



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 soon:

S. Miyazaki, K. Ohkubo, T. Kojima,* S. Fukuzumi*
**Modulation of Characteristics of a Ruthenium-Coordinated
 Flavin Analogue Showing an Unprecedented Coordination Mode**

M. L. Maddess, M. N. Tackett, H. Watanabe, P. E. Brennan,
 C. D. Spilling, J. S. Scott, D. P. Osborn, S. V. Ley*
Total Synthesis of Rapamycin

J. H. Lee, F. D. Toste*
Gold(I)-Catalyzed Synthesis of Functionalized Cyclopentadienes

E. Terreno, C. Cabella, C. Carrera, D. D. Castelli, R. Mazzon,
 S. Rollet, J. Stancanella, M. Visigalli, S. Aime*
**From “Spherical” to “Osmotically Shrunked” Paramagnetic
 Liposomes: An Improved Generation of LIPOCEST MRI Agents
 with Highly Shifted Water Protons**

W. H. Bernskoetter, E. Lobovsky, P. J. Chirik*
**Nitrogen–Carbon Bond Formation from N₂ and CO₂ Promoted by
 a Hafnocene Dinitrogen Complex Leads to the Liberation of a
 Substituted Hydrazine**

J. A. Teprovich, Jr., E. Prasad,* R. A. Flowers, II*
Solvation-Controlled Luminescence of Sm^{III} Complexes

News

Organic Materials:
 A. Hirsch awarded _____ 21

Asymmetric Catalysis:
 C. Bolm honored _____ 21

Peptide Chemistry:
 Prize for S. H. Gellman _____ 21

Books

Exploiting Chemical Diversity for Drug
 Discovery

Paul A. Bartlett, Michael Entzeroth

reviewed by A. Link _____ 22

Essays

History of Science

O. Krätz,* E. Vaupel* _____ 24–51

1807: Observations Regarding Chemistry
 in the Anglo-Saxon World during the
 Napoleonic Period

Far-reaching influence: How did the cul-
 tural atmosphere in the Anglo-Saxon
 world shape the sciences and in particular
 chemistry at the beginning of the
 19th century? Who were the most impor-
 tant figures, and what role did they play in
 academia as well as in the public?
 Impressions regarding these themes are
 given in this Essay.

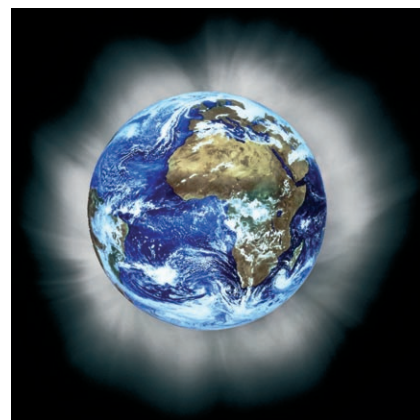


Renewable Energies

N. Armaroli,* V. Balzani* _____ 52–66

The Future of Energy Supply: Challenges
 and Opportunities

Energy for everybody? The ever increasing
 world energy demand cannot be satisfied
 much longer with fossil fuels; alternatives
 are required to limit the chance of a
 climate collapse and the spreading of
 wars for natural resources. The 21st
 century will be largely defined by the way
 we face and resolve the energy crisis. This
 is an intricate and fascinating scientific
 challenge, in which chemistry will play a
 fundamental role, and also an unprece-
 dented opportunity to shape a more
 peaceful world.

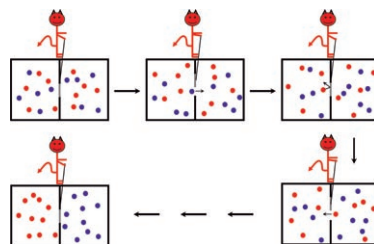


Reviews

Molecular Devices

E. R. Kay, D. A. Leigh,*
F. Zerbetto* — 72–191

Synthetic Molecular Motors and
Mechanical Machines



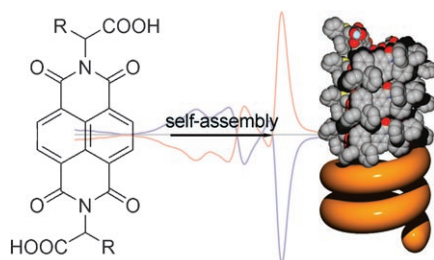
Exercising demons: Although the notion of synthetic molecular-level motors and machines has been around for 150 years (for example, Maxwell's demon, see picture), it is only recently that research in this area has flourished. The current state of the art in regard to how the components of molecular-level structures can be switched, rotated, speeded up, slowed down, and directionally driven in response to stimuli is described in the Review.

Communications

Nanotubes

G. D. Pantoş, P. Pengo,
J. K. M. Sanders* — 194–197

Hydrogen-Bonded Helical Organic
Nanotubes

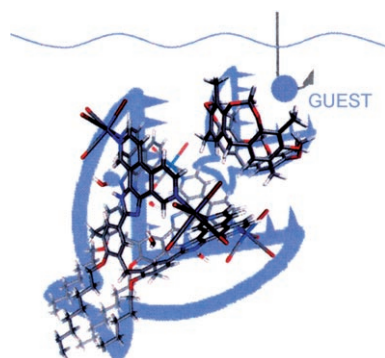


Twist your tubes: The self-assembly of small organic molecules is an entirely new approach to the synthesis of nanotubular structures possessing helical chirality. Amino acid derivatives of naphthalene-diimide form such assemblies both in solution and in the solid state. The chirality of the nanotubes is determined by the constituent amino acid but is independent of the nature of the side chains.

Inclusion Complexes

E. Botana, E. Da Silva, J. Benet-Buchholz,
P. Ballester, J. de Mendoza* — 198–201

Inclusion of Cavitands and Calix[4]arenes
into a Metallobridged *para*-(1*H*-
Imidazo[4,5-*f*][3,8]phenanthrolin-2-yl)-
Expanded Calix[4]arene



A hunter hunted! A highly preorganized, deep metallocavitand of nanoscale dimensions containing rhenium atoms at the four corners can be readily synthesized from a simple formyl-substituted calix[4]arene and 3,8-phenanthroquinone. Unsubstituted calix[4]arenes and cavitands without substituents on the lower rim are the ideal guests for such an expanded calixarene (see picture), and are included with binding constants of 10^3 – 10^5 M^{-1} .

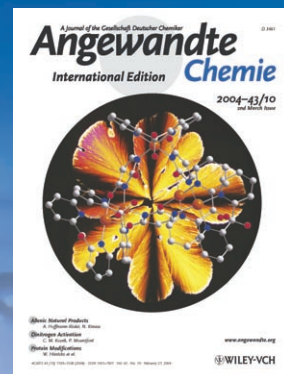
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1888: The beginning
of a success story

Constant Innovations

- 1962:** First issue of the
International Edition
- 1976:** Graphical abstracts
- 1979:** Cover pictures
- 1988:** Centenary of Angewandte
- 1989:** Routine use of color
- 1991:** New section: Highlights
- 1992:** Computerized editorial
tracking system
- 1995:** Internet service for readers
- 1998:** Regular press service;
full-text online
- 2000:** New section: Essays;
EarlyView: Communications
available online ahead of
the printed version
- 2001:** New section: Minireviews
- 2002:** Online submission
of manuscripts
- 2003:** Weekly publication; new
section: News; new layout
- 2004:** Backfiles (1962-1997);
ManuscriptXpress: Online
system for authors and
referees



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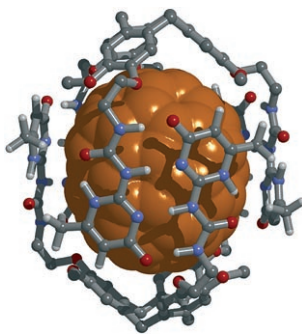
Hartmut Wiezer
Clariant International AG,
Sulzbach am Taunus

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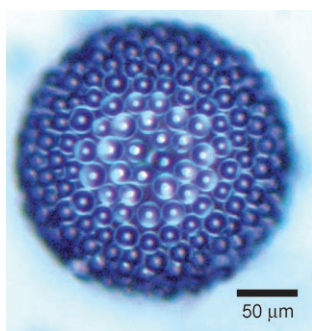
All wrapped up: An easy, highly selective separation of C_{70} and the higher fullerenes has been achieved by solid–liquid extraction with a 2-ureido-4-[1*H*]-pyrimidinone-based scaffold which wraps around the guest as a dimeric capsule (see picture), thereby solubilizing it in THF. Acidification disrupts the hydrogen-bonding network and allows easy recovery of the guest and recycling of the receptor without chromatography or tedious procedures.



Molecular Recognition

E. Huerta, G. A. Metselaar, A. Frago, E. Santos, C. Bo, J. de Mendoza* _____ **202–205**

Selective Binding and Easy Separation of C_{70} by Nanoscale Self-Assembled Capsules



Stick with me: Electrostatic charges can be induced in functionalized polystyrene beads. Oppositely charged beads then aggregate to form superstructures. A coat of small beads can self-assemble around a large bead (see optical microscopy image). After annealing, another layer of beads can be added. The technique, based on contact electrification, avoids the use of expensive equipment and enables the use of large quantities of material.

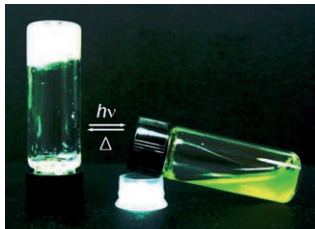
Self-Assembly

L. S. McCarty, A. Winkleman, G. M. Whitesides* _____ **206–209**

Electrostatic Self-Assembly of Polystyrene Microspheres by Using Chemically Directed Contact Electrification



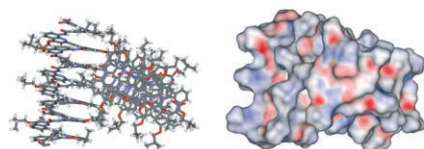
Without modification of its periphery, cucurbit[7]uril (a macrocyclic cavitand comprising seven glycoluril units) forms a hydrogel. The gelation is thermoreversible and sensitive to pH, but is inhibited by the presence of alkali-metal ions and shows guest-induced stimuli-responsive behavior: upon addition of a small amount of a guest, it undergoes a reversible gel–sol transition with alternating UV irradiation and heat treatment (see picture).



Hydrogels

I. Hwang, W. S. Jeon, H.-J. Kim, D. Kim, H. Kim, N. Selvapalam, N. Fujita, S. Shinkai, K. Kim* _____ **210–213**

Cucurbit[7]uril: A Simple Macrocyclic, pH-Triggered Hydrogelator Exhibiting Guest-Induced Stimuli-Responsive Behavior



Big is beautiful: A folded synthetic molecule with a conformation that compares in size with the tertiary folds of a small protein and yet only consist of non-natural units is described. By not controlling the helical handedness allows the effect of tertiary interactions between helical modules through helix–helix side-by-side induction of handedness to be observed.

Helical Structures

N. Delsuc, J.-M. Léger, S. Massip, I. Huc* _____ **214–217**

Proteomorphous Objects from Abiotic Backbones



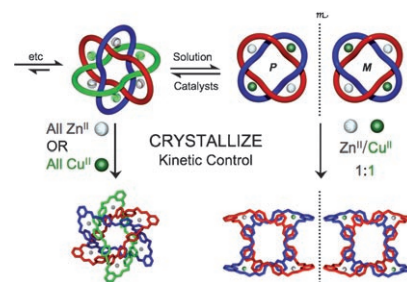
Supramolecular Chemistry

C. D. Pentecost, K. S. Chichak, A. J. Peters,
G. W. V. Cave, S. J. Cantrill,
J. F. Stoddart* _____ **218–222**



A Molecular Solomon Link

Knots galore: With a judicious choice of ions and solvents, it is possible to amplify a molecular Solomon link by kinetically controlled crystallization from a dynamic combinatorial library of molecular knots (see scheme).



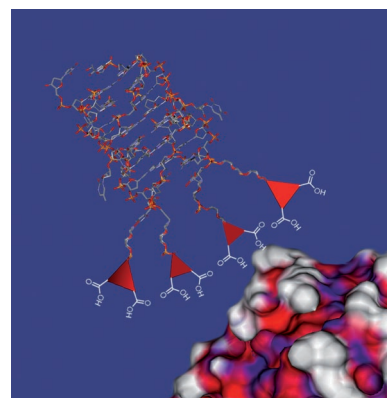
Self-Assembly

D. M. Tagore, K. I. Sprinz, S. Fletcher,
J. Jayawickramarajah,
A. D. Hamilton* _____ **223–225**



Protein Recognition and Denaturation by Self-Assembling Fragments on a DNA Quadruplex Scaffold

Recognize this face? Quadruplex DNA has been used as a noncovalent scaffold to project binding groups for protein recognition and denaturation, with the best quadruplex decreasing the melting temperature of cytochrome *c* by about 45 K.



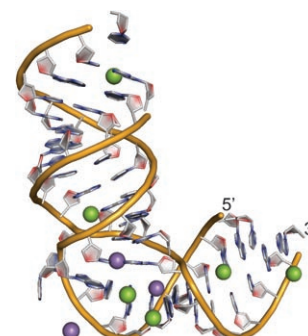
Molecular Recognition

S. M. Dibrov, H. Johnston-Cox, Y.-H. Weng,
T. Hermann* _____ **226–229**



Functional Architecture of HCV IRES Domain II Stabilized by Divalent Metal Ions in the Crystal and in Solution

Around the bend: A right-angled bend in the RNA of the hepatitis C virus is stabilized by a core of divalent metal ions (shown as green and violet spheres). Crystal-structure analysis and fluorescence labeling have been used to investigate the structure and metal-ion-dependent stabilization of the RNA domain that plays a key role in viral protein synthesis.

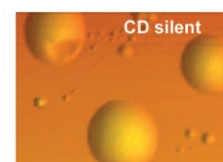
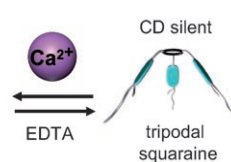
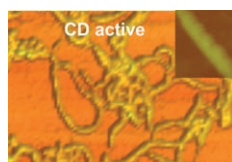


Helical Structures

A. Ajayaghosh,* P. Chithra,
R. Varghese _____ **230–233**

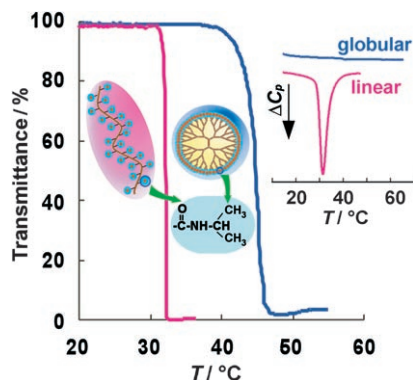


Self-Assembly of Tripodal Squaraines: Cation-Assisted Expression of Molecular Chirality and Change from Spherical to Helical Morphology



Let's do the twist: Tripodal squaraines self-assemble from acetonitrile to form hollow spheres, the complexation of which with Ca^{2+} or Mg^{2+} results in extended networks. An analogous chiral dye exhibits a bisignate CD couplet and a

helical morphology upon Ca^{2+} binding (see figure). Thus, the molecular chirality of a functional dye is expressed through specific cation binding and manifested in the form of supramolecular helicity.



The sensitive type: A lower critical solution temperature (LCST) is observed for dendrimers with *N*-isopropylamide (NIPAM) groups at all chain terminals and for poly(*N*-isopropylacrylamide) (PNIPAAm; see picture). A much smaller endothermic peak occurs around the LCST for NIPAM-terminated dendrimers. The globular structure of the dendrimers may cause inefficient hydration and dehydration around NIPAM groups below and above the LCST, respectively.

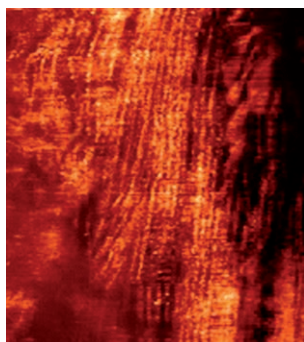
Thermosensitive Polymers

Y. Haba, C. Kojima, A. Harada, K. Kono* 234–237

Comparison of Thermosensitive Properties of Poly(amidoamine) Dendrimers with Peripheral *N*-Isopropylamide Groups and Linear Polymers with the Same Groups



Doped and wired: The organization of the π functional units in amide-functionalized tetrathiafulvalene in a gel by hydrogen-bonding interactions has given rise to nanofibers. Doping with iodine generates a conducting material, which upon annealing gives rise to nanowires with metal-like conductivity (see current-sensing AFM image).



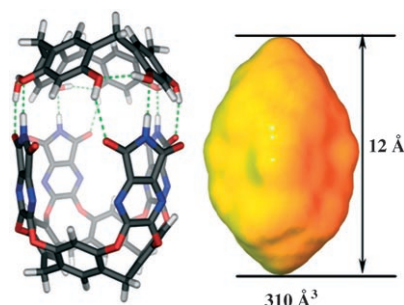
Electric Conductors

J. Puigmartí-Luis, V. Laukhin, Á. Pérez del Pino, J. Vidal-Gancedo, C. Rovira, E. Laukhina, D. B. Amabilino* 238–241

Supramolecular Conducting Nanowires from Organogels



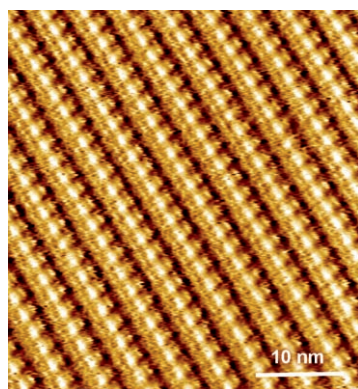
Different, yet compatible: A hybrid capsule is formed through hydrogen bonding between two different subunits, each of which is capable of self-assembly into homodimeric capsules. The hybrid forms in response to a guest that fills its space properly. Formation of the molecular capsule (see picture) is supported by ^1H NMR spectroscopy experiments.



Host–Guest Systems

D. Ajami, M. P. Schramm, A. Volonterio, J. Rebek, Jr.* 242–244

Assembly of Hybrid Synthetic Capsules



Nanopatterning of multifunctional architectures, that is, 1D or 2D arrays on surfaces, can be achieved through bottom-up fabrication of 1D coordination networks by self-assembly processes. A coordinating tecton bearing both monodentate and tridentate coordination poles is combined with suitable metal centers (see scanning tunneling microscopy image).

Supramolecular Chemistry

M. Surin, P. Samorì,* A. Jouaiti, N. Kyritsakas, M. W. Hosseini* 245–249

Molecular Tectonics on Surfaces: Bottom-Up Fabrication of 1D Coordination Networks That Form 1D and 2D Arrays on Graphite

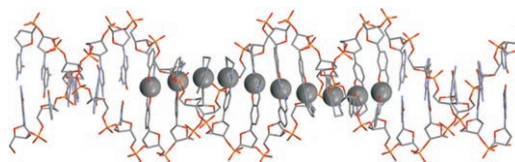


DNA Structures

G. H. Clever, T. Carell* — 250–253



Controlled Stacking of 10 Transition-Metal Ions inside a DNA Duplex



A helical turn full of metal ions! The metal–salen base-pair concept allows the incorporation of up to 10 transition-metal ions into double strands of DNA (see picture; Mn gray spheres, C gray, N blue,

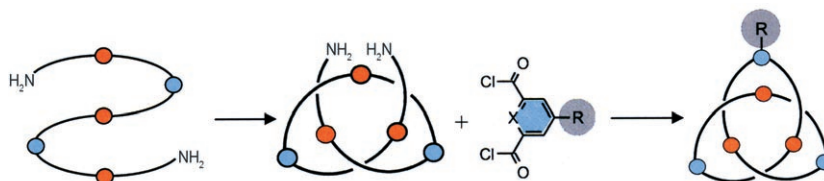
P orange, O red). The crosslinking provided by the metal–salen complexes conveys a high stability to the self-assembled systems.

Molecular Knots

J. Brüggemann, S. Bitter, S. Müller, W. M. Müller, U. Müller, N. M. Maier, W. Lindner,* F. Vögtle* — 254–259



Spontaneous Knotting—From Oligoamide Threads to Trefoil Knots



Tying up loose ends: Oligoamide thread molecules can spontaneously transform into open knots, whose terminal functional groups can subsequently be che-

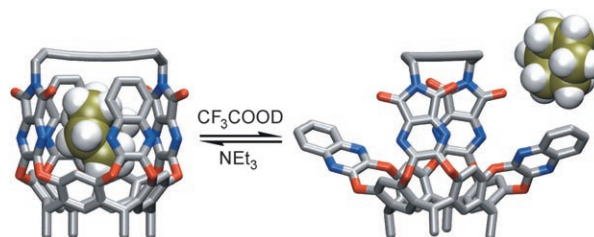
mically linked to form closed, cyclic knots (see scheme; left: threads; middle: open knots; right: molecular knots; X = N, C).

Switchable Supramolecular Systems

T. Gottschalk, B. Jaun, F. Diederich* — 260–264



Container Molecules with Portals: Reversibly Switchable Cycloalkane Complexation



A molecular basket (see picture) and a molecular tube can be reversibly switched between closed and open forms. In their closed forms, these novel container molecules encapsulate cycloalkanes such

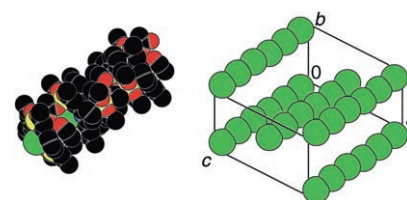
as cyclohexane. Their binding capabilities can be completely turned off by the addition of acid. Neutralization with base leads to restoration of the original complexes.

Coordination Polymers

R. W. Saalfrank,* A. Scheurer,* R. Puchta, F. Hampel, H. Maid, F. W. Heinemann — 265–268

Threading Cesium Ions: Metal, Host, and Ligand Control in Supramolecular Coordination Chemistry

Threads of cesium ions can be generated through supramolecular coordination chemistry in a one-pot synthesis. The cesium ions are threaded together, like in a pearl necklace, with surprisingly short interatomic distances. The figure shows the space-filling model of the dicationic repeating unit of the 1D coordination polymer (left) and the cesium threads alone in the unit cell (right). C black, Cs green, Cu yellow, O red, N blue.





The counterion, not the binding pocket, shifts the absorption of the protonated Schiff base of 11-*cis*-retinal into the visible region. This conclusion was drawn from high-level CASPT2 calculations on the visual pigment rhodopsin (the optimized structure of the binding pocket is shown).

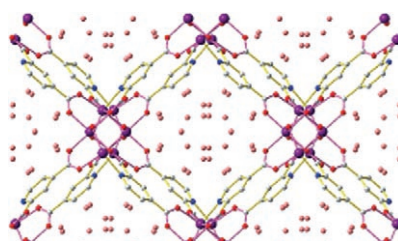
Chemistry of Vision

S. Sekharan, M. Sugihara,
V. Buss* ————— 269–271

Origin of Spectral Tuning in Rhodopsin—
It Is Not the Binding Pocket



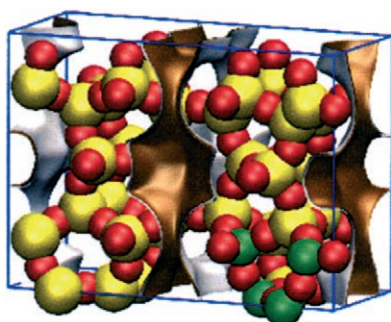
Resilient hosts: The porous coordination solids CUK-1 (see structure; Co purple, C gray, N blue, O red/pink) and CUK-2 are synthesized from unsymmetrical ligands and Co^{II} ions. Even after the removal of co-crystallized guests, the host frameworks are exceptionally stable. CUK-1 shows a high capacity for H₂ adsorption and is one of very few materials capable of separating N₂ from O₂.



Microporous Materials

S. M. Humphrey, J.-S. Chang,* S. H. Jung,
J. W. Yoon, P. T. Wood* ——— 272–275

Porous Cobalt(II)–Organic Frameworks
with Corrugated Walls: Structurally
Robust Gas-Sorption Materials



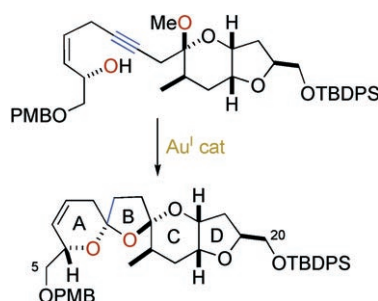
Aluminum sites in zeolites are difficult to locate experimentally, and hence an indirect theoretical approach is proposed that identifies the most likely positions of the aluminum atoms by matching simulation results with available experimental data. The picture shows a model unit cell of FER-type zeolite with the four distinct T-sites for aluminum in green.

Zeolites

E. García-Pérez, D. Dubbeldam, B. Liu,
B. Smit, S. Calero* ————— 276–278

A Computational Method To Characterize
Framework Aluminum in Aluminosilicates

Au-dacious ring synthesis: An efficient synthesis of the A–D rings of azaspiracid has been developed by using a Co-catalyzed oxaetherification to form the fused 2,5-*trans*-configured trisubstituted tetrahydrofuran D ring, and an unprecedented Au-catalyzed bis-spiroketal formation wherein a bridging alkyne served as a surrogate for the C10 ketal (see scheme; PMB = *para*-methoxybenzyl, TBDPS = *tert*-butyldiphenylsilyl).



Spiro Compounds

Y. Li, F. Zhou, C. J. Forsyth* — 279–282

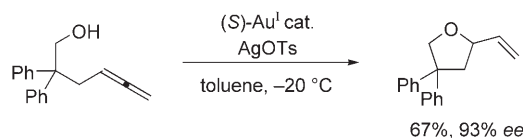
Gold(I)-Catalyzed Bis-Spiroketalization:
Synthesis of the Trioxadispiroketal-
Containing A–D Rings of Azaspiracid

Homogeneous Catalysis

Z. Zhang, R. A. Widenhoefer* **283–285**



Gold(I)-Catalyzed Intramolecular Enantioselective Hydroalkoxylation of Allenes



Turned by gold: The gold(I)-catalyzed enantioselective hydroalkoxylation of allenes proceeded rapidly to give useful oxygen heterocycles in high yields and with high stereoselectivity. The procedure

was also effective for the cyclization of γ -hydroxyallenes that possess an axially chiral allenyl moiety and for the cyclization of δ -hydroxyallenes.

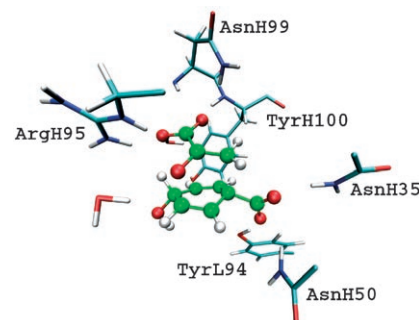
Computer Chemistry

S. Martí, J. Andrés, E. Silla, V. Moliner,*
I. Tuñón,* J. Bertrán **286–290**



Computer-Aided Rational Design of Catalytic Antibodies: The 1F7 Case

Thinking it through: Details of the transition-state structures of the chorismate to prephenate rearrangement in the active site of the 1F7 (N33S) mutant were obtained by computer-aided rational design. This method may be used to determine whether antibody scaffolds are evolutionary dead ends or if they can be further improved.



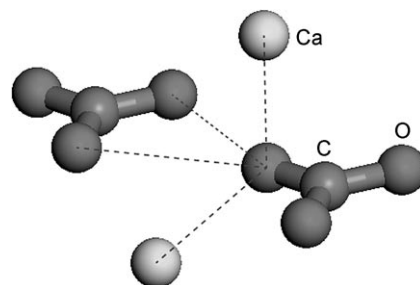
Calcite Structure

R. Gueta, A. Natan, L. Addadi, S. Weiner,
K. Refson, L. Kronik* **291–294**



Local Atomic Order and Infrared Spectra of Biogenic Calcite

Shining light on local order: The relations between local crystalline order and peak intensities in the infrared spectra of calcite are explained in terms of different sensitivities to Ca–O and O...O distances (see picture) by comparing ab initio phonon spectra for ideal and distorted calcite unit cells with experimental spectra of various biogenic and geological calcites.



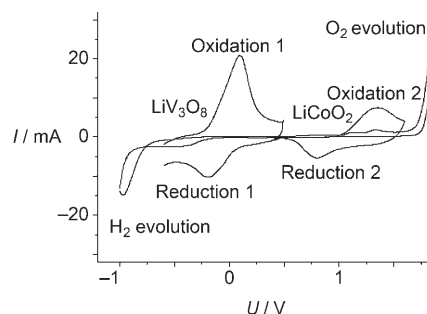
Batteries

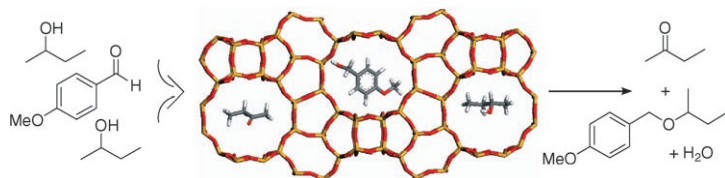
G. J. Wang, L. J. Fu, N. H. Zhao, L. C. Yang,
Y. P. Wu,* H. Q. Wu **295–297**



An Aqueous Rechargeable Lithium Battery with Good Cycling Performance

“Green” batteries: The cycling of an aqueous rechargeable lithium battery (ARLB) with an output voltage of 1.05 V is markedly improved by choosing the appropriate intercalation compounds as electrode materials (see diagram). This system is, in principle, very stable and provides a means to explore new energy-storage and conversion systems, especially for use in future electric vehicles.





This most ethereal of cascades: Water-resistant single isolated Lewis acids within the framework of molecular sieves act as excellent general catalysts for the synthesis of ethers (see scheme). On this

basis, an environmentally friendly process has been developed for the preparation of fine chemicals that involves a one-pot Meerwein–Ponndorf–Verley reduction/etherification cascade.

Etherification

A. Corma,* M. Renz* _____ 298–300

A General Method for the Preparation of Ethers Using Water-Resistant Solid Lewis Acids



Supporting information is available on the WWW (see article for access details).



A video clip is available as Supporting Information on the WWW (see article for access details).

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