



The following Communications have been judged by at least two referees to be “very important papers” and will be published online at [www.angewandte.org](http://www.angewandte.org) soon:

H. Jiang, P. Elsner, K. L. Jensen, A. Falcicchio, V. Marcos, K. A. Jørgensen\*

**Achieving Molecular Complexity by Organocatalytic One-Pot Strategies: A Fast Entry for the De Novo Synthesis of Sphingoids, Amino Sugars, and Polyhydroxylated  $\alpha$ -Amino Acids**

T. J. Kucharski, Z. Huang, Q.-Z. Yang, Y. Tian, N. C. Rubin, C. D. Concepcion, R. Boulatov\*

**Kinetics of Thiol/Disulfide Exchange Correlates Weakly with the Restoring Force in the Disulfide Moiety**

W. Xu, X. Xue, T. Li, H. Zeng, X. Liu\*

**Ultrasensitive and Selective Colorimetric DNA Detection by Nicking Endonuclease-Assisted Nanoparticle Amplification**

H. Ueda, H. Satoh, K. Matsumoto, K. Sugimoto, T. Fukuyama,\* H. Tokuyama\*

**Total Synthesis of (+)-Haplophytine**

G. A. Zelada, J. Riu,\* A. Düzgün, F. X. Rius\*

**Immediate Detection of Living Bacteria at Ultra-Low Concentrations Using a Carbon-Nanotube-Based Potentiometric Aptasensor**

K. Fuchibe, T. Kaneko, K. Mori, T. Akiyama\*

**Expedient Synthesis of N-Fused Indoles: A C–F Activation and C–H Insertion Approach**

A. Giannis,\* P. Heretsch, V. Sarli, A. Stössel

**Synthesis of Cycloamine Using a Biomimetic and Diastereoselective Approach**

W. A. Chalifoux, R. McDonald, M. J. Ferguson, R. R. Tykwinski  
***tert*-Butyl Endcapped Polyynes: Crystallographic Evidence of Reduced Bond-Length Alternation**



*“A good work day begins with a new and exciting experimental result.*

*The biggest challenge facing chemists is to understand the results and to convince other chemists that the unexpected chemical product was in fact desired. ...”*

This and more about Hans-Achim Wagenknecht can be found on page 5788.

## Author Profile

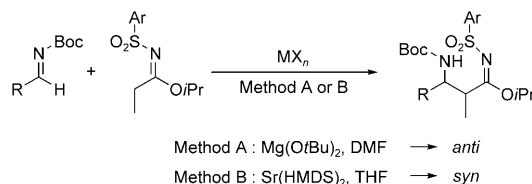
Hans-Achim Wagenknecht — 5788

Reagents for Radical and Radical Ion Chemistry

David Crich

## Books

reviewed by J. Hartung — 5789



**Trend-setting:** Alkaline earth metals are good catalysts for a number of direct addition reactions with carbonyl compounds. In Mannich reactions the stereochemical outcome can be controlled by

the reaction conditions and the alkaline earth metal used (see scheme: Boc = *tert*-butoxycarbonyl, HMDS = hexamethyldisilazide).

## Highlights

### Alkaline Earth Metal Catalysis

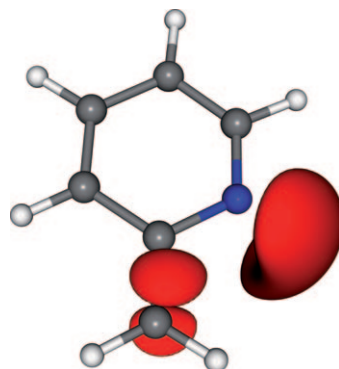
U. Kazmaier\* — 5790 – 5792

Direct Michael, Aldol, and Mannich Additions Catalyzed by Alkaline Earth Metals

## Electronic Structure

P. Macchi\* \_\_\_\_\_ 5793 – 5795

Resonance Structures and Electron Density Analysis



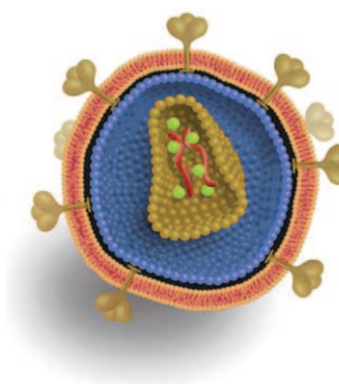
**In perfect resonance:** The electron density distribution is typically used to analyze chemical bonding, even if strong electron delocalization occurs. The electron densities and electric potentials of picoline and the picolyl anion (see picture) have been analyzed and a detailed description of picolyl lithium complexes has been derived. The next goal is to predict chemical reactivity from electron density.

## Reviews

### Cancer Research

H. zur Hausen\* \_\_\_\_\_ 5798 – 5808

The Search for Infectious Causes of Human Cancers: Where and Why (Nobel Lecture)



**Viruses** are the uniting theme of the 2008 Nobel Prize for Physiology or Medicine. Françoise Barré-Sinoussi and Luc Montagnier received their Prize for the discovery of the human immunodeficiency virus (HIV), and Harald zur Hausen identified that cervical cancer is triggered by papillomaviruses. The Nobel Laureates describe their research first-hand.

### HIV/AIDS

F. Barré-Sinoussi\* \_\_\_\_\_ 5809 – 5814

HIV: A Discovery Opening the Road to Novel Scientific Knowledge and Global Health Improvement (Nobel Lecture)

L. Montagnier\* \_\_\_\_\_ 5815 – 5826

25 Years after HIV Discovery: Prospects for Cure and Vaccine (Nobel Lecture)

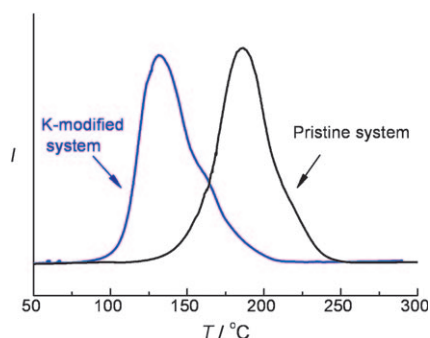
### For the USA and Canada:

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## Communications

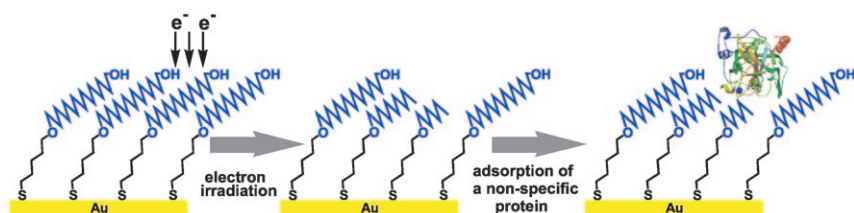


**Using KH as an additive** to  $\text{Mg}(\text{NH}_2)_2/\text{LiH}$  drastically improves hydrogen desorption, which begins at ca. 80 °C (see graph). Circa 5 wt % of hydrogen can be reversibly desorbed and absorbed at about 107 °C. The presence of potassium in the reacting system weakens the amide N–H and imide Li–N bonds, leading to enhanced reaction kinetics.

### Hydrogen Storage

J. Wang, T. Liu, G. Wu, W. Li, Y. Liu, C. M. Araújo, R. H. Scheicher, A. Blomqvist, R. Ahuja, Z. Xiong, P. Yang, M. Gao, H. Pan, P. Chen\* — **5828–5832**

Potassium-Modified  $\text{Mg}(\text{NH}_2)_2/2\text{LiH}$  System for Hydrogen Storage



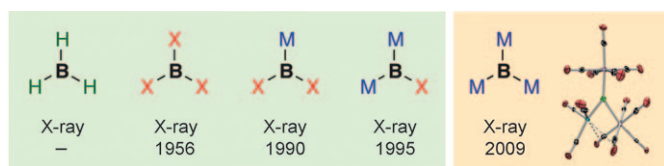
**Write on target:** An efficient and versatile approach to fabricate protein patterns of any shape on a variable length scale is developed. The patterns are directly writ-

ten in an oligo- or poly(ethylene glycol)-based protein-repelling film by electron-beam lithography.

### Protein Patterns

N. Ballav, H. Thomas, T. Winkler, A. Terfort, M. Zharnikov\* — **5833–5836**

Making Protein Patterns by Writing in a Protein-Repelling Matrix



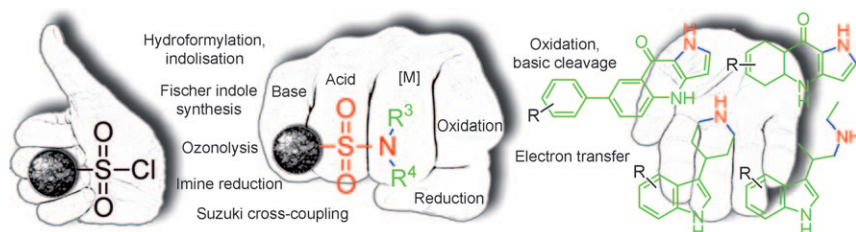
**Boron trifecta:** The first true trimetallo-borane has been synthesized by simple salt elimination from a dimanganese bromoborylene and  $\text{Na}[\text{Co}(\text{CO})_4]$ . The complex was structurally characterized,

and features only first-row transition metals, a planar boron atom, and two semi-bridging CO ligands between the cobalt and one manganese atom (see picture).

### Boride Ligands

H. Braunschweig,\* R. D. Dewhurst, K. Kraft, K. Radacki — **5837–5840**

Low-Coordinate Boride Ligands: A True Trimetalloborane



**One linker, broad application:** A simple sulfonamide linker for primary and secondary amines was used for the construction of small libraries of privileged indole and quinolone structures on a solid

phase. After the synthesis, the products can be liberated in a traceless manner under electron transfer conditions or according to a “safety catch” principle.

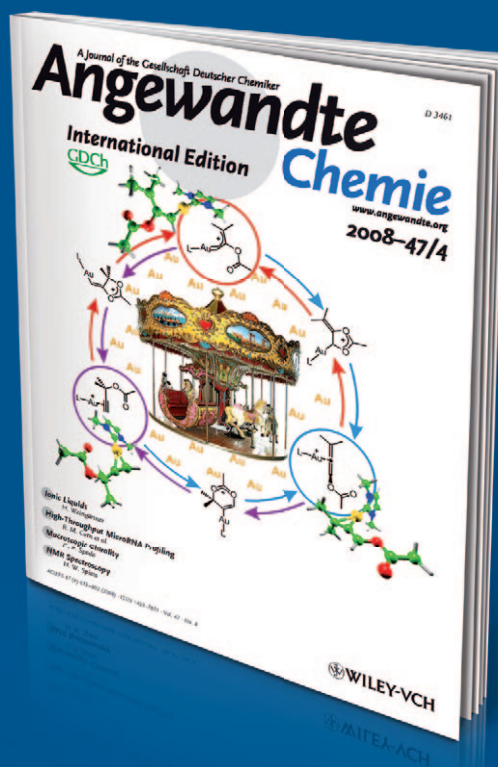
### Solid-Phase Synthesis

M. Mentel, A. M. Schmidt, M. Gorray, P. Eilbracht, R. Breinbauer\* — **5841–5844**

Polystyrene Sulfonamide: A Highly Orthogonal Linker Resin for the Synthesis of Nitrogen-Containing Heterocycles



# *Incredibly* **versatile**



**Theme variety** on the one hand: Many articles in *Angewandte Chemie* cover the classical themes such as organic synthesis or coordination chemistry. Besides these, current topics like **(bio)nanotechnology, chemical biology, and sustainable chemistry** are well represented. And then there are the „must-see articles“, such as those on the detection of anthrax spores\*, or the characteristic scent of iron,\*\* or the artificial lily-of-the-valley flavor\*\*\*

**Section variety** on the other: Communications, Reviews, Highlights, Essays, Obituaries, Meeting Reviews, as well as Website and Book Reviews are regularly found in *Angewandte*.

\* M. Tamborrini, D.B. Werz, J. Frey, G. Pluschke, P.H. Seeberger, *Angew. Chem. Int. Ed.* 2006, 45, 6581--6582.

\*\* D. Glindemann, A. Dietrich, H.-J. Staerk, P. Kusch, *Angew. Chem. Int. Ed.* 2006, 45, 7006--7009.

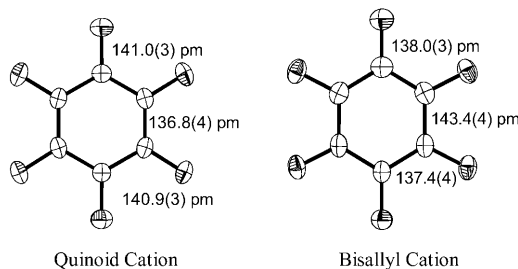
\*\*\* L. Doszczak, P. Kraft, H.-P. Weber, R. Bertermann, A. Triller, H. Hatt, R. Tacke, *Angew. Chem. Int. Ed.* 2007, 46, 3367--3371.



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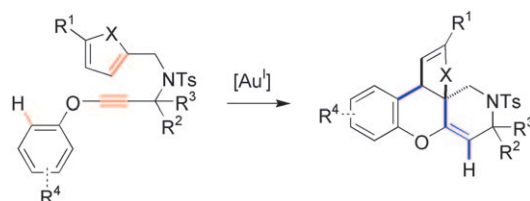
**Ring, ring!**  $C_6F_6^{+}$   $Os_2F_{11}^{-}$  and  $C_6F_6^{+}Sb_2F_{11}^{-}$  have isomorphous crystal structures and each contain two different  $C_6F_6^{+}$  cations. One is a quinoid structure, the other bisallyl structure. Calculations

show that indeed two such Jahn–Teller distorted structures coexist with essentially the same energy. This seems to be a case of bond-stretch isomerism.

### Bond-Stretch Isomerism

H. Shorafa, D. Mollenhauer, B. Paulus, K. Seppelt\* — 5845 – 5847

The Two Structures of the Hexafluorobenzene Radical Cation  $C_6F_6^{+}$



**Changing tracks:** By the use of alkynyl ethers as directing elements, the furan-yne cyclization enters a new reaction

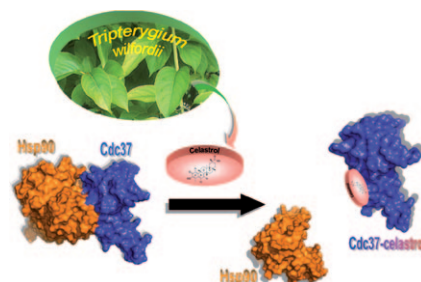
pathway. Instead of phenols, tetracycles containing two heteroatoms and two new stereocenters are formed (see scheme).

### Synthetic Methods

A. S. K. Hashmi,\* M. Rudolph, J. Huck, W. Frey, J. W. Bats, M. Hamzić — 5848 – 5852

Gold Catalysis: Switching the Pathway of the Furan-Yne Cyclization

**The correct target:** The cell division cycle protein 37 (Cdc37) and the heat shock protein (Hsp90) are molecular chaperones crucial for the folding and stabilization of protein kinases including the oncogenic kinases. NMR studies show that celastrol, a recently identified triterpene targeting Hsp90, in fact binds to Cdc37 and disrupts the Cdc37–Hsp90 complex. Celastrol inactivates Cdc37 through a thiol-mediated mechanism.

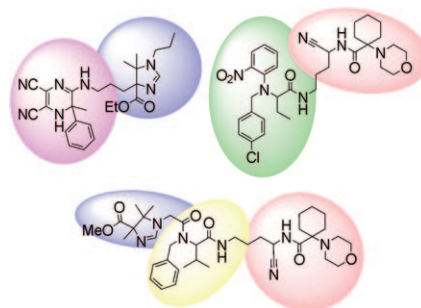


### Protein–Protein Complex Inhibition

S. Sreeramulu, S. L. Gande, M. Göbel, H. Schwalbe\* — 5853 – 5855

Molecular Mechanism of Inhibition of the Human Protein Complex Hsp90–Cdc37, a Kinome Chaperone–Cochaperone, by Triterpene Celastrol

**E = MCR<sup>2</sup>!** The introduction of orthogonal functional groups in multicomponent reactions (MCRs) with unique solvent and functional-group compatibility enables their combination with other multicomponent reactions in one pot. The resulting novel 5- and 6CRs and an unprecedented 8CR afford very complex products in up to 80% yields (see picture), with up to nine new bond formations and eleven diversity points in a single reaction.



### Multicomponent Reactions

N. Elders, D. van der Born, L. J. D. Hendrickx, B. J. J. Timmer, A. Krause, E. Janssen, F. J. J. de Kanter, E. Ruijter, R. V. A. Orru\* — 5856 – 5859

The Efficient One-Pot Reaction of up to Eight Components by the Union of Multicomponent Reactions

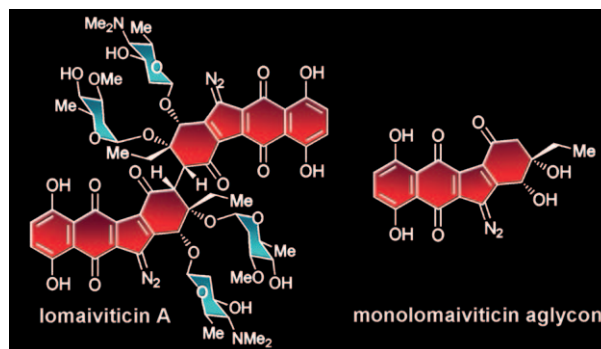


## Natural Products

K. C. Nicolaou,\* A. L. Nold,  
H. Li \_\_\_\_\_ 5860–5863



Synthesis of the Monomeric Unit of the  
Lomaiviticin Aglycon



**The right building blocks:** The monomeric unit of the lomaiviticin aglycon (see structures) was synthesized through an enantioselective route featuring an Ull-

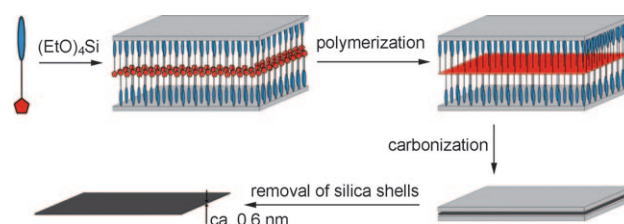
mann coupling, a benzoin-type cyclization, and a novel  $\text{SmI}_2$ -mediated allylic alcohol formal transposition.

## Graphene

W. Zhang, J. Cui, C. Tao, Y. Wu, Z. Li, L. Ma,  
Y. Wen, G. Li\* \_\_\_\_\_ 5864–5868



A Strategy for Producing Pure Single-Layer  
Graphene Sheets Based on a Confined  
Self-Assembly Approach



**Carbon sandwich:** When a pyrrole-containing surfactant is polymerized between layers of silica (see picture; pyrrole is red), subsequent carbonization and removal of the silica template yields large, pure,

single-layer graphene sheets. The procedure, which employs mild conditions, is controllable and can be used to produce micrometer-sized graphene sheets on a gram scale.

## Spontaneous Resolution

A. Lennartson,  
M. Håkansson\* \_\_\_\_\_ 5869–5871

Total Spontaneous Resolution of  
Five-Coordinate Complexes



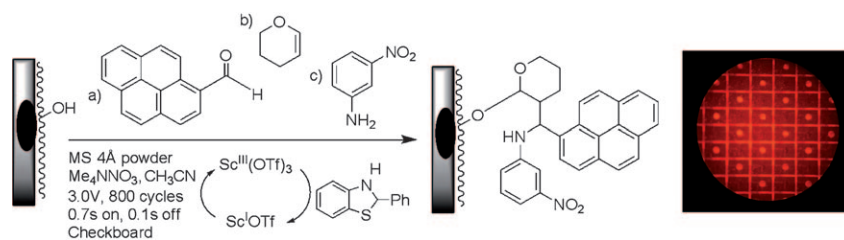
**Talking about a resolution:** Bulk quantities of five-coordinate complexes have been resolved for the first time using zinc and cadmium diethyldithiocarbamate species. The stereochemical outcome can be controlled by seeding with the desired isomer, giving access to either enantiomer in high enantiomeric excess and yield.

## Microelectrode Arrays

B. Bi, K. Maurer,  
K. D. Moeller\* \_\_\_\_\_ 5872–5874

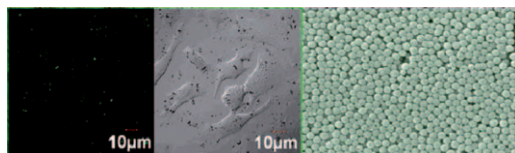


Building Addressable Libraries: Site-  
Selective Lewis Acid (Scandium(III))  
Catalyzed Reactions



**Reagent confinement:** Lewis acid catalyzed reactions have been conducted on arrays with either 1024 or 12544 microelectrodes  $\text{cm}^{-2}$ . A  $\text{Sc}^{\text{III}}$  species generated at the electrodes is employed as the Lewis acid, and the reagent is confined to the

electrodes through the use of a solution-phase reductant. A multicomponent synthesis of a tetrahydropyran (see scheme), a Diels-Alder reaction, and an esterification reaction are all compatible with this strategy.



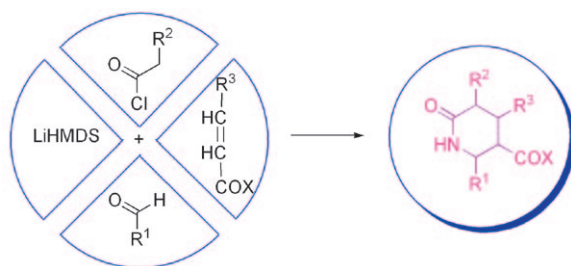
**Uniform magnetite particles** stabilized by citrate groups were successfully synthesized by a modified high-temperature solvothermal reaction. Cell imaging reveals that the water-dispersible particles

can readily penetrate into cells without destroying them, indicating an excellent biocompatibility. A high enrichment capacity of the magnetite particles for separation of trace peptides is observed.

### Magnetic Colloids

J. Liu, Z. K. Sun, Y. H. Deng,\* Y. Zou, C. Y. Li, X. H. Guo, L. Q. Xiong, Y. Gao, F. Y. Li, D. Y. Zhao\* — 5875 – 5879

Highly Water-Dispersible Biocompatible Magnetite Particles with Low Cytotoxicity Stabilized by Citrate Groups



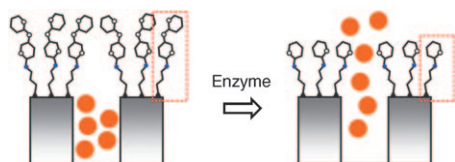
**Creating diversity:** Multicomponent reactions for the synthesis of complex piperidine scaffolds lead to high levels of skeletal, functional, and stereochemical diversity in an efficient way (see scheme,

X = OR, NR<sub>2</sub>). Connecting the acid chloride component to the dienophile generates polycyclic piperidine scaffolds by an intramolecular Diels–Alder reaction of the in situ generated azadienes.

### Synthetic Methods

W. Zhu, M. Mena, E. Jnoff, N. Sun, P. Pasau, L. Ghosez\* — 5880 – 5883

Multicomponent Reactions for the Synthesis of Complex Piperidine Scaffolds



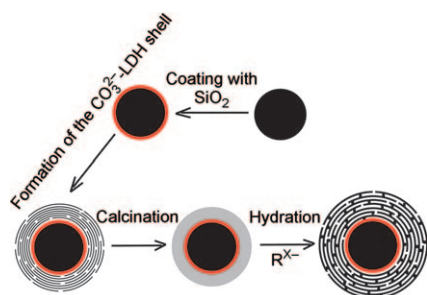
**The great escape:** A biocontrolled gated material has been prepared by grafting a lactose derivative onto the pore outlets of a mesoporous support. The galactosidase-induced hydrolysis of the  $\beta 1 \rightarrow 4$

glycosidic bond in the lactose moiety (red box in picture) allows the release of a dye entrapped in the pores of the hybrid material to the bulk solution.

### Molecular Gates

A. Bernardos, E. Aznar, M. D. Marcos, R. Martínez-Máñez,\* F. Sancenón, J. Soto, J. M. Barát,\* P. Amorós\* — 5884 – 5887

Enzyme-Responsive Controlled Release Using Mesoporous Silica Supports Capped with Lactose



**Layering up:** The title nanocomposite shows high anion loading capacity. The demonstration of the assembly of a  $W_{7}O_{24}^{6-}$  catalyst by this method may provide a general route to the facile and direct fabrication of composite structures with magnetic cores and shells functionalized with various anions (see scheme; LDH = layered double hydroxide).

### Magnetic Materials

L. Li,\* Y. Feng, Y. Li, W. Zhao, J. Shi\* — 5888 – 5892

Fe<sub>3</sub>O<sub>4</sub> Core/Layered Double Hydroxide Shell Nanocomposite: Versatile Magnetic Matrix for Anionic Functional Materials

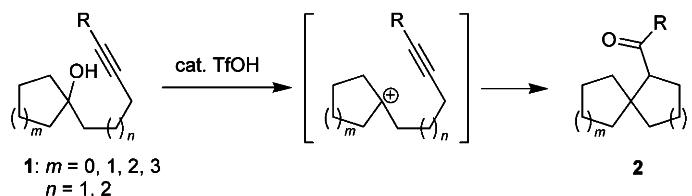


## Spirocyclization

T. Jin,\* M. Himuro,  
Y. Yamamoto\* 5893 – 5896



Triflic Acid Catalyzed Synthesis of  
Spirocycles via Acetylene Cations



**Rings of various shapes and sizes:** Spirocyclic hydrocarbons **2** were obtained in good to excellent yield through the triflic acid (TfOH) catalyzed cyclization of alkynyl-substituted cyclic tertiary alcohols

**1** under mild conditions with good control of ring size (see scheme). The method was extended to the synthesis of bridged bicyclic ketones with high stereoselectivity.

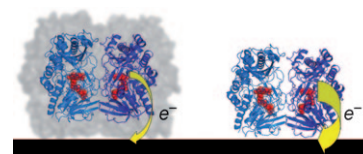
## Direct Electron Transfer

O. Courjean, F. Gao,  
N. Mano\* 5897 – 5899



Deglycosylation of Glucose Oxidase for  
Direct and Efficient Glucose  
Electrooxidation on a Glassy Carbon  
Electrode

**Down to the bare bones:** When a glucose oxidase (GOx, left) was deglycosylated, the modified enzyme (right) immobilized on a vitreous carbon electrode came into closer electrical contact with the surface than the native enzyme. Glucose was electrooxidized directly on a monolayer of deglycosylated GOx on a carbon electrode at the unprecedented reducing potential of  $-200$  mV versus Ag/AgCl and with a current density of  $235 \mu\text{A cm}^{-2}$ .



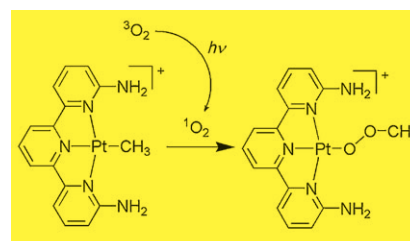
## Insertion Reactions

R. A. Taylor, D. J. Law, G. J. Sunley,  
A. J. P. White,  
G. J. P. Britovsek\* 5900 – 5903



Towards Photocatalytic Alkane Oxidation:  
The Insertion of Dioxygen into a  
Platinum(II)–Methyl Bond

**Always look on the bright side:** The light-driven insertion of dioxygen into a platinum–methyl bond results in a methylperoxo complex (see picture) which decomposes to formaldehyde and a platinum hydroxo complex. This reaction occurs at 1 atm  $\text{O}_2$  and room temperature within minutes, and proceeds via the formation of singlet oxygen.



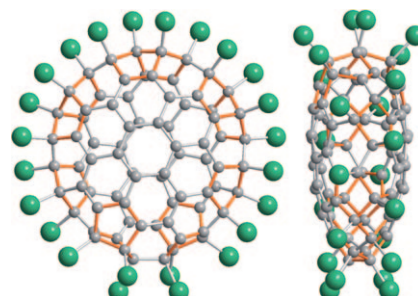
## Halogenated Fullerenes

I. N. Ioffe, A. A. Goryunkov, N. B. Tamm,  
L. N. Sidorov, E. Kemnitz,\*  
S. I. Troyanov\* 5904 – 5907

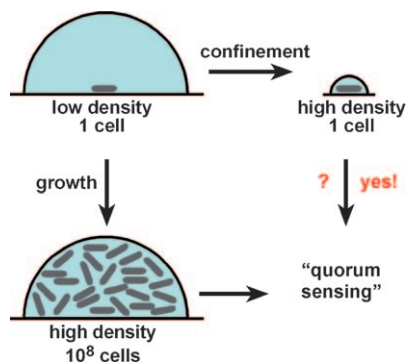


Fusing Pentagons in a Fullerene Cage by  
Chlorination: IPR  $\text{D}_2\text{-C}_{76}$  Rearranges into  
non-IPR  $\text{C}_{76}\text{Cl}_{24}$

**Spectacular skeletal rearrangement** of the  $\text{C}_{76}$  fullerene cage was observed as a result of chlorination of  $\text{D}_2\text{-C}_{76}$  to give  $\text{C}_{76}\text{Cl}_{24}$  (see structure; gray C, green Cl, orange bonds highlight the pentagons), which features a significantly flattened carbon cage that violates the isolated pentagon rule. This transformation is likely to include seven single Stone–Wales rearrangements, which are facilitated by chlorination of the fullerene cage.





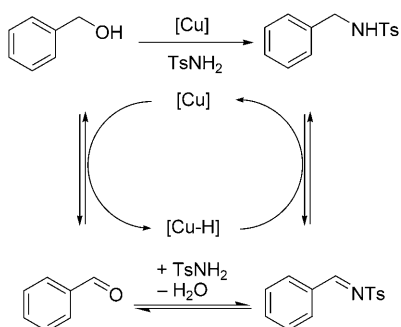


**One is a quorum:** As few as one to three cells of *Pseudomonas aeruginosa* bacteria are confined in small volumes by the use of microfluidics. These small numbers of cells are able to activate quorum sensing (QS) pathways and achieve QS-dependent growth. The results also show that at low numbers of cells, initiation of QS is highly variable within a clonal population.

### Microfluidics

J. Q. Boedicker, M. E. Vincent, R. F. Ismagilov\* — 5908 – 5911

Microfluidic Confinement of Single Cells of Bacteria in Small Volumes Initiates High-Density Behavior of Quorum Sensing and Growth and Reveals Its Variability



**Water is the only by-product** in an efficient and atom-economical Cu(OAc)<sub>2</sub>-catalyzed coupling of alcohols with sulfonamides (see proposed mechanism; Ts = *p*-toluenesulfonyl). It was discovered that bissulfonylated amidines formed as intermediates when the transhydrogenative C–N bond-forming reaction is carried out in air act as novel ligands to stabilize the catalyst.

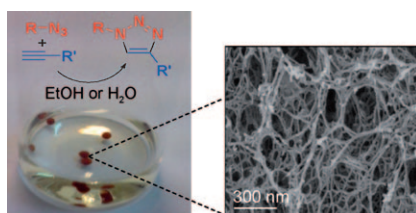
### C–N Bond Formation

F. Shi,\* M. K. Tse, X. Cui, D. Gördes, D. Michalik, K. Thürow, Y. Deng, M. Beller\* — 5912 – 5915

Copper-Catalyzed Alkylation of Sulfonamides with Alcohols



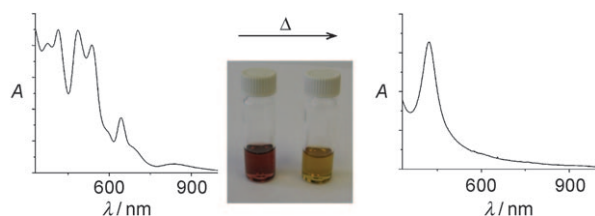
**Clean and green:** Copper(I) complexes of phenanthroline-based ligands anchored on the chitosan polymer are good catalysts for the “click” cycloaddition of azides with terminal alkynes (see scheme; the scanning electron microscopy image shows the porous structure of the catalyst). These heterogeneous catalytic systems do not require a base or reducing agent and operate in alcohol or water.



### Heterogeneous Catalysis

M. Chtchigrovsky, A. Primo, P. Gonzalez, K. Molvinger, M. Robitzer, F. Quignard,\* F. Taran\* — 5916 – 5920

Functionalized Chitosan as a Green, Recyclable, Biopolymer-Supported Catalyst for the [3+2] Huisgen Cycloaddition



**A simple one-pot method** produces silver nanoparticles coated with aryl thiols that show intense, broad nonplasmonic optical properties. The synthesis works with many aryl-thiol capping ligands, including

water-soluble 4-mercaptobenzoic acid. The nanoparticles produced show linear absorption that is broader, stronger, and more structured than most conventional organic and inorganic dyes.

### Metal Nanoparticles

O. M. Bakr, V. Amendola, C. M. Aikens, W. Wenseleers, R. Li, L. Dal Negro, G. C. Schatz, F. Stellacci\* — 5921 – 5926

Silver Nanoparticles with Broad Multiband Linear Optical Absorption

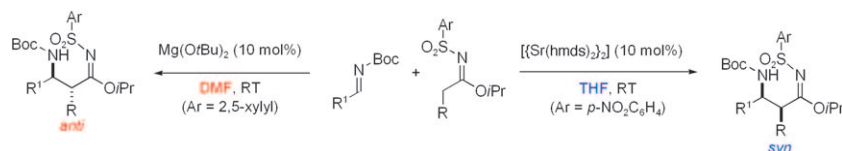


## Homogeneous Catalysis

H. Van Nguyen, R. Matsubara,  
S. Kobayashi\* \_\_\_\_\_ **5927 – 5929**



Addition Reactions of Sulfonylimidates with Imines Catalyzed by Alkaline Earth Metals



**Cheaper, safer:** Addition reactions of sulfonylimidates to imines are catalyzed by alkaline-earth-metal alkoxide salts, which are abundant, inexpensive, and nontoxic. Diastereoselectivity is highly dependent on solvent and catalyst, and

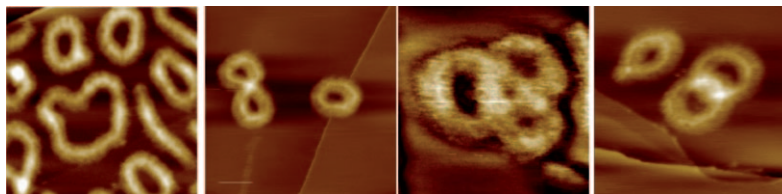
both *syn* and *anti* adducts are obtained in high yields and with high diastereoselectivity (see scheme). The first catalytic asymmetric Mannich-type reaction of a sulfonylimidate is also presented.

## Macromolecular Architectures

M. Schappacher,  
A. Deffieux\* \_\_\_\_\_ **5930 – 5933**



Imaging of Catenated, Figure-of-Eight, and Trefoil Knot Polymer Rings



**A knotty problem:** Macrocyclic topological isomers formed during the end-to-end cyclization of linear polymer chains are imaged by using atomic force microscopy (AFM). Images of isolated molecules (see

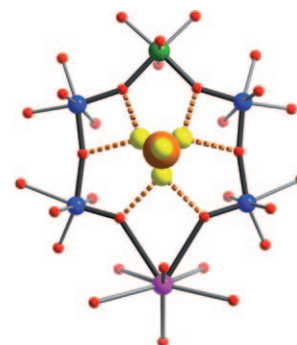
picture) were obtained after magnification of the initial polymer rings by grafting polystyrene oligomers to the macrocycles. This technique allows the visualization of nontrivial macrocyclic architectures.

## Polyoxometalates

A. Müller,\* F. L. Sousa, A. Merca,  
H. Bögge, P. Miró, J. A. Fernández,  
J. M. Poblet, C. Bo \_\_\_\_\_ **5934 – 5937**

Supramolecular Chemistry on a Cluster Surface: Fixation/Complexation of Potassium and Ammonium Ions with Crown-Ether-Like Rings

**Integrated but separate:** A strongly nucleophilic cluster surface allows the selective complexation and separation of ammonium and potassium ions. Six {Mo<sub>4</sub>VKO<sub>6</sub>} rings with crown-ether-like functionality (see picture; Mo blue, V green, K pink, O red) present in the holes of the investigated cluster complex integrate six ammonium ions (N orange, H yellow).



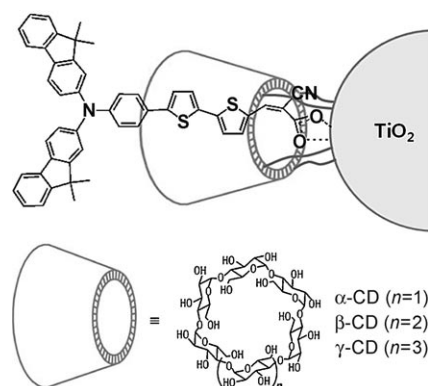
## Solar Cells

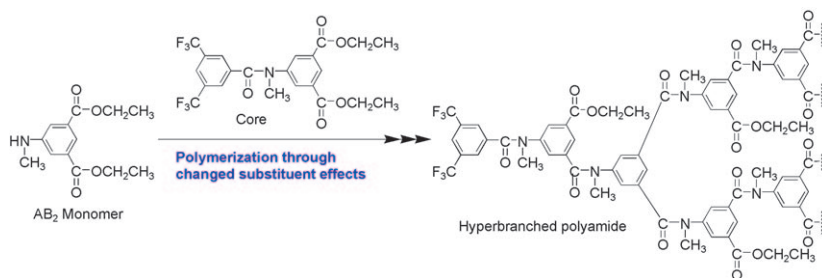
H. Choi, S. O. Kang, J. Ko,\* G. Gao,  
H. S. Kang, M.-S. Kang,  
M. K. Nazeeruddin,  
M. Grätzel \_\_\_\_\_ **5938 – 5941**



An Efficient Dye-Sensitized Solar Cell with an Organic Sensitizer Encapsulated in a Cyclodextrin Cavity

**Dying to get inside:** Charge recombination is retarded and dye aggregation is prevented in solar cells that contain the JK-2 dye encapsulated in a cyclodextrin (CD) cavity (see picture). The β-CD/JK-2 device with a polymer gel electrolyte gave an overall conversion efficiency of 7.40%, which is the highest value reported to date for DSSCs based on the organic sensitizers, and showed excellent stability.





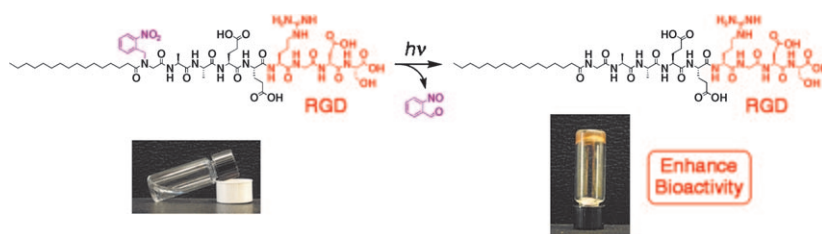
**Branching out:** Condensation polymerization of AB<sub>2</sub> monomer proceeds selectively from a core molecule owing to the change of substituent effects between the monomer and the polymer (see scheme).

Hyperbranched polyamides are obtained with very low polydispersity and controlled molecular weight determined by the monomer/core feed ratio.

## Hyperbranched Polymers

Y. Ohta, S. Fujii, A. Yokoyama,  
T. Furuyama, M. Uchiyama,  
T. Yokozawa\* 5942 – 5945

Synthesis of Well-Defined Hyperbranched Polyamides by Condensation Polymerization of AB<sub>2</sub> Monomer through Changed Substituent Effects



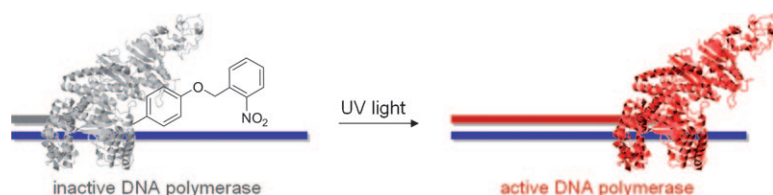
**Photocleavage** of a 2-nitrobenzyl group in a bioactive peptide amphiphile containing the Arg-Gly-Asp (RGD) epitope triggers a sol-to-gel transition as nanospheres are

converted to nanofibers (see picture). This morphological change enhances the bioactivity of the nanostructures surrounding cells in three dimensions.

## Nanostructures

T. Muraoka, C.-Y. Koh, H. Cui,  
S. I. Stupp\* 5946 – 5949

Light-Triggered Bioactivity in Three Dimensions



**When the time is right:** The widely applied *Thermus aquaticus* DNA polymerase was rendered light-activatable by incorporation of the photocaged amino acid *ortho*-nitrobenzyl tyrosine in place of a key

tyrosine residue in the active site (see picture). As the modified enzyme was completely inactive until irradiated with UV light, temporal regulation of polymerase activity was possible.

## Photocaging

C. Chou, D. D. Young,  
A. Deiters\* 5950 – 5953

A Light-Activated DNA Polymerase

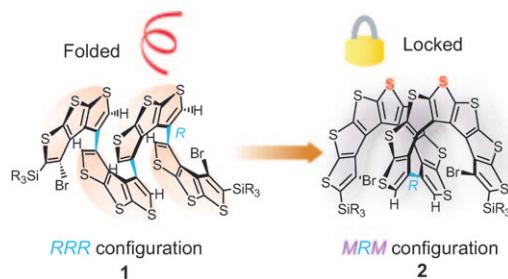


## Oligohelices

M. Miyasaka, M. Pink, S. Rajca,  
A. Rajca\* 5954–5957



Noncovalent Interactions in the  
Asymmetric Synthesis of Rigid,  
Conjugated Helical Structures



**From helical folding to helical locking:**  
Tetrakis( $\beta$ -trithiophene) **1** folds into a  
helical conformation (*RRR*) that facilitates  
double ring annelation, with high diaste-  
reoselectivity and modest enantioselectivity,

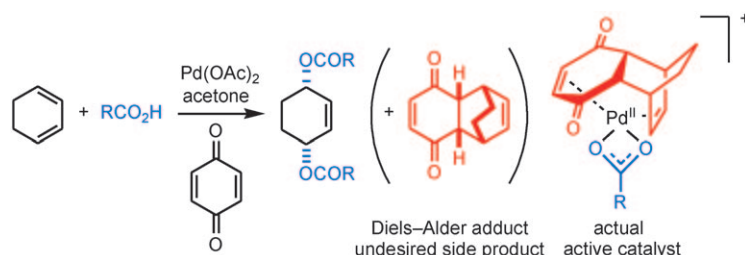
to provide bis[7]helicene **2** (*MRM*).  
This rigid, helically locked structure has  
enhanced chiroptical properties similar to  
the corresponding [15]helicene.

## Diene Oxidation

M. D. Eastgate,\*  
F. G. Buono 5958–5961



Mechanistic Insight into the Palladium-  
Catalyzed 1,4-Oxidation of 1,3-Dienes to  
1,4-Dicarboxy-alk-2-enes



**Side products get involved:** The 1,4-oxi-  
dation of a diene transforms a simple  
hydrocarbon into an extremely useful  
intermediate. A complex formed in situ  
between palladium and a bicyclic Diels–

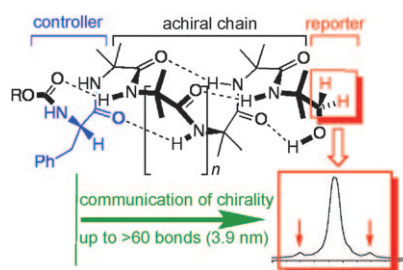
Alder adduct, which is produced as a side  
product during the reaction, was respon-  
sible for the high rate and high dia-  
stereoselectivity observed in the oxidation  
of cyclohexadiene (see scheme).

## Chirality Transfer

J. Clayden,\* A. Castellanos, J. Solà,  
G. A. Morris 5962–5965



Quantifying End-to-End Conformational  
Communication of Chirality through an  
Achiral Peptide Chain



**Successful communication:** Two diaste-  
reotopic protons more than 60 bonds  
from the nearest chiral center appear as  
an AB system, showing that the interven-  
ing structure is a well-ordered helix. Decay  
of anisochronicity quantifies the linear  
persistence of a helix of achiral amino  
acids: as little as 3.5 % of the chiral  
influence is lost with each additional  
achiral residue.



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



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## Corrigendum

The authors of this Communication have recognized an error in Equation (2). The correct Equation (2) is therefore as follows:

$$\chi_M = \frac{1}{k_B(T-\theta)} \frac{2 N_A g^2 \mu_B^2}{3 + \exp\left(-\frac{2J}{k_B T}\right)} \quad (2)$$

Moreover, in the right-hand column on page 923, the optimized value for the exchange coupling  $J$  should be corrected to  $J = 11.2 \text{ cm}^{-1}$  ( $= 16.0 \text{ K}$ ), and Ref. [3] cited in this paragraph should be Ref. [6].

A Spiro-Fused Triarylammonium Radical Cation with a Triplet Ground State

A. Ito, M. Urabe, K. Tanaka\* — 921–924

*Angew. Chem. Int. Ed.* **2003**, 42

DOI 10.1002/anie.200390244

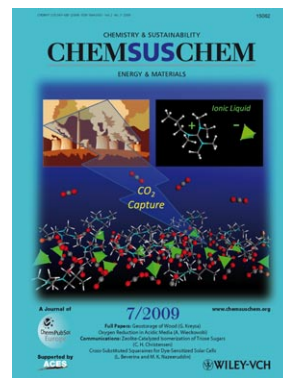
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