



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:

I. Garcia-Bosch, A. Company, C. W. Cady, S. Styring, W. R. Browne, X. Ribas, M. Costas\*

**Evidence for a Precursor Complex in C–H Hydrogen-Atom-Transfer Reactions Mediated by a Manganese(IV) Oxo Complex**

G. N. Newton, S. Yamashita, K. Hasumi, J. Matsuno, N. Yoshida, M. Nihei, T. Shiga, M. Nakano, H. Nojiri, W. Wernsdorfer, H. Oshio\*

**Redox-Controlled Optimization of the Magnetic Properties of Keggin-Type  $\{Mn_{13}\}$  Clusters**

J. J. Murphy, A. Quintard, P. McArdle, A. Alexakis,\* J. C. Stephens\*  
**Asymmetric Organocatalytic 1,6-Conjugate Addition of Aldehydes to Dienic Sulfones**

S. Zhou, S. Fleischer, K. Junge, M. Beller\*  
**Cooperative Transition-Metal and Chiral Brønsted Acid Catalysis: Enantioselective Hydrogenation of Imines to Amines**

J. M. Lee, W. Shim, J.-S. Noh, W. Lee\*  
**Highly Mobile Thin Films on an Elastomeric Substrate as Gas Sensors: Palladium-Based Nanogap Hydrogen-Gas Sensors**



Angewandte Chemie International Edition Celebrates Its 50th Birthday

## Editorial

Michael Dröscher \_\_\_\_\_ 4718



*“My favorite subjects at school were the sciences and geography.*

*When I was eighteen I wanted to be an engineer or a scientist. ...”*

This and more about Takashi Kato can be found on page 4740.

## Author Profile

Takashi Kato \_\_\_\_\_ 4740



*“If I were not scientist, I would be an architect.*

*When I wake up I have a big breakfast and think about what I will be doing during the day ...”*

This and more about Buxing Han can be found on page 4741.

Buxing Han \_\_\_\_\_ 4741

Chemical Synthesis of Hormones, Pheromones and Other Bioregulators

Kenji Mori

## Books

reviewed by S. Schulz \_\_\_\_\_ 4742

## Highlights

### Nanotechnology

L. Dai\* ————— 4744–4746

Carbon Nanotube Rubber Stays Rubbery in Extreme Temperatures



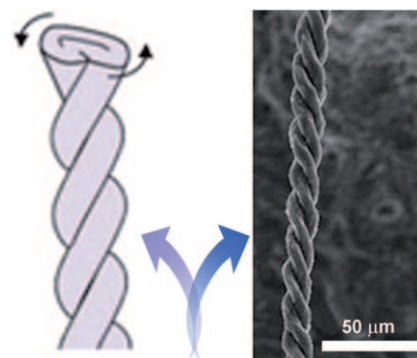
**Extreme elastic:** A new viscoelastic material has recently been developed from carbon nanotubes (CNT rubber; see picture). This material is similar to silicone rubber but maintains its viscoelasticity from  $-196$  to  $1000^{\circ}\text{C}$  in an oxygen-free environment. CNT rubber is promising for a wide range of applications, including use in high-vacuum furnaces and even aerospace vehicles that travel to the cold interstellar space.

### Inorganic Double Helices

D. S. Su\* ————— 4747–4750

Inorganic Materials with Double-Helix Structures

**Two different methods** recently yielded inorganic materials with double-helix structures: Silicon microtubes (see picture) formed when high inner pressure forced NaSi melt through an opening in the surface of a disc, and carbon nanotubes were prepared when plates of layered double hydroxide coated with active catalyst particles were used as substrate. These reports open the door for the application of double-helical inorganic materials in chemistry and biology.



## Essays

### History of Chemistry

C. Friedrich,\* H. Remane\* — 4752–4758

Marie Curie: Recipient of the 1911 Nobel Prize in Chemistry and Discoverer of the Chemical Elements Polonium and Radium

**Déjà vu all over again:** When the Polish-born scientist Marie Skłodowska-Curie traveled from Paris to Stockholm in December 1911 to receive the Nobel Prize in Chemistry, it was the second time that she had been recognized with the sciences' top honor; she had already received the Nobel Prize in Physics in 1903. Madame Curie's contributions included her pioneering investigations of radioactivity and the discovery of the radioactive elements radium and polonium.



**For the USA and Canada:** ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, 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 POSTMASTER: 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\$ 9442/8583 (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.

# Asymmetric Catalysis Atom Economy

**Give me an H:** The sophisticated synergism of the two concepts of asymmetric catalysis and atom economy offers a truly efficient synthetic strategy for the production of requisite chemical entities with

high enantiomeric purity. Recent advances in this field are highlighted, with a particular emphasis on catalytic asymmetric reactions that proceed under proton-transfer conditions.

## Minireviews

### Cooperative Catalysis

N. Kumagai,\*  
M. Shibasaki\* \_\_\_\_\_ 4760–4772

Recent Advances in Direct Catalytic Asymmetric Transformations under Proton-Transfer Conditions

**What makes a living thing alive?** *Caenorhabditis elegans* is a popular model organism for genetic research. Although the worm (see picture) is a simple organism, it still exhibits many of the complex phenomena found in higher organisms, including aging, behavior, cognition, and susceptibility to disease. This review provides an introduction to worm biology and argues that *C. elegans* is a useful system for the examination of complex biological phenomena from a chemical perspective.

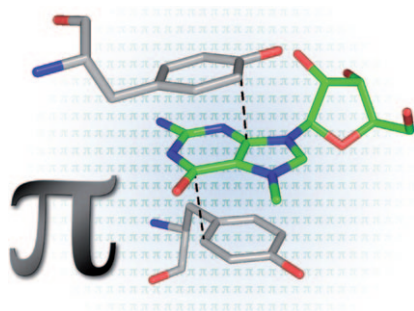


## Reviews

### Chemical Biology

S. E. Hulme,  
G. M. Whitesides\* \_\_\_\_\_ 4774–4807

Chemistry and the Worm: *Caenorhabditis elegans* as a Platform for Integrating Chemical and Biological Research



**The role of aromatic rings in chemical and biological recognition** is explored with a multidimensional approach, which includes synthetic host–guest studies, small-molecule crystallography, investigations with biological receptors and biostructural analysis, and database mining in the Cambridge Structural Database (CSD) and the Protein Data Bank (PDB). Topics covered are arene–arene, perfluoroarene–arene, S $\cdots$ aromatic, cation– $\pi$ , and anion– $\pi$  interactions, as well as hydrogen bonding to  $\pi$  surfaces. Shown here is the complexation of a cationic 7-methylguanosine ring in the human nuclear cap-binding complex.

### Aromatic Rings

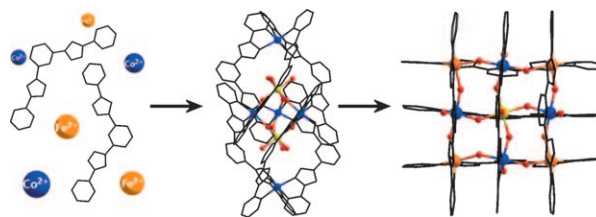
L. M. Salonen, M. Ellermann,  
F. Diederich\* \_\_\_\_\_ 4808–4842

Aromatic Rings in Chemical and Biological Recognition: Energetics and Structures

## Communications

### Self-Assembly

G. N. Newton, T. Onuki, T. Shiga,  
M. Noguchi, T. Matsumoto,  
J. S. Mathieson, M. Nihei, M. Nakano,  
L. Cronin,\* H. Oshio\* — 4844–4848



**Two iron/cobalt** mixed-valence clusters were synthesized using multidentate polypyridyl ligands (see picture: Fe<sup>II</sup> orange, Fe<sup>III</sup> yellow, Co<sup>II</sup> blue, O red). A heptanuclear helix and a [3 × 3] grid com-

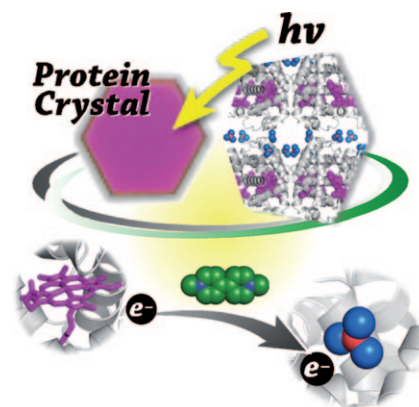
plex form depending on the metal ion stoichiometry. ESI-MS measurements suggest that the helical cluster is an intermediate to the grid complex.



Mapping the Sequential Self-Assembly of Heterometallic Clusters: From a Helix to a Grid

### Protein Engineering

T. Koshiyama, M. Shirai, T. Hikage,  
H. Tabe, K. Tanaka, S. Kitagawa,\*  
T. Ueno\* — 4849–4852



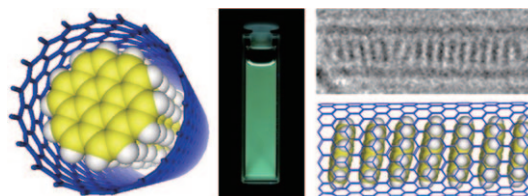
**An artificial photoinduced** electron-transfer system has been constructed by accumulating redox cofactors in a myoglobin crystal. The crystal space allowed the construction of a site-specific dense array, and the different redox cofactors had low reorganization energies, as observed in native photosynthesis. A charge-separated state with a half-life 2800 times longer than that of one previously reported in organic solution was achieved.



Post-Crystal Engineering of Zinc-Substituted Myoglobin to Construct a Long-Lived Photoinduced Charge-Separation System

### Carbon Nanotubes

T. Okazaki,\* Y. Iizumi, S. Okubo,  
H. Kataura, Z. Liu, K. Suenaga, Y. Tahara,  
M. Yudasaka, S. Okada,  
S. Iijima — 4853–4857



**Pancakes in tubes:** Coronenes, a class of planar  $\pi$ -conjugated molecules, organize in 1D structures when using single-walled carbon nanotubes (SWCNTs) as templates (see picture). Coronene columns with coaxial stacking in SWCNTs exhibit

characteristic fluorescence spectra that significantly differ from those of isolated coronene molecules and three-dimensional crystals and that are related to their well-ordered 1D structure.

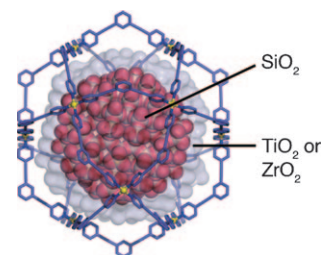


Coaxially Stacked Coronene Columns inside Single-Walled Carbon Nanotubes

### Core-Shell Nanoparticles

K. Suzuki, K. Takao, S. Sato,  
M. Fujita\* — 4858–4861

**The synthesis within:** Highly monodisperse core-shell nanoparticles (SiO<sub>2</sub>/TiO<sub>2</sub>, SiO<sub>2</sub>/ZrO<sub>2</sub>) with a polydispersity index of < 1.01 and a diameter of 3 nm were synthesized within structurally exact self-assembled spherical Pd complexes that act as three-dimensional templates (see picture; gray spheres: TiO<sub>2</sub> or ZrO<sub>2</sub>, purple spheres: SiO<sub>2</sub>, yellow spheres: Pd).



The Precise Synthesis and Growth of Core-Shell Nanoparticles within a Self-Assembled Spherical Template





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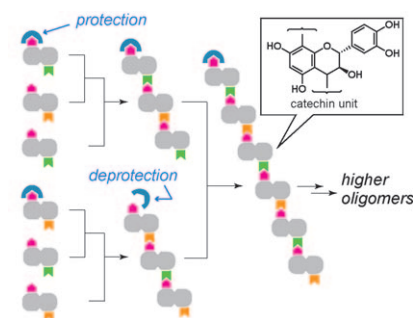
## Oligocatechins

K. Ohmori, T. Shono, Y. Hatakoshi,  
T. Yano, K. Suzuki\* — 4862–4867



Integrated Synthetic Strategy for Higher  
Catechin Oligomers

**Chain linked:** An integrated strategy for the rapid assembly of catechin oligomers has been developed, thus enabling access to higher oligomers ranging from 6- to 24-mers. The method exploits an orthogonal, block-type coupling strategy (see scheme).

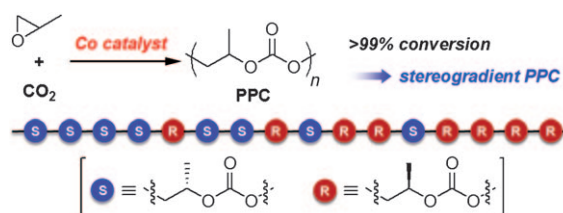


## Polycarbonate Synthesis

K. Nakano, S. Hashimoto, M. Nakamura,  
T. Kamada, K. Nozaki\* — 4868–4871



Stereocomplex of Poly(propylene carbonate): Synthesis of Stereogradient Poly(propylene carbonate) by Regio- and Enantioselective Copolymerization of Propylene Oxide with Carbon Dioxide



**Cobalt(III)–salen complexes** with ammonium arm(s) have been used to catalyze the title transformation. Higher thermal decomposition temperatures than those

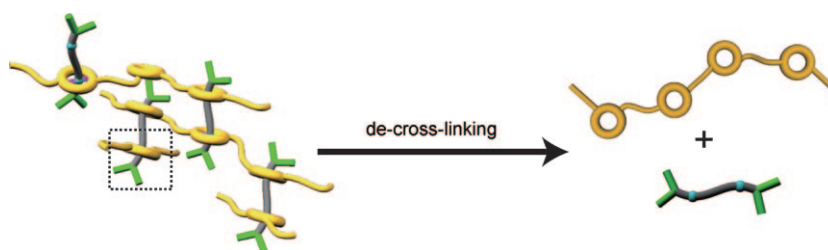
of typical poly(propylene carbonate)s (PPCs) were observed for the stereogradient and the stereoblock PPCs obtained by this method.

## Supramolecular Gels

Y. Kohsaka, K. Nakazono, Y. Koyama,  
S. Asai, T. Takata\* — 4872–4875



Size-Complementary Rotaxane Cross-Linking for the Stabilization and Degradation of a Supramolecular Network



**Break it down:** Gels formed from rotaxane cross-linkers with end groups that are size-complementary to the macrocyclic cavity of wheel components (see picture) were prepared. The network structure was

maintained in polar organic solvents or in the presence of a base to prevent hydrogen bonding. Anion exchange enabled the selective and efficient de-cross-linking of the gels.

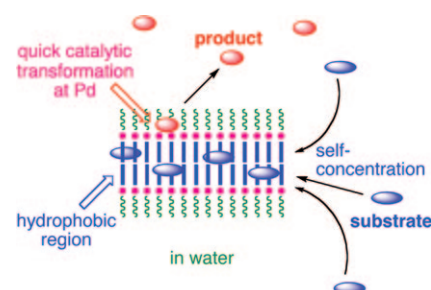
## Vesicular Catalyst

G. Hamasaka, T. Muto,  
Y. Uozumi\* — 4876–4878

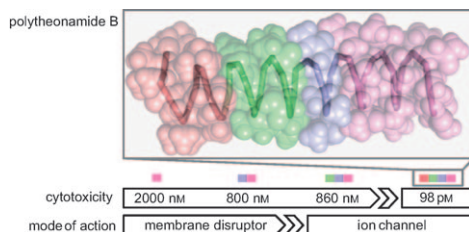


Molecular-Architecture-Based Administration of Catalysis in Water: Self-Assembly of an Amphiphilic Palladium Pincer Complex

**Testing the waters:** An architecture-based system for transition-metal catalysis consisting of a self-assembled amphiphilic pincer palladium complex bearing hydrophilic and hydrophobic chains has been developed. Self-assembly of the bilayer vesicles of the complex, concentration of the organic substrates within the hydrophobic region of the bilayer membrane, and catalytic transformation of the substrate all occur sequentially in water (see scheme).







**Longer is better:** Polytheonamide B, the largest nonribosomal linear peptide identified to date, is a transmembrane channel-forming peptide. Nine of its substructures have now been chemically

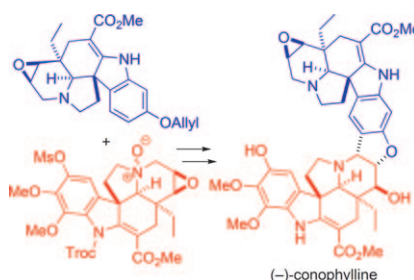
synthesized. The membrane-disrupting and ion-channel-forming sequences as well as the cytotoxicity-enhancing sequence have been identified.

## Natural Products

S. Matsuoka, N. Shinohara, T. Takahashi, M. Iida, M. Inoue\* 4879–4883

Functional Analysis of Synthetic Substructures of Polytheonamide B: A Transmembrane Channel-Forming Peptide

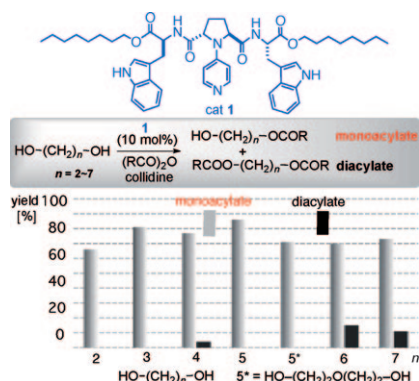
**Double take:** The total syntheses of the title compounds were accomplished in a highly convergent manner. The approach features the regio- and diastereoselective Polonovski–Potier-type reaction for the coupling of two aspidosperma skeletons and the formation of the dihydrofuran ring. Troc = 2,2,2-trichloroethoxycarbonyl.



## Natural Products Synthesis

Y. Han-ya, H. Tokuyama, T. Fukuyama\* 4884–4887

Total Synthesis of (–)-Conophylline and (–)-Conophyllidine

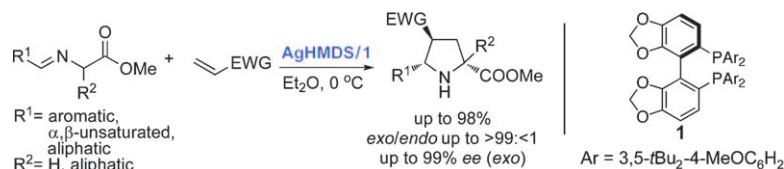


**Matters of length:** Exclusive or predominant monoacylation of 1,*n*-linear diols took place in the presence of **1** when the chain length of linear diols was equal to or shorter than five carbon atoms. The chemoselectivity of acylation between 1,5-pentanediol (*n* = 5) and 1,6-hexanediol (*n* = 6) was 5.2, and that between 1,5-pentanediol and its monoacylate was 113.

## Chemoselective Catalysis

K. Yoshida, T. Furuta, T. Kawabata\* 4888–4892

Organocatalytic Chemoselective Monoacylation of 1,*n*-Linear Diols



**Silver lining:** Highly *exo*-selective asymmetric [3+2] cycloaddition of  $\alpha$ -amino ester Schiff bases with activated olefins proceeds in the presence of AgHMDS/**1**. The  $\alpha$ -amino ester Schiff bases including those derived from aliphatic imines suc-

cessfully reacted to afford the corresponding pyrrolidine derivatives in high yield with high *exo*- and enantioselectivities. EWG = electron-withdrawing group, HMDS = hexamethyldisilazide.

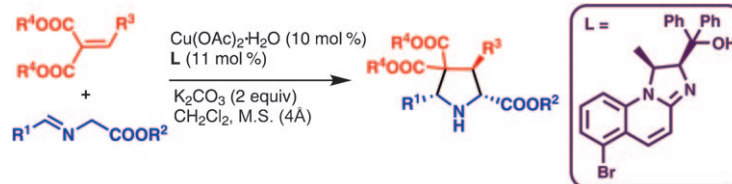
## Asymmetric Catalysis

Y. Yamashita, T. Imaizumi, S. Kobayashi\* 4893–4896

Chiral Silver Amide Catalyst for the [3+2] Cycloaddition of  $\alpha$ -Amino Esters to Olefins

## Copper Catalysis

M. Wang, Z. Wang, Y.-H. Shi, X.-X. Shi,  
J. S. Fossey, W.-P. Deng\* — 4897–4900

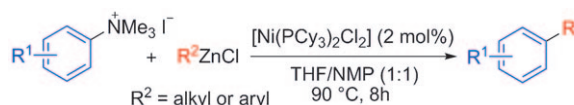


**An *exo*-lent catalyst:** An N,O-ligand/Cu-(OAc)<sub>2</sub> derived chiral complex is an excellent catalyst for inducing asymmetry in the catalytic enantioselective 1,3-dipolar cycloadditions of azomethine ylides with various alkylidene malonates. A

series of highly functionalized *exo*-pyrrolidines were obtained in excellent yields (80–99 %) and enantioselectivities (91–99 % *ee*; see scheme; M.S.: molecular sieve).

## C–N Activation

L.-G. Xie, Z.-X. Wang\* — 4901–4904

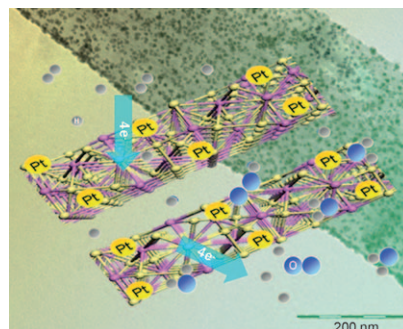


**Broad scope and good tolerance:** An efficient cross-coupling of aryltrimethylammonium iodide salts with aryl-, methyl-, and benzylzinc chlorides catalyzed by [Ni(PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] has been achieved

(see scheme). The reaction involves cleavage of the C–N bond and displays broad substrate scope and good functional group tolerance. NMP = *N*-methylpyrrolidine.

## Fuel-Cell Catalysts

M.-R. Gao, Q. Gao, J. Jiang, C.-H. Cui,  
W.-T. Yao, S. H. Yu\* — 4905–4908

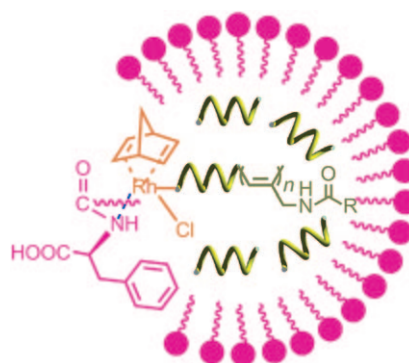


A Methanol-Tolerant Pt/CoSe<sub>2</sub> Nanobelt Cathode Catalyst for Direct Methanol Fuel Cells

**High alcohol tolerance:** A Pt/CoSe<sub>2</sub> nanobelt cathode catalyst for direct methanol fuel cells was prepared by in situ loading of Pt nanoparticles on CoSe<sub>2</sub>/diethylene-triamine nanobelts through a polyol reduction approach. The resulting functionalized nanobelts (see picture) exhibit high activity in the four-electron oxygen reduction reaction and are highly methanol tolerant.

## Chirality

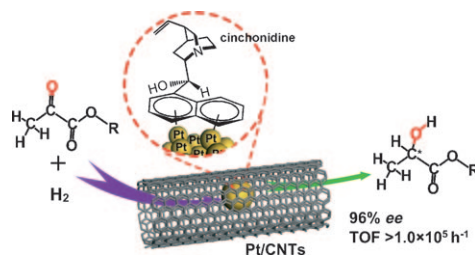
X. F. Luo, J. P. Deng,\*  
W. T. Yang — 4909–4912



Helix-Sense-Selective Polymerization of Achiral Substituted Acetylenes in Chiral Micelles

**Hold that shape:** An achiral acetylene underwent helix-sense-selective polymerization in chiral micelles consisting of [{(nbd)RhCl}<sub>2</sub>] (nbd = 2,5-norbornadiene) and dodecylphenylalanine as a chiral emulsifier to produce optically active helical polymers and polymeric emulsions.





**Going through the proper channels:** A highly active and enantioselective heterogeneous asymmetric catalyst was fabricated by confining Pt nanoparticles that are modified with cinchonidine within the

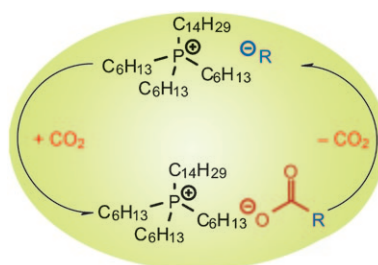
channels of carbon nanotubes. A high turnover frequency (TOF) and enantioselectivity are achieved when using this catalyst for the asymmetric hydrogenation of  $\alpha$ -ketoesters.

## Asymmetric Hydrogenation

Z. J. Chen, Z. H. Guan, M. R. Li,  
Q. H. Yang, C. Li\* 4913–4917

Enhancement of the Performance of a Platinum Nanocatalyst Confined within Carbon Nanotubes for Asymmetric Hydrogenation

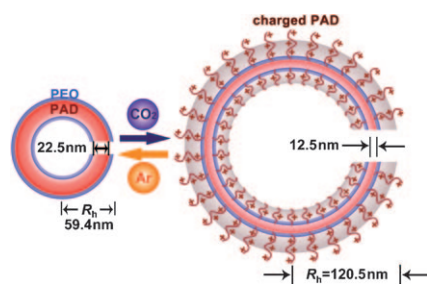
**What a catch!** Basic ionic liquids (ILs) based on a phosphonium hydroxide derivative can be tuned for CO<sub>2</sub> capture by varying the weak proton donors, which have different  $pK_a$  values. The stability, absorption capacity, and absorption enthalpy of the ILs could be easily tuned: the best IL for CO<sub>2</sub> capture has good stability (> 300 °C), energy saving (ca. 56 kJ mol<sup>-1</sup>), and equimolar absorption capability.



## Carbon Capture

C. Wang,\* X. Luo, H. Luo, D. Jiang, H. Li,  
S. Dai\* 4918–4922

Tuning the Basicity of Ionic Liquids for Equimolar CO<sub>2</sub> Capture

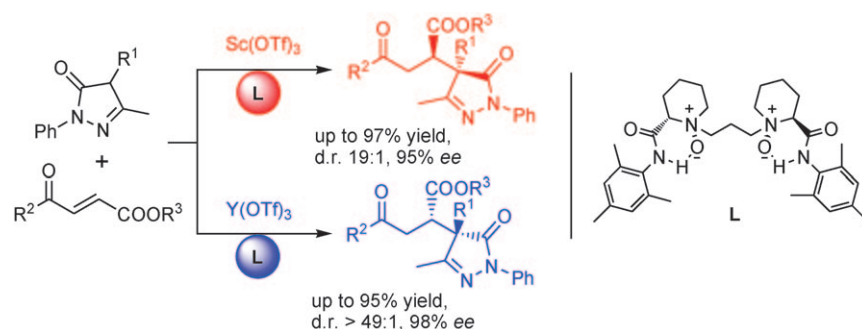


**Vesicles breathe CO<sub>2</sub>!** A new type of vesicle that self-assembles from amidine-containing diblock copolymer displays “breathing” features. Treating the vesicles with CO<sub>2</sub> or Ar can reversibly tune the expansion and contraction of the vesicular volume, as if a bubble is breathing (see picture, PAD = poly((*N*-amidino)dodecyl acrylamide), PEO = poly(ethylene oxide),  $R_h$  = hydrodynamic radius).

## Tunable Vesicles

Q. Yan, R. Zhou, C. K. Fu, H. J. Zhang,  
Y. W. Yin, J. Y. Yuan\* 4923–4927

CO<sub>2</sub>-Responsive Polymeric Vesicles that Breathe



**Make the switch:** The first example of a switch in enantioselectivity in the asymmetric Michael addition of pyrazolin-5-ones to 4-oxo-4-arylbutenoates that is controlled by the metal center of the

catalyst is reported. By using the same *N,N'*-dioxide ligand **L** with different metals the respective enantiomers of various 4-substituted 5-pyrazolone derivatives were obtained. Tf = trifluoromethanesulfonyl.

## Asymmetric Synthesis

Z. Wang, Z. G. Yang, D. H. Chen,  
X. H. Liu, L. L. Lin,  
X. M. Feng\* 4928–4932

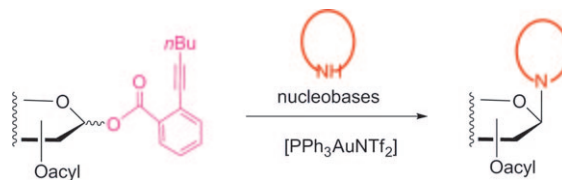
Highly Enantioselective Michael Addition of Pyrazolin-5-ones Catalyzed by Chiral Metal/*N,N'*-Dioxide Complexes: Metal-Directed Switch in Enantioselectivity

## Nucleoside Synthesis

Q. Zhang, J. Sun,\* Y. Zhu, F. Zhang,  
B. Yu\* ————— 4933 – 4936



An Efficient Approach to the Synthesis of Nucleosides: Gold(I)-Catalyzed N-Glycosylation of Pyrimidines and Purines with Glycosyl *ortho*-Alkynyl Benzoates



**Persuaded with gold:** The title reaction in the presence of  $[\text{Ph}_3\text{PAuNTf}_2]$  (Tf = trifluoromethanesulfonyl) led conveniently to the corresponding nucleosides with excellent regioselectivity (see scheme).

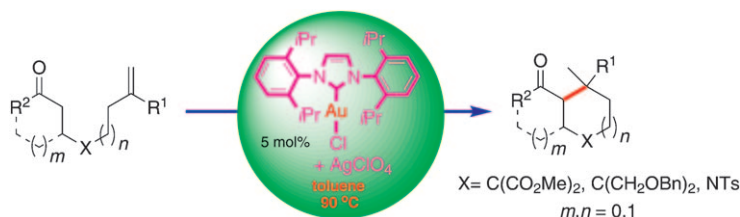
Even purine derivatives underwent this transformation owing to the mild conditions, which enabled the use of protecting groups that would not usually be compatible with N-glycosylation conditions.

## Gold Catalysis

Y.-P. Xiao, X.-Y. Liu,  
C.-M. Che\* ————— 4937 – 4941



Efficient Gold(I)-Catalyzed Direct Intramolecular Hydroalkylation of Unactivated Alkenes with  $\alpha$ -Ketones



**Easy access by gold:** The  $\text{Au}^{\text{I}}$ -catalyzed title reaction provides simple and efficient access to highly substituted cyclic compounds with excellent yields and good diastereoselectivity. This transformation

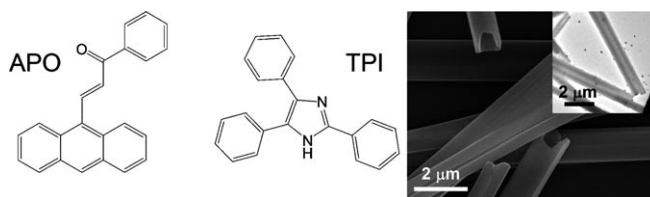
constitutes the first example of transition-metal-catalyzed direct hydroalkylation of unactivated alkenes with simple  $\alpha$ -ketone groups in the absence of additive reagents. Bn = benzyl, Ts = tosyl.

## Self-Assembly

Q. Liao, H. B. Fu,\* C. Wang,  
J. N. Yao\* ————— 4942 – 4946



Cooperative Assembly of Binary Molecular Components into Tubular Structures for Multiple Photonic Applications



**Take the tube:** Tubular structures can be fabricated by the cooperative self-assembly of the binary molecular components TPI and APO (see picture). This method can also be used to make a single binary

tube capable of performing multiple photonic functions, such as an annular microcavity waveguide, waveguide modulation, and a controllable waveguide switch.

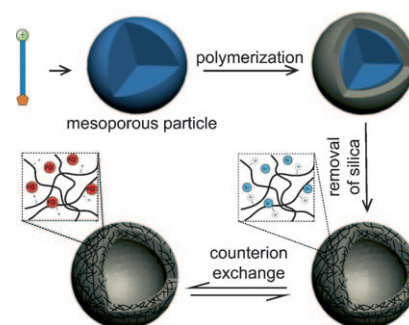
## Polymer Capsules

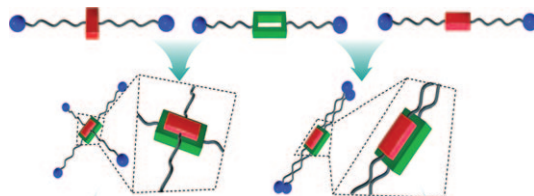
C. Lin, W. Zhu, H. Yang, Q. An, C. Tao,  
W. Li, J. Cui, Z. Li, G. Li\* — 4947 – 4951



Facile Fabrication of Stimuli-Responsive Polymer Capsules with Gated Pores and Tunable Shell Thickness and Composite

**A hollow victory:** A multifunctional polymerizable ionic liquid (IL)-based surfactant is used in the synthesis of silica spheres with tunable size. Hollow capsules with a mesoporous polymer-network shell and pendant IL moieties are then fabricated by template synthesis (see picture). The pore size of the shell is reversibly adjustable by exchange of counteranions (blue and red circles) of the pendant IL units.





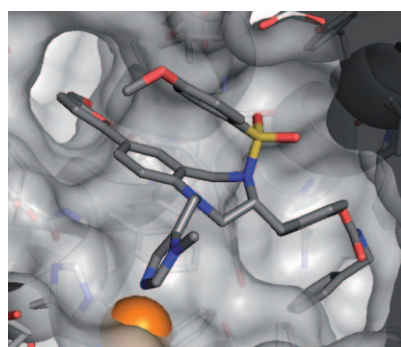
**Give and take:** X- or H-shape superamphiphiles form on the basis of directional charge-transfer complexes and lead to the formation of one-dimensional nanorods and two-dimensional nanosheets,

respectively (see picture, blue: pyridinium ion, red: naphthalene derivatives, green: naphthalene diimide). The superstructures form after elaborate tuning of the building block structures.

### Self-Assembly

K. Liu, C. Wang, Z. B. Li,  
X. Zhang\* — 4952 – 4956

Superamphiphiles Based on Directional Charge-Transfer Interactions: From Supramolecular Engineering to Well-Defined Nanostructures

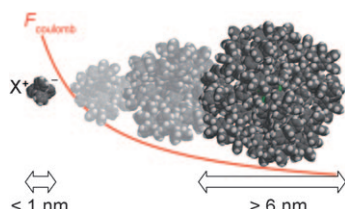


**Designing for selectivity:** A combination of protein crystal-structure analysis, virtual screening, and synthetic chemistry has been used to develop noncytotoxic inhibitors of RabGGTase ( $IC_{50}$ : 42 nM for the example shown; red O, blue N, yellow S) that are selective over FTase and GGTase I. Furthermore, the inhibitors display cellular activity and inhibit cancer cell proliferation.

### Inhibitor Design

R. S. Bon, Z. Guo, E. A. Stigter, S. Wetzel,  
S. Menninger, A. Wolf, A. Choidas,  
K. Alexandrov, W. Blankenfeldt,  
R. S. Goody, H. Waldmann\* — 4957 – 4961

Structure-Guided Development of Selective RabGGTase Inhibitors

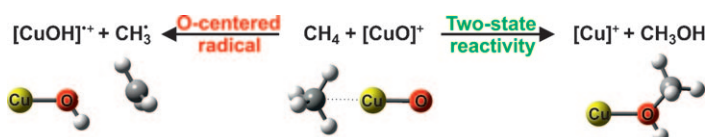


**Size matters:** The strategy of divergent dendronization allows for the synthesis of unprecedented large, rigid, and bulky anions (see picture). Their size, density, and chemical nature of surface can be tailored to obtain more hydrophobic, less nucleophilic, and more weakly coordinating anions.

### Dendronized Anions

D. Türp, M. Wagner, V. Enkelmann,  
K. Müllen\* — 4962 – 4965

Synthesis of Nanometer-Sized, Rigid, and Hydrophobic Anions



**The final piece in an intriguing puzzle:** More than ten years after its theoretical prediction to serve as a powerful converter of methane to methanol, the bare  $[CuO]^+$  cation has been successfully generated in

the gas phase. A combination of mass spectrometry and DFT calculations revealed the crucial role of two-state reactivity and oxygen-centered radicals in the selectivity in the oxidation of methane.

### Methane Activation

N. Dietl, C. van der Linde, M. Schlangen,  
M. K. Beyer, H. Schwarz\* — 4966 – 4969

Diatomic  $[CuO]^+$  and Its Role in the Spin-Selective Hydrogen- and Oxygen-Atom Transfers in the Thermal Activation of Methane



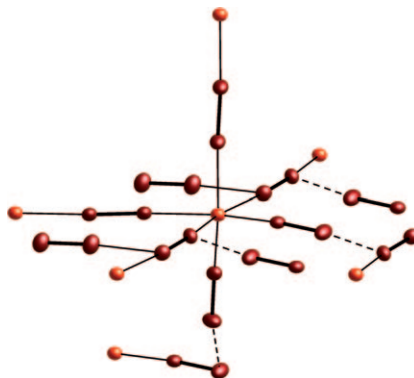


## Polybromides

M. Wolff, J. Meyer,  
C. Feldmann\* \_\_\_\_\_ 4970–4973



$[C_4MPyr]_2[Br_{20}]$ : Ionic-Liquid-Based Synthesis of a Three-Dimensional Polybromide Network



**A Br stunt:** The first three-dimensional polybromide network is found in  $[C_4MPyr]_2[Br_{20}]$  (see structure of the  $[Br_{20}]^{2-}$  network). The compound was obtained in an ionic-liquid-based synthesis—and with 18:2 contains the highest  $Br^0:Br^-$  ratio ever observed.

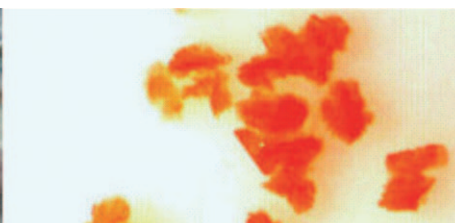
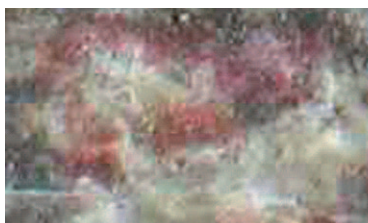


## Coordination Chemistry

X. Wurzenberger, H. Piotrowski,  
P. Klüfers\* \_\_\_\_\_ 4974–4978



A Stable Molecular Entity Derived from Rare Iron(II) Minerals: The Square-Planar High-Spin- $d^6$   $Fe^{II}O_4$  Chromophore



**The odd couple:** The red chromophore of both the rare silicate mineral gillespite ( $BaFeSi_4O_{10}$ ; see picture, left, on sanbornite,  $BaSi_2O_5$ ) and the bis(*meso*-oxolanediolato)ferrate(II) anion in its lithium salt (right) is the square-planar, high-spin-

$d^6$  ferrous center. The unusual combination of structure and spin state for the  $FeO_4$  moiety is not forced by a rigid environment of the central metal, but rather results from an intrinsically stable entity.

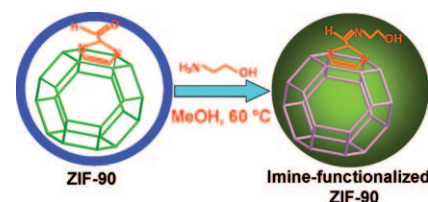
## Selective Membranes

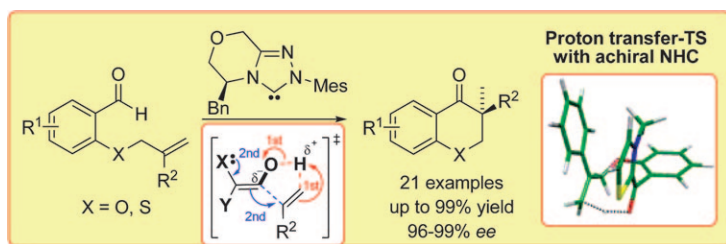
A. Huang,\* J. Caro\* \_\_\_\_\_ 4979–4982



Covalent Post-Functionalization of Zeolitic Imidazolate Framework ZIF-90 Membrane for Enhanced Hydrogen Selectivity

**MOF constrictor:** Covalent modification of a ZIF-90 membrane was achieved by imine condensation of the aldehyde groups of the metal–organic framework (MOF) linker by ethanolamine (see picture). The modification leads to constriction of the pore apertures and prevents unselective permeation through defect pores, thus improving gas separation performance. For a  $H_2/CO_2$  mixture, selectivity can be increased from 7.3 to 62.5.





**NHC-catalysis proto(n)type:** The title reaction produces 21 different chroman-4-one-type products in good yields and excellent enantioselectivities, in each case building up a new all-carbon quaternary

stereocenter (see scheme). Based on DFT calculations a mechanistic scenario involving proton transfer, possible transition states, and a mode of enantioinduction is presented.

## Asymmetric Organocatalysis



I. Piel, M. Steinmetz, K. Hirano,  
R. Fröhlich, S. Grimme,\*  
F. Glorius\* \_\_\_\_\_ 4983 – 4987

Highly Asymmetric NHC-Catalyzed  
Hydroacylation of Unactivated Alkenes



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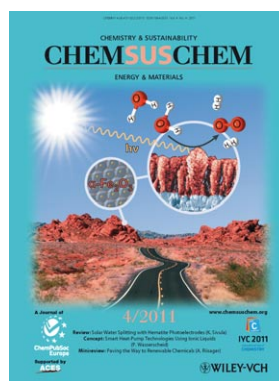
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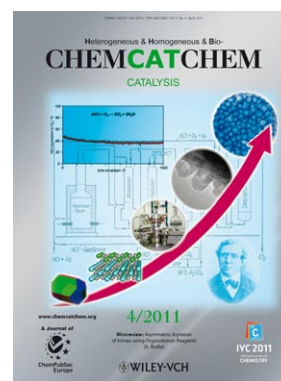
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