Brown,  
A. N. Khlobystov\* — 2051–2054



Assembly and Magnetic Bistability of  
Mn<sub>3</sub>O<sub>4</sub> Nanoparticles Encapsulated in  
Hollow Carbon Nanofibers

**Effects of confinement:** Magnetic nanoparticles are encapsulated within hollow carbon nanofibers. The density and orientation of the guest Mn<sub>3</sub>O<sub>4</sub> nanoparticles depend crucially on the internal structure of the host carbon nanocontainer, which enables tuning functional magnetic properties of the composite material.



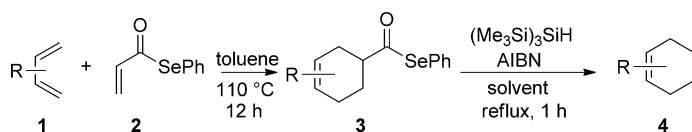


**Spontaneous polarization reversal:** Saturated polarization–electric field loops with a concave region were obtained from diphenylalanine peptide microtubes (FF PMTs) by combining the action of light during the hysteresis loop measurements (see picture;  $E_c$  = coercive field). The existence of ferroelectricity in FF peptide nanostructures was shown experimentally. The ferroelectricity of the FF PMTs is expected to extend their applications to biomedicine and microelectronics.

### Ferroelectric Materials

Z. X. Gan, X. L. Wu,\* X. B. Zhu,  
J. C. Shen \_\_\_\_\_ 2055 – 2059

Light-Induced Ferroelectricity in  
Bioinspired Self-Assembled  
Diphenylalanine Nanotubes/Microtubes



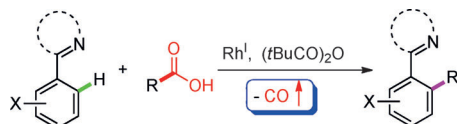
**Reactive:** Se-phenyl prop-2-ene selenoate (phenyl selenoacrylate) **2**, readily prepared from acryloyl chloride, is a very reactive dienophile in Diels–Alder reactions, and more reactive than acrylates. Its cyclo-adducts **3** with many dienes **1** can be

easily reduced to the hydrocarbons **4** under radical conditions. This process works even in cases where there is an adjacent group that can be easily eliminated, e.g., an allylic ether.

### Synthetic Methods

M. E. Jung,\* F. Perez, C. F. Regan, S. W. Yi,  
Q. Perron \_\_\_\_\_ 2060 – 2062

Se-Phenyl Prop-2-ene selenoate: An  
Ethylene Equivalent for Diels–Alder  
Reactions



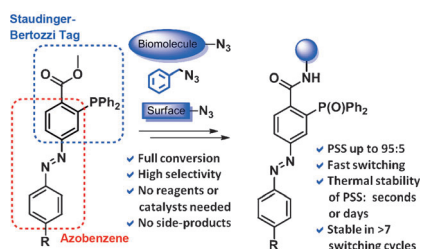
**Marked absent:** The pseudo-oxidative decarboxylative coupling of carboxylic acids and arenes using rhodium(I) in the

absence of an oxidant is described. The study offers a new convenient method for the construction of  $C_{sp^2}$ – $C_{sp^2}/C_{sp^3}$  bonds.

### C–H Activation

F. Pan, Z.-Q. Lei, H. Wang, H. Li, J. Sun,\*  
Z.-J. Shi\* \_\_\_\_\_ 2063 – 2067

Rhodium(I)-Catalyzed Redox-Economic  
Cross-Coupling of Carboxylic Acids with  
Arenes Directed by N-Containing Groups



**Click to switch:** A novel family of azobenzenes containing residues needed for aqueous Staudinger–Bertozzi ligation to azides was designed (see scheme). The resulting photochromes show stable and reversible switching behavior in water, with a photostationary state (PSS) of up to 95:5 *cis/trans*. Applications in model systems include the modification of azide-bearing surfaces and proteins.

### Photochromism

W. Szymański, B. Wu, C. Poloni,  
D. B. Janssen,  
B. L. Feringa\* \_\_\_\_\_ 2068 – 2072

Azobenzene Photoswitches for  
Staudinger–Bertozzi Ligation





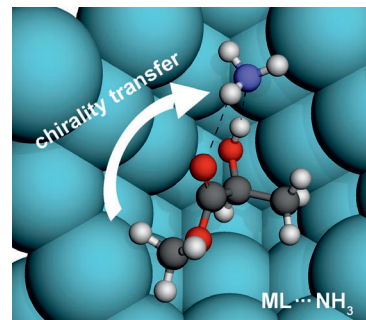
## Chirality Transfer

C. Merten, Y. Xu\* — 2073 – 2076



Chirality Transfer in a Methyl Lactate–Ammonia Complex Observed by Matrix-Isolation Vibrational Circular Dichroism Spectroscopy

**Hand-me-down chirality:** Chirality transfer from methyl lactate to ammonia has been investigated and the mirror-imaged vibrational circular dichroism (VCD) spectra of a pair of enantiomers of a flexible chiral molecular complex are presented. The distinct VCD spectral pattern provides decisive evidence for the existence of two dominant and subtly different conformers of the complex.



Back Cover

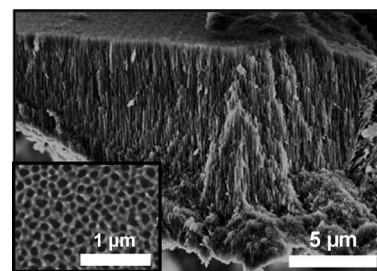
## Electrochemistry

C.-Y. Lee, K. Lee,  
P. Schmuki\* — 2077 – 2081



Anodic Formation of Self-Organized Cobalt Oxide Nanoporous Layers

**Nanoporous materials:** High-aspect-ratio, ordered porous  $\text{Co}_3\text{O}_4$  layers were formed by self-organizing anodization of a cobalt substrate and subsequent annealing. The key for successful formation of such layers is to sufficiently suppress competing oxygen evolution during anodization. The aligned  $\text{Co}_3\text{O}_4$  channel layers behave as a highly efficient water oxidation catalyst (see picture).

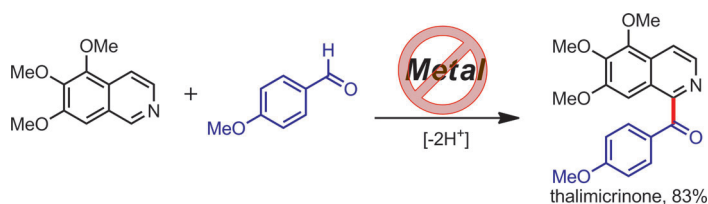


## C–H Functionalization

K. Matcha,  
A. P. Antonchick\* — 2082 – 2086



Metal-Free Cross-Dehydrogenative Coupling of Heterocycles with Aldehydes



A range of heterocyclic compounds were synthesized by a novel, metal-free cross-dehydrogenative coupling between heterocycles and aldehydes under mild reaction conditions that are not sensitive to moisture. The products are formed

smoothly and regioselectively at room temperature by a hypervalent iodine mediated transformation. This method has a broad substrate scope and was used in the highly efficient, one-step synthesis of natural products.

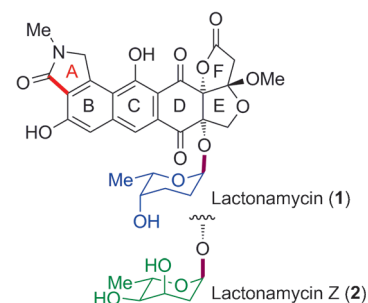
## Natural Product Synthesis

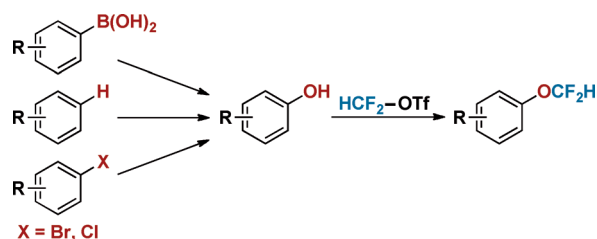
S. Adachi, K. Watanabe, Y. Iwata,  
S. Kameda, Y. Miyaoka, M. Onozuka,  
R. Mitsui, Y. Saikawa,\*  
M. Nakata\* — 2087 – 2091



Total Syntheses of Lactonamycin and Lactonamycin Z with Late-Stage A-Ring Formation and Glycosylation

**The highly oxygenated** polyketide antibiotics, lactonamycin and lactonamycin Z were synthesized. The BCDEF ring system was constructed by a cycloaddition and a palladium-catalyzed cyclization and a Bischler–Napieralski-type cyclization was used for the formation of the A ring. The glycosylation of the aglycon with the appropriate sugar gave lactonamycin and lactonamycin Z.





**The difluoromethylation of phenols** with a simple, non-ozone-depleting reagent is described. The reaction occurs within minutes at room temperature with exceptional functional-group tolerance,

which makes possible tandem processes for the conversion of arylboronic acids, aryl halides, and arenes to difluoromethyl ethers.

## Difluoromethylation

P. S. Fier, J. F. Hartwig\* — 2092–2095

Synthesis of Difluoromethyl Ethers with Difluoromethyltriflate



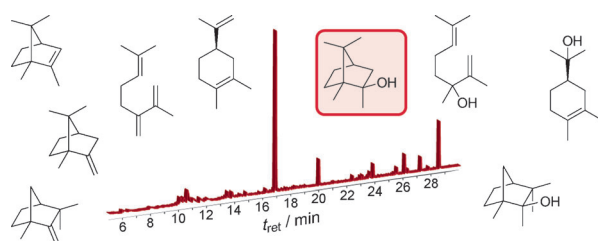
**Three in the spotlight:** Irradiation promotes a general, three-component reaction between diazoketones, carboxylic acids, and isocyanides. The highly functionalized captodative olefin products of this reaction are versatile synthons for organic synthesis.



## Synthetic Methods

A. Basso,\* L. Banfi, S. Garbarino, R. Riva — 2096–2099

Ketene Three-Component Reaction: A Metal-Free Multicomponent Approach to Stereodefined Captodative Olefins



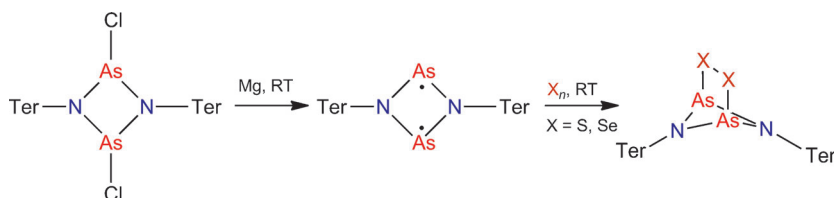
**Odor of earth:** Several homomonoterpenes were identified in actinomycetes that produce 2-methylisoborneol (2-MIB, see scheme, which is responsible for an earthy odor in drinking water). Their occurrence clarifies the 2-MIB pathway,

because they are derived from cationic intermediates that are otherwise difficult to detect. A highly sensitive method using feeding experiments with  $^{13}\text{C}$ -labeled precursors gives detailed insights into 2-MIB biosynthesis.

## Terpene Biosynthesis

N. L. Brock, S. R. Ravella, S. Schulz,\* J. S. Dickschat\* — 2100–2104

A Detailed View of 2-Methylisoborneol Biosynthesis



**As you like it:** The first reported four-membered heterocycle  $[\text{As}(\mu\text{-Nter})]_2$ , which can be referred to as a high-temperature stable biradicaloid, is formed, when a bulky substituent, such as the

terphenyl group, prevents dimerization. Addition reactions of elemental sulfur and selenium (see scheme) as well as the double bond of  $\text{CS}_2$  demonstrate that  $[\text{As}(\mu\text{-Nter})]_2$  has radical-type behavior.

## Biradicaloids

S. Demeshko, C. Godemann, R. Kuzora, A. Schulz,\* A. Villinger — 2105–2108

An Arsenic–Nitrogen Biradicaloid: Synthesis, Properties, and Reactivity

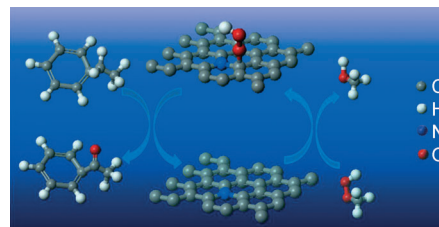


## Heterogeneous Catalysis

Y. Gao, G. Hu, J. Zhong, Z. Shi, Y. Zhu,  
D. S. Su,\* J. Wang,\* X. Bao,  
D. Ma\* 2109–2113



Nitrogen-Doped  $sp^2$ -Hybridized Carbon  
as a Superior Catalyst for Selective  
Oxidation



**Thanks to nitrogen** introduced into the layered carbon framework of graphite, the chemical reactivity of the carbon atoms was increased. N-doped graphitic cata-

lysts generate reactive oxygen species and display excellent activity for hydrocarbon activation even at room temperature.

## Surface Catalysis

L. Shao, B. Zhang, W. Zhang, S. Y. Hong,  
R. Schlögl, D. S. Su\* 2114–2117



The Role of Palladium Dynamics in the  
Surface Catalysis of Coupling Reactions



**More than scratching the surface:** The mechanism by which supported Pd nanoparticles (PdNPs) catalyze cross-coupling reactions is the subject of debate. The changes in supported PdNPs during coupling reactions are studied by

exploiting modified carbon nanotubes (CNTs) as support materials. After catalysis, CNTs with scratched walls and PdNPs with surface crystalline distortions were discovered, offering insights into the catalytic mechanism.

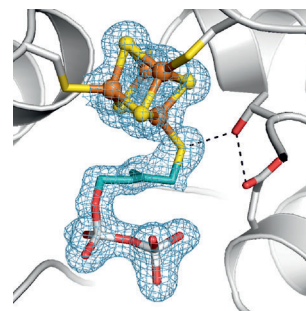
## Biosynthesis

I. Span,\* K. Wang, W. Wang, J. Jauch,  
W. Eisenreich, A. Bacher, E. Oldfield,  
M. Groll\* 2118–2121



Structures of Fluoro, Amino, and Thiol  
Inhibitors Bound to the  $[Fe_4S_4]$  Protein  
IspH

**The iron–sulfur protein IspH** catalyzes a key step in isoprenoid biosynthesis in bacteria and malaria parasites. Crystal structures of IspH complexed with three substrate analogues reveal their mode of binding and suggest new routes to inhibitor design.

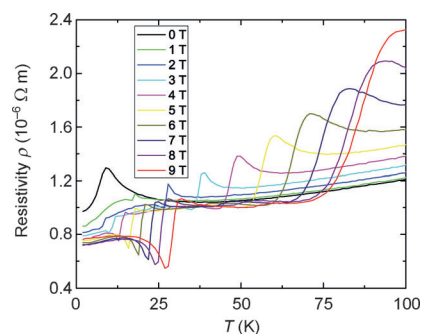


## Magnetic Zintl Phases

A. Slabon, C. Mensing, C. Kubata,  
E. Cuervo-Reyes,  
R. Nesper\* 2122–2125



Field-Induced Inversion of the  
Magnetoresistive Effect in the Zintl Phase  
 $Eu_{5+x}Mg_{18-x}Si_{13}$  ( $x=2.2$ )



**Watch the signs!** The new Zintl phase  $Eu_{5+x}Mg_{18-x}Si_{13}$  ( $x=2.2$ ) displays a negative as well as a positive magnetoresistive effect depending on the temperature. The maximal value of the magnetoresistivity of 92% occurs at 100 K and 9 T (see plot).



Supporting information is available  
on [www.angewandte.org](http://www.angewandte.org)  
(see article for access details).



A video clip is available as Supporting  
Information on [www.angewandte.org](http://www.angewandte.org)  
(see article for access details).



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



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