



*"... In judging researchers early in their career, the h-index seems to be a poor measure. It is more a trailing, rather than a leading, indicator of professional success ..."*  
Read more in the Editorial by Richard N. Zare.

## Editorial

R. N. Zare\* \_\_\_\_\_ 7338

Assessing Academic Researchers



*"The word 'scientist' means to be creative and innovative. My secret/not-so-secret passion is art in the form of modern paintings, graphics, and rock music. ..."*  
This and more about Karl Anker Jørgensen can be found on page 7364.

## Author Profile

Karl Anker Jørgensen \_\_\_\_\_ 7364



D. A. Evans



O. Ozerov



P. T. Anastas

## News

Welch Award:

D. A. Evans ausgezeichnet \_\_\_\_\_ 7365

Hackerman Award:

O. Ozerov \_\_\_\_\_ 7365

Wöhler Prize:

Paul T. Anastas \_\_\_\_\_ 7365

## Obituaries

Horst Weller \_\_\_\_\_ 7366 – 7367



Arnim Henglein, who died on January 5, 2012, was a pioneer in numerous fields of research. He laid foundations for nanoscience when he reduced silver ions in solution with pulsed electron beams, forming homogeneously distributed silver atoms that grew into silver clusters and nanoparticles.

## Books

Metal–Fluorocarbon Based Energetic  
Materials

Ernst-Christian Koch

reviewed by S. Cudzilo \_\_\_\_\_ 7368

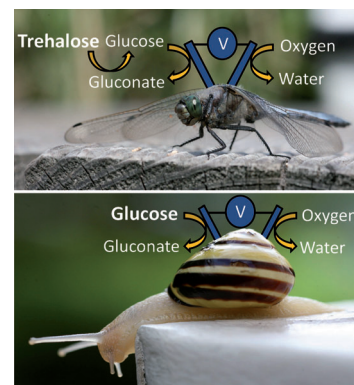
## Highlights

### Biofuel Cells

U. Schröder\* ————— 7370–7372

From In Vitro to In Vivo—Biofuel Cells Are Maturing

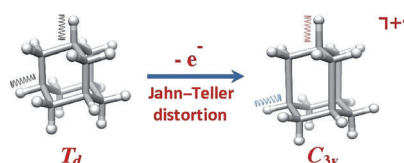
**Insects and molluscs** as future biological drones for military purposes or environmental monitoring systems (see picture)? Two research groups have demonstrated the successful implantation and operation of biofuel cells in snails, clams, and cockroaches. Owing to their simple circulatory systems, these invertebrates could be used in implantation studies without serious physical damage.



### Vibrational Spectroscopy

M. E. Crestoni,  
S. Fornarini\* ————— 7373–7375

Jahn–Teller Distortion of Hydrocarbon Cations Probed by Infrared Photodissociation Spectroscopy



**Frozen distortion or fluxional system?** The IR spectrum of ionized adamantane probes the distorted geometry predicted by the Jahn–Teller theorem, testifying the potential of infrared photon dissociation action spectroscopy in revealing fundamental vibrational and electronic features of isolated charged molecules (see picture).

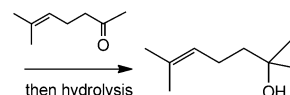
## Essays

### History of Science

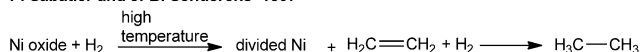
H. B. Kagan\* ————— 7376–7382

Victor Grignard and Paul Sabatier: Two Showcase Laureates of the Nobel Prize for Chemistry

V. Grignard 1910



P. Sabatier and J.-B. Senderens 1897



**Looking back one hundred years:** The two 1912 Nobel Laureates of Chemistry are featured within the context of the academic world in France. Grignard discovered the preparation and use of organo-

magnesium reagents (see scheme). Sabatier established the addition of hydrogen to unsaturated compounds in the presence of catalytic amounts of nickel.

#### For the USA and Canada:

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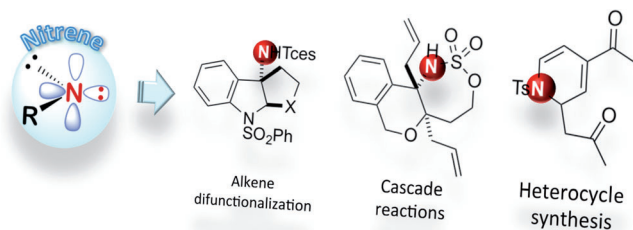
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## Minireviews

### Nitrenes

G. Dequierez, V. Pons,  
P. Dauban\* \_\_\_\_\_ 7384–7395

Nitrene Chemistry in Organic Synthesis:  
Still in Its Infancy?



Long regarded as highly reactive but poorly selective species, nitrenes have recently emerged as useful tools for C–N bond-forming reactions. Their capacity to insert into various bonds has led to the

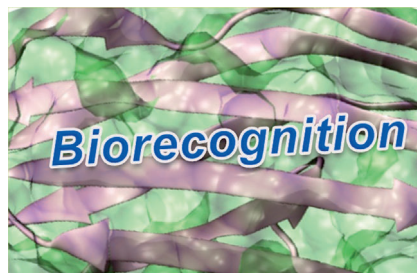
development of efficient catalytic C–H amination and alkene aziridination reactions. In recent work several click-type reactions using nitrenes have been developed.

## Reviews

### Biorecognition

J. Kopeček, J. Yang \_\_\_\_\_ 7396–7417

Smart Self-Assembled Hybrid Hydrogel Biomaterials



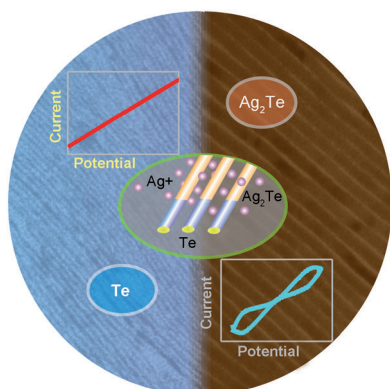
**Hybrid biomaterials:** The self-assembly of macromolecules composed of two or more distinct classes of molecules by biorecognition results in new materials with high degree of organization. This Review focuses on synthetic macromolecules and peptide motifs. Approaches to the design of hybrid systems are evaluated, followed by a discussion on similarity of designs of biomaterials and nanomedicines.

## Communications

### Nanotechnology

J.-W. Liu, J. Xu, H.-W. Liang, K. Wang,  
S. H. Yu\* \_\_\_\_\_ 7420–7425

Macroscale Ordered Ultrathin Telluride Nanowire Films, and Tellurium/Telluride Hetero-Nanowire Films



**Films to order:** Macroscale ordered ultrathin telluride nanowire films and tellurium/telluride hetero-nanowire films can be rapidly fabricated using more reactive nanowire patterns as a template. This method provides a new route to nanowire films with tailored properties.

Frontispiece





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Bertozzi



François  
Diederich



Alois  
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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)

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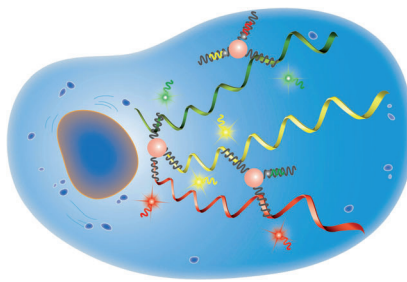


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**Multidetector:** A novel nanoprobe, based on multicolor nanoflares, for the simultaneous detection and imaging of three tumor-related mRNAs in living cells has been developed. The nanoprobe possesses high specificity, nuclease stability, and good biocompatibility. It can also effectively distinguish cancer cells from normal cells and identify changes in the levels of mRNA expression.

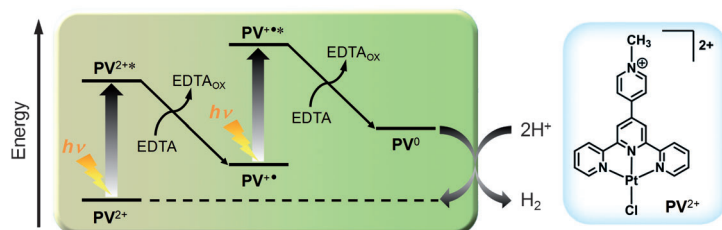


### Cancer Cell Detection

N. Li, C. Chang, W. Pan,  
B. Tang\* 7426–7430

A Multicolor Nanoprobe for Detection and Imaging of Tumor-Related mRNAs in Living Cells

Inside Back Cover



**Mimicking nature:** The photochemical  $H_2$  evolution from water catalyzed by a platinum(II)-based metalloviologen ( $PV^{2+}$ ) proceeds via the photoexcited state of the one-electron-reduced species ( $PV^{\bullet+}$ ; see

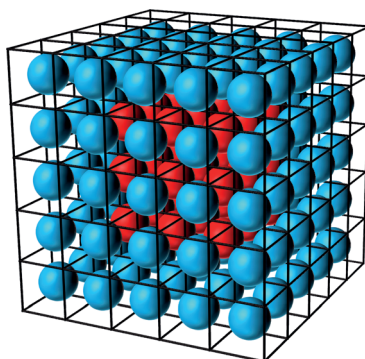
picture, EDTA = ethylenediaminetetraacetic acid). This artificial photosynthesis is reminiscent of the “Z-scheme photosynthesis” in green plants.

### Photocatalysis

M. Kobayashi, S. Masaoka,  
K. Sakai\* 7431–7434

Photoinduced Hydrogen Evolution from Water by a Simple Platinum(II) Terpyridine Derivative: A Z-Scheme Photosynthesis

**Location, location, location:** The combination of reaction and diffusion has been used to deposit nanoparticles (red and blue) inside of cyclodextrin MOFs (black), either uniformly or in a core/shell manner. Such processes can also be combined with galvanic exchange reactions to provide a flexible route to the location-specific post-processing of MOFs. When dissolved, the core/shell MOFs liberate nanoparticles of different types sequentially.



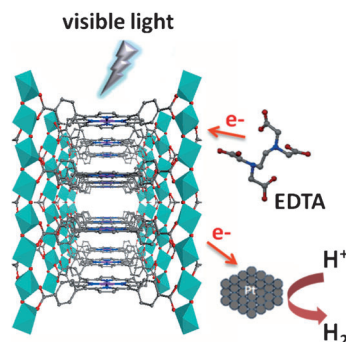
### Nanoparticles in MOFs

Y. Wei, S. Han, D. A. Walker, P. E. Fuller,  
B. A. Grzybowski\* 7435–7439

Nanoparticle Core/Shell Architectures within MOF Crystals Synthesized by Reaction Diffusion

Inside Cover

**Light-harvesting MOFs:** A new porous porphyrinic metal–organic framework (MOF; see picture) was obtained by hydrothermal synthesis. The chemical and thermal stability of the material allows a postsynthetic insertion of zinc in the center of the porphyrin. The visible-light photocatalytic activity of this porphyrin-based material is shown for the sacrificial hydrogen evolution from water.



### Metal–Organic Frameworks

A. Fateeva, P. A. Chater, C. P. Ireland,  
A. A. Tahir, Y. Z. Khimyak, P. V. Wiper,  
J. R. Darwent,  
M. J. Rosseinsky\* 7440–7444

A Water-Stable Porphyrin-Based Metal–Organic Framework Active for Visible-Light Photocatalysis

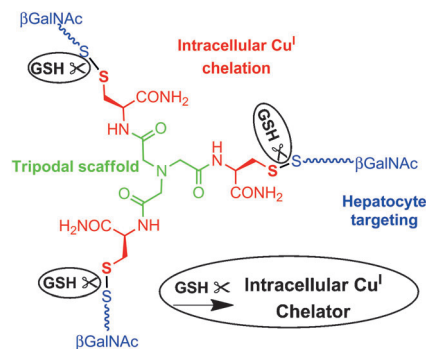
### Bioinorganic Chemistry

A. M. Pujol, M. Cuillel, A.-S. Jullien,  
C. Lebrun, D. Cassio, E. Mintz,\*  
C. Gateau, P. Delangle\* — 7445 – 7448



A Sulfur Tripod Glycoconjugate that  
Releases a High-Affinity Copper Chelator  
in Hepatocytes

**Released in the cell:** Three *N*-acetylgalactosamine units, which recognize the asialoglycoprotein receptor, were tethered through disulfide bonds to the three coordinating thiol functions of a sulfur tripod ligand that has a high affinity for Cu<sup>I</sup> (see scheme). The resulting glycoconjugate can be considered as a prodrug, because after uptake by hepatic cells the intracellular reducing glutathione (GSH) releases the high-affinity intracellular Cu<sup>I</sup> chelator.



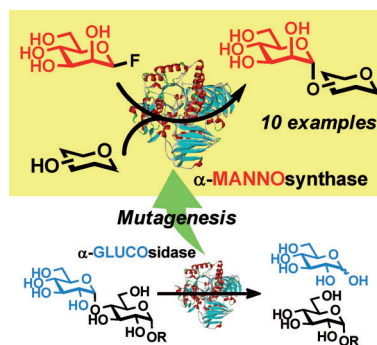
### Biocatalysts

K. Yamamoto, B. G. Davis\* 7449 – 7453



Creation of an  $\alpha$ -Mannosynthase from  
a Broad Glycosidase Scaffold

**$\alpha$ -Mannosides made easy:** Mutation of a family-GH31  $\alpha$ -glucosidase that displays plasticity to alterations at the 2-OH position of donor substrates created an efficient  $\alpha$ -mannoside-synthesizing biocatalyst. A simple fluoride donor reagent was used for the synthesis of a range of mono- $\alpha$ -mannosylated conjugates using the  $\alpha$ -mannosynthase displaying low (unwanted) oligomerization activity.

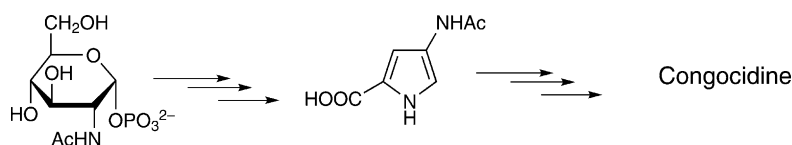


### Biosynthetic Pathways

S. Lautru,\* L. Song, L. Demange,  
T. Lombès, H. Galons, G. L. Challis,  
J.-L. Pernodet — 7454 – 7458



A Sweet Origin for the Key Congocidine  
Precursor 4-Acetamidopyrrole-2-  
carboxylate



**Feeding (*Streptomyces*) frenzy:** Natural products belonging to the pyrrolamide family are defined by their pyrrole-2-carboxamide moiety. 4-acetamidopyrrole-2-carboxylate is identified as the key pyrrolamide congoicidine precursor (see

scheme) through feeding studies using *Streptomyces ambofaciens*. The biosynthetic pathway of congoicidine starts with the carbohydrate *N*-acetylglucosamine and involves carbohydrate-processing enzymes.

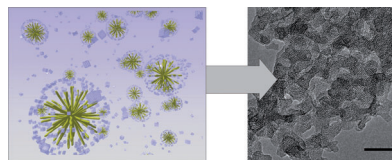
### Ultrafast Lithium Insertion

J. M. Feckl, K. Fominykh, M. Döblinger,  
D. Fattakhova-Rohlfing,\*  
T. Bein\* — 7459 – 7463



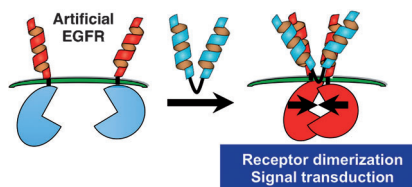
Nanoscale Porous Framework of Lithium  
Titanate for Ultrafast Lithium Insertion

**Mesoporous lithium titanate** has been prepared with a titanate morphology that leads to the fastest insertion of lithium. It features a gravimetric capacity of about 175 mAhg<sup>-1</sup> and delivers up to 73 % of the maximum capacity at up to 800 C (4.5 s) without deterioration over 1000 cycles. A key feature is a fully crystalline interconnected porous framework composed of spinel nanocrystals of only a few nanometers in size. Scale bar: 10 nm.





**Examine your zipper:** An artificial receptor system composed of an extracellular leucine-zipper domain (red helices) fused to the transmembrane and cytoplasmic domains of the epidermal growth factor receptor (EGFR) is shown (see scheme). Dimerization and activation of the receptor is induced by a bivalent leucine-zipper ligand (blue helices), leading to phosphorylation of the cytoplasmic domain of the receptor, and eliciting a signaling cascade.



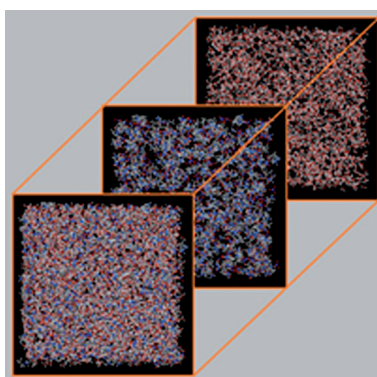
### Artificial Receptors

I. Nakase, S. Okumura, G. Tanaka,  
K. Osaki, M. Imanishi,  
S. Futaki\* \_\_\_\_\_ **7464–7467**

Signal Transduction Using an Artificial  
Receptor System that Undergoes  
Dimerization Upon Addition of a Bivalent  
Leucine-Zipper Ligand



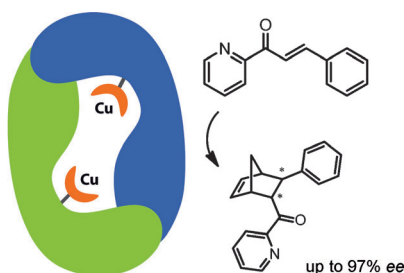
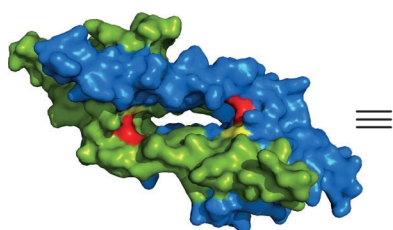
**Water in ionic liquids:** When equal masses of water and the protic ionic liquid ethylammonium nitrate are mixed a bicontinuous nanostructure results. This nanostructure resembles aqueous surfactant mesophases but has length scales at least an order of magnitude smaller. The local structure of both the water and the ionic liquid are strikingly similar to that found in the pure liquids (see picture).



### Nanostructures

R. Hayes, S. Imberti, G. G. Warr,  
R. Atkin\* \_\_\_\_\_ **7468–7471**

How Water Dissolves in Protic Ionic  
Liquids



**A game of two halves:** Artificial metalloenzymes are generated by forming a novel active site on the dimer interface of the transcription factor LmrR. Two copper centers are incorporated by bind-

ing to ligands in each half of the dimer. With this system up to 97% *ee* was obtained in the benchmark Cu<sup>II</sup> catalyzed Diels–Alder reaction (see scheme).

### Artificial Metalloenzymes

J. Bos, F. Fusetti, A. J. M. Driessen,  
G. Roelfes\* \_\_\_\_\_ **7472–7475**

Enantioselective Artificial  
Metalloenzymes by Creation of a Novel  
Active Site at the Protein Dimer Interface

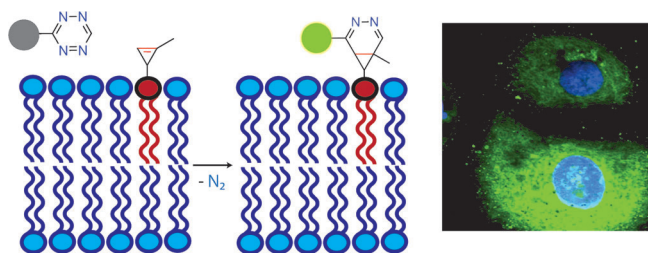


## Fluorogenic Mini-Tags

J. Yang, J. Šečutě, C. M. Cole,  
N. K. Devaraj\* 7476–7479



Live-Cell Imaging of Cyclopropene Tags  
with Fluorogenic Tetrazine Cycloadditions



**Spotlight on lipids:** One of the major limitations of tetrazine bioorthogonal cycloadditions is the requirement of bulky dienophile reaction partners. Methylcyclopropene tags were designed capable of reacting rapidly with tetrazines while

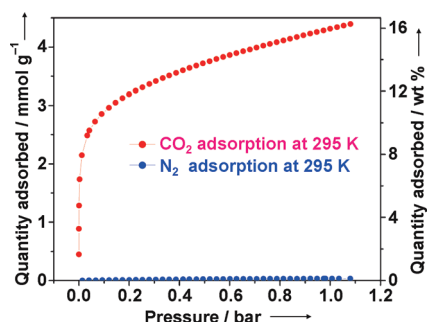
maintaining stability in aqueous solution. The suitability of these probes for bioconjugation is shown by imaging cyclopropene-modified phospholipids in live human cancer cells (see picture).

## CO<sub>2</sub> Capture

W. Lu, J. P. Sculley, D. Yuan, R. Krishna,  
Z. Wei H.-C. Zhou\* 7480–7484



Polyamine-Tethered Porous Polymer  
Networks for Carbon Dioxide Capture  
from Flue Gas



**Gas guzzler:** The introduction of polyamines in porous polymer networks results in significant enhancement of CO<sub>2</sub>-uptake capacities at low pressures. The best substituted network was found to exhibit high adsorption enthalpies for CO<sub>2</sub> and the largest selectivity (see graph) of any porous material reported to date. It also had outstanding physicochemical stability and could be regenerated under mild conditions.

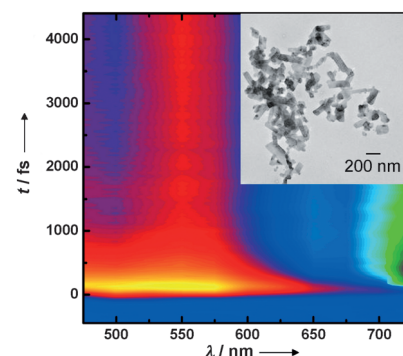
## Ultrafast Photoswitching

R. Bertoni, M. Lorenc,\* A. Tissot,  
M. Servol, M.-L. Boillot,  
E. Collet\* 7485–7489



Femtosecond Spin-State Photoswitching  
of Molecular Nanocrystals Evidenced by  
Optical Spectroscopy

**Quick change:** Femtosecond optical pump–probe spectroscopy is used to study the photoswitching dynamics of Fe<sup>III</sup> spin-crossover nanocrystals. Results indicate that up to 10% of the molecules can be photoswitched from low-spin to high-spin states within less than one picosecond.



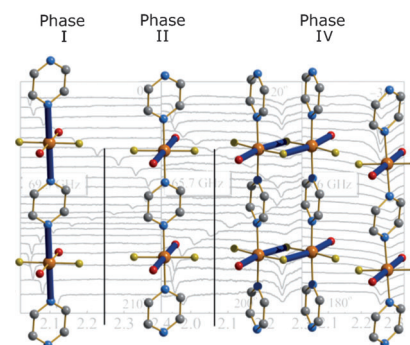
## Controlled Under Pressure

A. Prescimone, C. Morien, D. Allan,  
J. A. Schlueter, S. W. Tozer, J. L. Manson,  
S. Parsons,\* E. K. Brechin,\*  
S. Hill\* 7490–7494

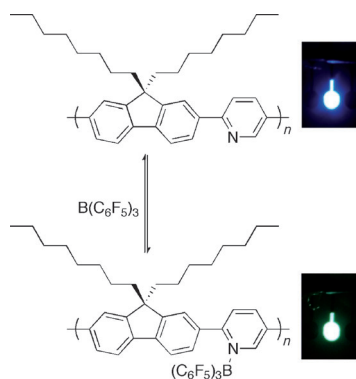


Pressure-Driven Orbital Reorientations  
and Coordination-Sphere Reconstructions  
in [CuF<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(pyz)]

**Successive reorientations of the Jahn–Teller axes** associated with the Cu<sup>II</sup> ions accompany a series of pronounced structural transitions in the title compound, as is shown by X-ray crystallography and high-frequency EPR measurements. The second transition forces a dimerization involving two thirds of the Cu<sup>II</sup> sites due to ejection of one of the water molecules from the coordination sphere.





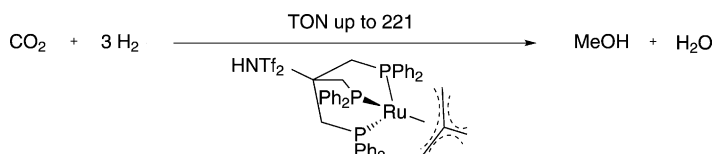


**The right mix:** By mixing a Lewis basic polymer with a Lewis acid, the optical properties of the polymer can be tuned. The formation of an adduct results in red-shifted absorbance and photoluminescence spectra, increase in the emission yield, and a longer excited-state lifetime. This strategy was successfully implemented to modulate the electroluminescence of a polymer light-emitting diode.

### Conjugated Polymers

P. Zalar, Z. B. Henson, G. C. Welch, G. C. Bazan,\*  
T.-Q. Nguyen\* \_\_\_\_\_ **7495 – 7498**

Color Tuning in Polymer Light-Emitting Diodes with Lewis Acids



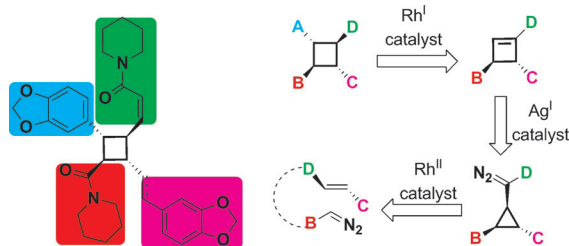
**Simply efficient:** The homogeneously catalyzed hydrogenation of CO<sub>2</sub> to methanol is achieved by using a ruthenium phosphine complex under relatively mild conditions (see scheme; HNTf<sub>2</sub> = bis(trifluoromethane)sulfonimide). This is the first

example of CO<sub>2</sub> hydrogenation to methanol by using a single molecularly defined catalyst.

### Hydrogenation of CO<sub>2</sub>

S. Wesselbaum, T. vom Stein, J. Klankermayer,\*  
W. Leitner\* \_\_\_\_\_ **7499 – 7502**

Hydrogenation of Carbon Dioxide to Methanol by Using a Homogeneous Ruthenium–Phosphine Catalyst



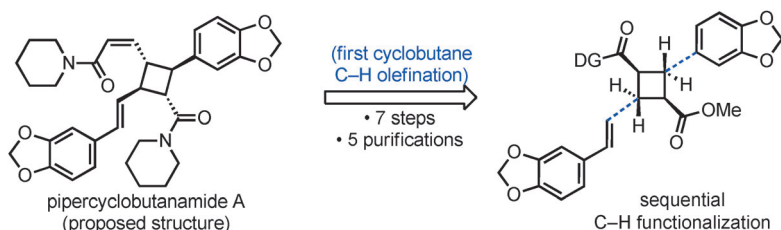
**Squared away:** A general strategy was developed for the diastereo- and enantioselective synthesis of cyclobutanes having four different substituents (see scheme). The strategy involves a Rh<sup>II</sup>-catalyzed cyclopropanation, a Ag<sup>I</sup>-catalyzed regio-

selective and stereospecific ring expansion, and a Rh<sup>I</sup>-catalyzed addition reaction. The structures of pipericyclobutanamide A and piperchabamide G were synthesized and revised.

### Cyclobutanes

R. Liu, M. Zhang, T. P. Wyche, G. N. Winston-McPherson, T. S. Bugni, W. Tang\* \_\_\_\_\_ **7503 – 7506**

Stereoselective Preparation of Cyclobutanes with Four Different Substituents: Total Synthesis and Structural Revision of Pipericyclobutanamide A and Piperchabamide G



**Hip to be square:** A strategy for assembling tetrasubstituted cyclobutanes is reported in the context of a short, protecting-group-free synthesis of the proposed structure of pipericyclobutanamide A. The route features sequential C–H

functionalizations on an unactivated cyclobutane wherein C–C bonds to aryl and styryl groups are made one by one in a stereocontrolled fashion. DG = directing group.

### Natural Products

W. R. Gutekunst, R. Gianatassio, P. S. Baran\* \_\_\_\_\_ **7507 – 7510**

Sequential C<sub>sp</sub><sup>3</sup>–H Arylation and Olefination: Total Synthesis of the Proposed Structure of Pipericyclobutanamide A



## Synthetic Methods

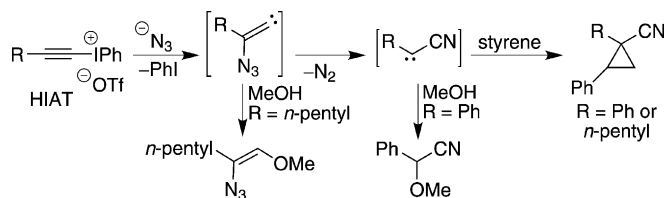
I. F. D. Hyatt, M. P. Croatt\* 7511–7514



Reactions of Hypervalent Iodonium Alkynyl Triflates with Azides: Generation of Cyanocarbenes



Front Cover



**HIAT me, baby, one more time:** Cyano-carbenes have been formed by the reaction of azides with hypervalent iodonium alkynyl triflates (HIATs). Experimental evidence supports the potential intermediacy of an azide-substituted vinylidene or

alkynyl azide, both of which could form a cyanocarbene. Trapping of the vinylidene and cyanocarbene includes O–H insertion, dimethyl sulfoxide coordination, and cyclopropanation reactions.

## Ethynyl Azides

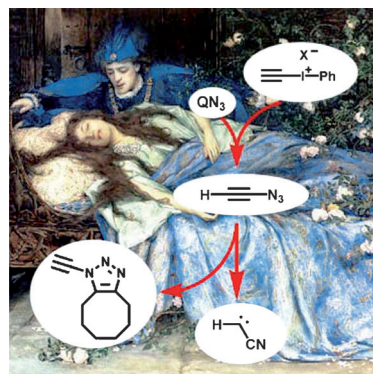
K. Banert,\* R. Arnold, M. Hagedorn, P. Thoss, A. A. Auer\* 7515–7518



1-Azido-1-Alkynes: Synthesis and Spectroscopic Characterization of Azidoacetylene



Front Cover



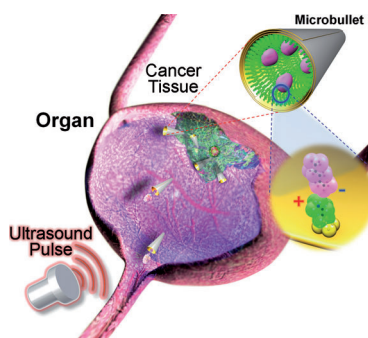
**Sleeping Beauty awakes:** After 102 years of unsuccessful attempts to synthesize azidoacetylene, spectroscopic evidence for this compound has been shown. This highly explosive compound was synthesized by the treatment of ethynyl iodide salts with azide ( $\text{QN}_3 = n\text{-C}_{16}\text{H}_{33}\text{Bu}_3\text{PN}_3$ ). Azidoacetylene can be trapped by a cycloaddition reaction to yield a stable triazole, otherwise cleavage to generate cyanocarbene dominates.

## Micromachines

D. Kagan, M. J. Benchimol, J. C. Claussen, E. Chuluun-Erdene, S. Esener,\* J. Wang\* 7519–7522



Acoustic Droplet Vaporization and Propulsion of Perfluorocarbon-Loaded Microbullets for Targeted Tissue Penetration and Deformation



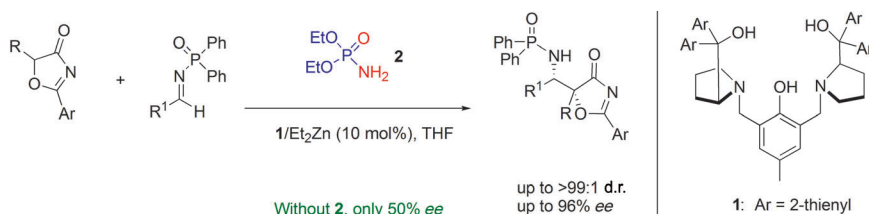
**Bullets and rockets:** Ultrasound-triggered vaporization of a perfluorocarbon compound loaded into microbullets provides the necessary force for the microbullets to penetrate, cleave, and deform cellular tissue for potential targeted drug delivery and precision nanosurgery. The microbullets have an inner Au layer that allows conjugation of a monolayer of thiolated cysteamine (green in picture) for electrostatic attachment of perfluorocarbon droplets (purple droplets).

## Asymmetric Catalysis

D. Zhao, L. Wang, D. Yang, Y. Zhang, R. Wang\* 7523–7527

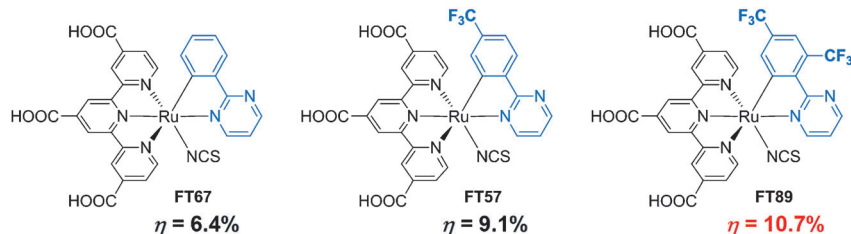


Highly Diastereo- and Enantioselective Synthesis of  $\alpha$ -Alkyl Norstatine Derivatives: Catalytic Asymmetric Mannich Reactions of 5H-Oxazol-4-ones



**Going Mannich:** The title reaction results in the first catalytic asymmetric synthesis of *syn*- $\alpha$ -alkyl norstatine derivatives. Excellent enantioselectivities and diastereoselectivities were achieved with a series of *N*-diphenylphosphino-yl-pro-

TECTED imines and 5H-oxazol-4-ones by using the catalyst 1/Zn. Importantly, the involvement of the diethyl phosphoramidate 2 was critical to achieve good enantioselectivities in the present Mannich reaction.



**Efficient light harvesting:** Cyclometalated ruthenium complexes were synthesized and evaluated in a dye-sensitized solar cell as near-IR sensitizers. Tuning of the

HOMO energy level by structural modifications of the ligand improved the conversion efficiency of the cells based on these complexes to up to 10.7%.

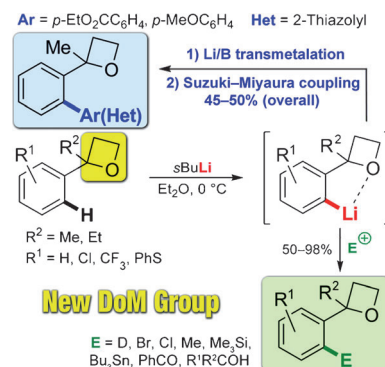
## Dye-Sensitized Solar Cells

T. Funaki,\* H. Funakoshi, O. Kitao, N. Onozawa-Komatsuzaki, K. Kasuga, K. Sayama, H. Sugihara\* — **7528–7531**

Cyclometalated Ruthenium(II) Complexes as Near-IR Sensitizers for High-Efficiency Dye-Sensitized Solar Cells

## Oxetane nudges in the DoM direction!

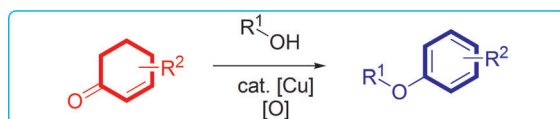
Regioselective *ortho*-lithiation induced by an oxetane ring has been achieved. The reaction provides easy access to *ortho*-functionalized 2-aryloxetanes also through a lithiation/borylation Suzuki–Miyaura cross-coupling. The lithiation-directing ability of oxetane and the proton transfer mechanism have been investigated by competitive metalation and kinetic isotope effect studies.



## Lithiation Chemistry

D. I. Coppi, A. Salomone, F. M. Perna, V. Capriati\* — **7532–7536**

Exploiting the Lithiation-Directing Ability of Oxetane for the Regioselective Preparation of Functionalized 2-Aryloxetane Scaffolds under Mild Conditions



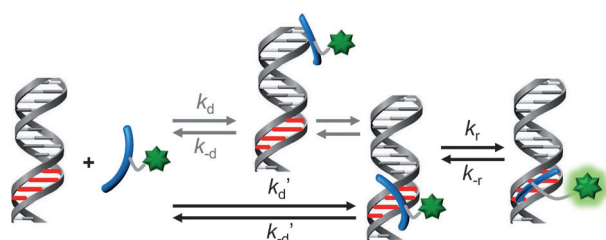
**Only little waste:** Aryl ether formation is accomplished by oxidative condensation of alcohols and 2-cyclohexenones. The reaction complements the existing methods used by synthetic chemists to obtain aryl ethers, and allows a straightforward

access to a wide range of functionalized products. In addition, the catalytic reaction with O<sub>2</sub> as the oxidant generates water as the only by-product and provides a “greener” approach to aryl ethers.

## Aryl Ether Formation

M.-O. Simon, S. A. Girard, C.-J. Li\* — **7537–7540**

Catalytic Aerobic Synthesis of Aromatic Ethers from Non-Aromatic Precursors



**Getting in the groove:** Fluorescence correlation spectroscopy reveals that the dynamics of the association process of the bisbenzamidine minor-groove binder BBA-OG (blue with green star, see

scheme) to dsDNA is not controlled by diffusion, but by the insertion of the binder into the groove at the specific site (red), as shown by the rate constants for each step of the binding event.

## DNA Binding Dynamics

J. Bordello, M. I. Sánchez, M. E. Vázquez, J. L. Mascareñas, W. Al-Soufi, M. Novo\* — **7541–7544**

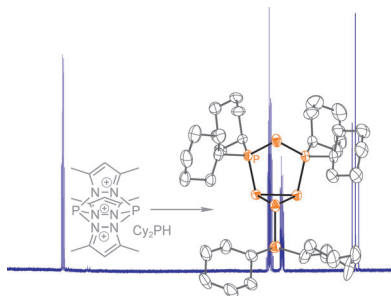
Single-Molecule Approach to DNA Minor-Groove Association Dynamics

## Phosphorus Compounds

K.-O. Feldmann,  
J. J. Weigand\* 7545 – 7549



One-Pot Syntheses of Cationic Polyphosphorus Frameworks with Two-, Three-, and Four-Coordinate Phosphorus Atoms by One-Pot Multiple P–P Bond Formations from a P<sub>1</sub> Source



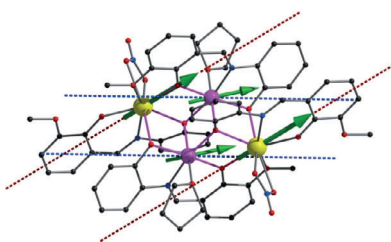
**Accessible complexity:** Polyphosphorus frameworks [R<sub>4</sub>P<sub>4</sub>pyr]<sup>+</sup> and [R<sub>6</sub>P<sub>7</sub>]<sup>+</sup> (R = Cy, Ph; pyr = 3,5-dimethylpyrazolyl) were prepared from a P<sub>1</sub> source, R<sub>2</sub>PH. In a one-pot reaction, eight P–P bonds are formed via a unique combination of substitution and base-induced reductive P–P coupling.

## Single-Molecule Magnets

K. C. Mondal, A. Sundt, Y. Lan,  
G. E. Kostakis, O. Waldmann,\* L. Ungur,  
L. F. Chibotaru,\* C. E. Anson,  
A. K. Powell\* 7550 – 7554



Coexistence of Distinct Single-Ion and Exchange-Based Mechanisms for Blocking of Magnetization in a Co<sup>II</sup><sub>2</sub>Dy<sup>III</sup><sub>2</sub> Single-Molecule Magnet



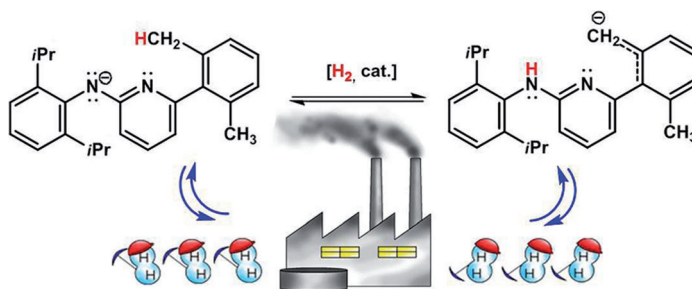
**Two ways to relax:** A defect-dicubane Co<sub>2</sub>Dy<sub>2</sub> single-molecule magnet (SMM) displays slow relaxation of magnetization with a blocking temperature of 22 K (at 1500 Hz), the highest reported for a 3d–4f-based SMM. Analysis of the relaxation reveals two distinct blocking regimes, one of which is intraionic, localized on the Dy<sup>III</sup> ions, while the other is exchange-based.

## Dihydrogen Catalysis

J. E. V. Valpuesta, N. Rendón,  
J. López-Serrano, M. L. Poveda,  
L. Sánchez, E. Álvarez,  
E. Carmona\* 7555 – 7557



Dihydrogen-Catalyzed Reversible Carbon–Hydrogen and Nitrogen–Hydrogen Bond Formation in Organometallic Iridium Complexes



**Dihydrogen at work!** H<sub>2</sub> catalyzes with high efficiency a prototropic rearrangement of aminopyridinate ligands bound to a {(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ir<sup>III</sup>} unit. The catalytic iso-

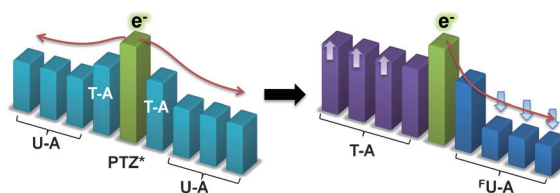
merization implies reversible formation and cleavage of H–H, C–H, and N–H bonds.

## Electron Transport in DNA

T. Ito,\* Y. Hamaguchi, K. Tanabe,  
H. Yamada, S. Nishimoto\* 7558 – 7561



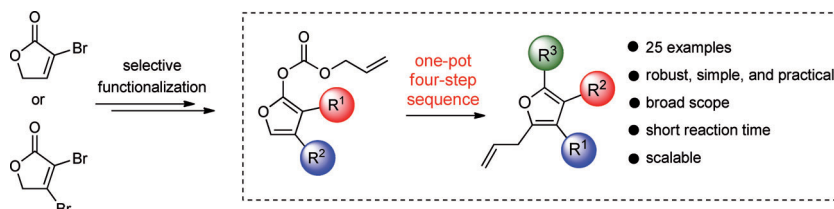
Transporting Excess Electrons along Potential Energy Gradients Provided by 2'-Deoxyuridine Derivatives in DNA



**LUMO-level dependent:** Chemically modified DNA molecules containing 2'-deoxyuridine (dU) derivatives with various LUMO energy levels have been synthesized to manipulate electron-transfer efficiencies. By arranging thymidine, the dU

derivatives, and 5-fluoro-2'-deoxyuridine in order of their LUMO levels, the efficiency and the directionality of photoinduced electron transport in DNA could be regulated.





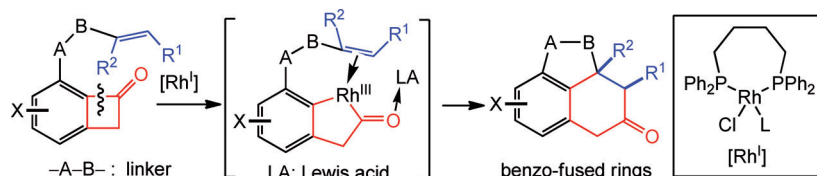
**One for all:** Allyl dienol carbonates can be readily converted into diversely substituted furans by a one-pot four-step sequence featuring a palladium-catalyzed decarboxylative allylic alkylation, a microwave-mediated Cope rearrangement,

a nucleophilic addition, and a dehydration reaction (see scheme). The protocol is operationally simple, highly flexible, and provides di-, tri-, and tetrasubstituted furans starting from readily available materials.

## Furan Synthesis

J. Fournier, S. Arseniyadis,\*  
J. Cossy\* ————— 7562 – 7566

A Modular and Scalable One-Pot  
Synthesis of Polysubstituted Furans



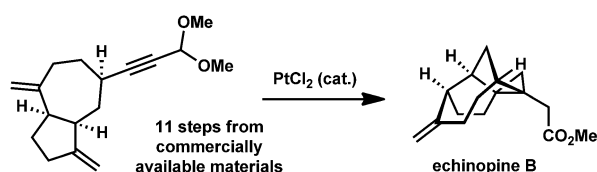
**Cut and sew:** A rhodium-catalyzed regioselective carboacylation reaction of benzocyclobutenones was developed (see scheme). Directed by the pendant olefins, the C1–C2 bond is selectively cleaved rather than the C1–C8 bond. Subsequent

alkene insertion leads to complex fused-ring systems. This reaction provides facile access to natural-product-like polycyclic structures in a chemoselective and atom-economic fashion.

## C–C Activation

T. Xu, G. Dong\* ————— 7567 – 7571

Rhodium-Catalyzed Regioselective  
Carboacylation of Olefins: A C–C Bond  
Activation Approach for Accessing Fused-  
Ring Systems



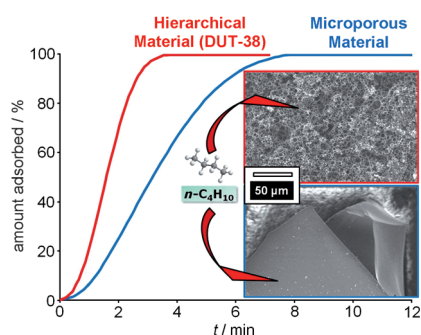
**In a short synthesis** of echinopine B, a guaiaine-like intermediate was generated through a methylenecyclopentane annulation onto a substituted cycloheptenone. The resulting bicyclic compound was

converted into the natural product by a  $\text{PtCl}_2$ -catalyzed enyne cycloisomerization (see scheme). Several late-stage polycyclic rearrangement products were isolated and characterized.

## Natural Product Synthesis

T. D. Michels, M. S. Dowling,  
C. D. Vanderwal\* ————— 7572 – 7576

A Synthesis of Echinopine B



**Sierpinski carbon:** Macroporous carbide-derived carbon monoliths (DUT-38) were synthesized starting from SiC-PolyHIPEs, resulting in a hierarchical micro-, meso-, and macroporous structure. The high specific surface area and high macropore volume renders PolyHIPE-CDC an excellent adsorbent combining high storage capacity with excellent adsorption rates in gas storage and air filtration.

## Porous Materials

M. Oschatz, L. Borchardt, M. Thommes,  
K. A. Cychosz, I. Senkovska, N. Klein,  
R. Frind, M. Leistner, V. Presser,  
Y. Gogotsi, S. Kaskel\* ————— 7577 – 7580

Carbide-Derived Carbon Monoliths with  
Hierarchical Pore Architectures



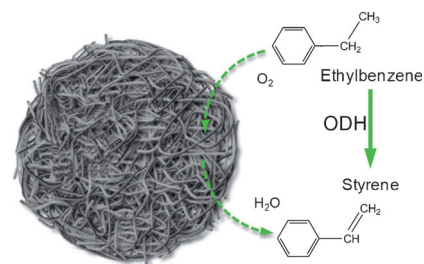
## Nanocarbon Synthesis

J. Zhang, R. Wang, E. Z. Liu, X. F. Gao,  
Z. H. Sun, F. S. Xiao,\* F. Girgsdies,  
D. S. Su\* 7581 – 7585



Spherical Structures Composed of  
Multiwalled Carbon Nanotubes:  
Formation Mechanism and Catalytic  
Performance

**Structured catalyst:** A new strategy was used to produce carbon nanotube mono-liths by a solid-phase process that was well characterized by in situ techniques. The synthesized spherical nanoparticles display extremely high selectivity in the oxidative dehydrogenation (ODH) of ethylbenzene (see scheme).



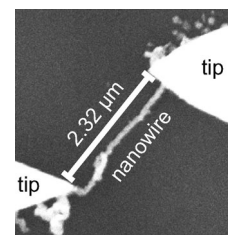
## DNA Nanowires

J. Timper, K. Gutmiedl, C. T. Wirges,  
J. Broda, M. Noyong, J. Mayer, T. Carell,  
U. Simon\* 7586 – 7588



Surface “Click” Reaction of DNA followed  
by Directed Metalization for the  
Construction of Contactable Conducting  
Nanostructures

**Investment in copper, silver, and gold:** A difunctional DNA template is first immobilized on a functionalized substrate by a copper-catalyzed reaction, modified with silver nucleation centers, and then metalized by gold deposition. The diameter of the resulting metallically conductive nanowires can be adjusted.

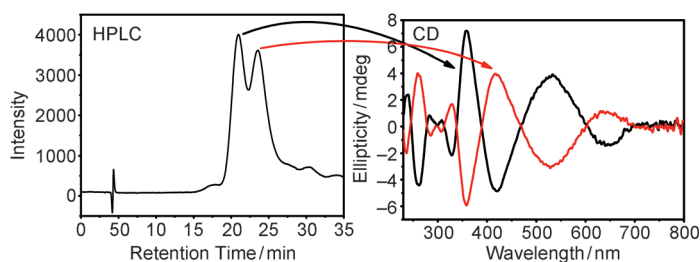


## Gold Clusters

S. Knoppe, I. Dolamic, A. Dass,  
T. Bürgi\* 7589 – 7591



Separation of Enantiomers and CD  
Spectra of  $\text{Au}_{40}(\text{SCH}_2\text{CH}_2\text{Ph})_{24}$ :  
Spectroscopic Evidence for Intrinsic  
Chirality



**Chirality unveiled:** Thiolate-protected  $\text{Au}_{40}(\text{SR})_{24}$  clusters were enantioenriched using an HPLC approach. CD spectra show strong mirror-image responses,

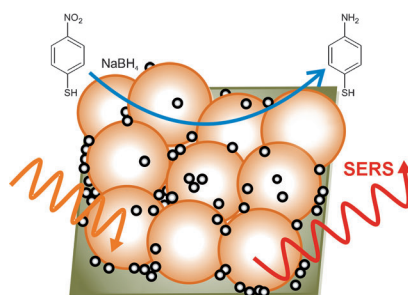
indicating the intrinsic chirality of a cluster of unknown structure protected with achiral ligands.

## Reaction Kinetics

V. Joseph, C. Engelbrekt, J. Zhang,  
U. Gernert, J. Ulstrup,  
J. Kneipp\* 7592 – 7596



Studying the Kinetics of Nanoparticle-  
Catalyzed Reactions by Surface-Enhanced  
Raman Scattering



**Separate gold and platinum nanoparticles** simultaneously immobilized on a glass surface used to study the kinetics of a catalytic reaction directly. Owing to the proximity of the platinum and gold nanoparticles, the analyte molecules can interact with the platinum nanoparticles whilst they reside in the local optical fields of the gold nanoparticles.

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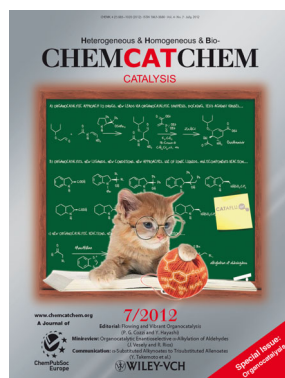
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