



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:

C. Coleman, D. van der Spoel*

Picosecond Melting of Ice by an Infrared Laser Pulse: A Simulation Study

T. Amaya, H. Sakane, T. Hirao*

A Concave-Bound CpFe Complex of Sumanene as a Dished-up Metal in a π -Bowl

A. M. Brizard, M. C. Stuart, K. J. v. Bommel, A. Friggeri, M. R. de Jong, J. H. v. Esch*

Nanostructures by Orthogonal Self-Assembly of Hydrogelators and Surfactants

H.-C. Chiu,* Y.-W. Lin, Y.-F. Huang, C.-K. Chuang, C.-S. Chern
Polymer Vesicles Containing Small Vesicles within Interior Aqueous Compartments and pH-Responsive Transmembrane Channels

M. J. Hanguer, C. R. Bertozzi*

A FRET-Based Fluorogenic Phosphine for Live-Cell Imaging with the Staudinger Ligation

A. Baumgartner, K. Sattler, J. Thun, J. Breu*

A Novel Route to Microporous Materials: Oxidative Pillaring of Mic

Integrated Approach to Coordination Chemistry

Rosemary A. Marusak, Kate Doan, Scott D. Cummings

Books

reviewed by A. Klein 438

Highlights

Ionothermal Synthesis

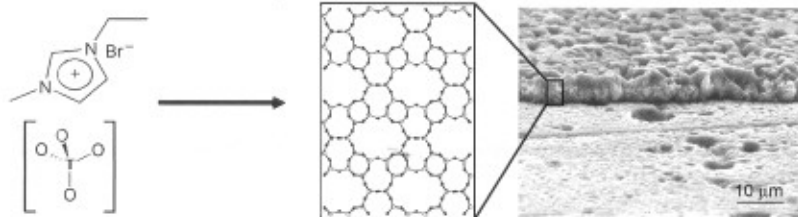
R. E. Morris* 442–444

Ionic Liquids and Microwaves—Making Zeolites for Emerging Applications

Microporous Materials

M. Mastalerz* 445–447

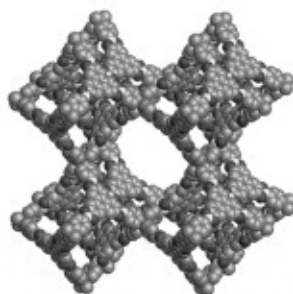
The Next Generation of Shape-Persistent Zeolite Analogues: Covalent Organic Frameworks



Not much pressure: Taking advantage of the low volatility of ionic liquids, together with their excellent absorption of microwave radiation, highly oriented coatings of zeolites on metals have been prepared at ambient pressure (see picture; O red,

Al blue, P yellow, T = Al, P), thus circumventing the usual high pressures associated with zeolite synthesis. This technique offers a simplified synthesis that may be used in many other applications of zeolites.

Porous and highly ordered: After metal-organic frameworks (MOFs), which were first described over ten years ago, a new class of porous materials has been introduced: covalent organic frameworks (COFs), which are distinguished by high thermostabilities, large specific surface areas, and low densities. The example shows a model structure of COF-108.

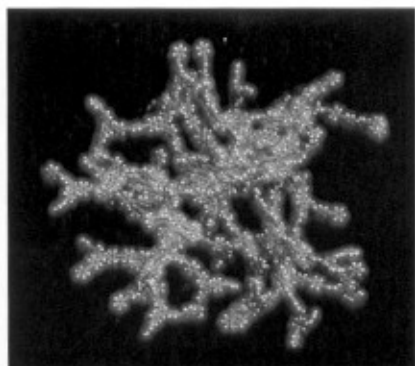


Microporous Materials

C. Weder* ————— 448–450

Hole Control in Microporous Polymers

Amorphous, but defined: The control of pore size in microporous polymers represents an important problem that is relevant to many applications. Several approaches have recently emerged to solve this problem. Highlighted here is a new study which shows that control over pore size can be achieved in amorphous conjugated polymer networks.



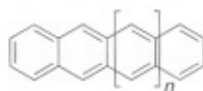
Reviews

Organic Electronics

J. E. Anthony* ————— 452–483

The Larger Acenes: Versatile Organic Semiconductors

Making acene: Semiconducting acenes are well suited for numerous organic electronic components, and their functionalization allows improvements in stability, solubility, and compatibility. Most importantly, however, the lifetime of the electronic components must be improved. Derivatives of acenes larger than pentacene have recently become available.



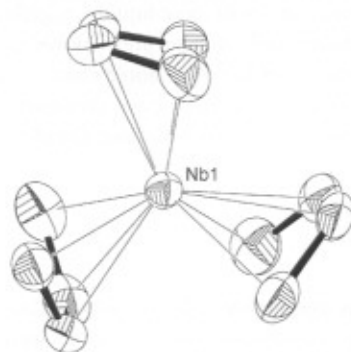
Communications

VIP Metalate Complexes

V. J. Sussman, J. E. Ellis* — 484–489

 From Storable Sources of Atomic Nb³⁺ and Ta³⁺ Ions to Isolable Anionic Tris(1,3-butadiene)metal Complexes: [M(η⁴-C₄H₆)₃][−], M = Nb, Ta

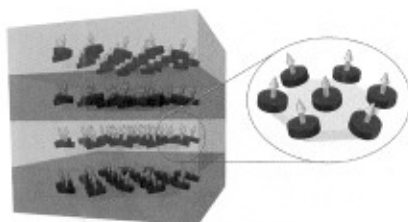
Hat trick: Homoleptic butadienemetalates of 4d and 5d metals have for the first time been structurally characterized. The niobium–naphthalene species [Nb(η⁴-C₁₀H₈)₂(PMe₃)₂][−] functions as a useful source of “naked” Nb³⁺ ions in its reaction with 1,3-butadiene to afford an unprecedented homoleptic niobium–butadiene complex [Nb(η⁴-C₄H₆)₃][−] (see structure). The tantalum analogue [Ta(η⁴-C₄H₆)₃][−] was obtained by a similar route.



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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.

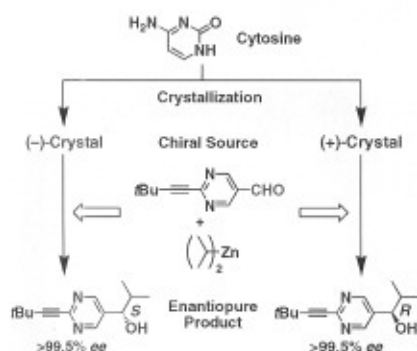


Layering up: The single-molecule magnets (SMMs) $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$ have been shown to exhibit liquid-crystalline phases. The mesophases can be smectic or cubic depending on the surface functionality imparted by the R group. A local squarelike arrangement of the cluster cores is observed within the smectic layers. This result is a first step towards the self-assembly of SMMs on surfaces by a bottom-up approach.

Single-Molecule Magnets

E. Terazzi, C. Bourgogne, R. Welter, J.-L. Gallani, D. Guillon, G. Rogez,*
B. Donnio* 490–495

Single-Molecule Magnets with Mesomorphic Lamellar Ordering



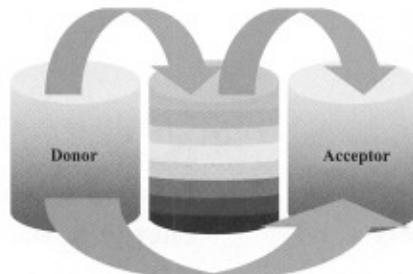
Crystals to add chirality: Cytosine, a prebiotic achiral biomolecule and an essential nucleobase, spontaneously forms enantioenriched crystals if stirring is applied during crystallization. The chiral crystal of achiral cytosine is a chiral initiator for asymmetric autocatalysis of a pyrimidyl alkanol with amplification of the *ee* value, which provides a nearly enantiopure alcohol with an absolute configuration correlated to that of the cytosine crystal.

Homochirality

T. Kawasaki, K. Suzuki, Y. Hakoda, K. Soai* 496–499

Achiral Nucleobase Cytosine Acts as an Origin of Homochirality of Biomolecules in Conjunction with Asymmetric Autocatalysis

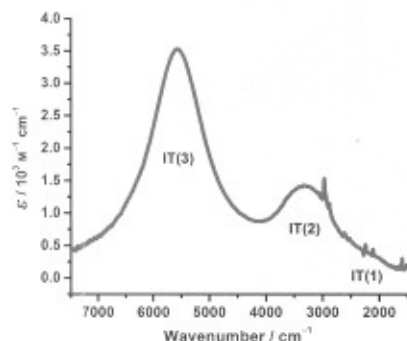
Donor, acceptor, and tuner: FRET-based ratiometric live-cell imaging captures emissions of two fluorophores within the constraints of a FRET pair. A method for engineering FRET-circuit-based biosensors has been developed by introducing an intermediate fluorophore, which facilitates energy transfer and allows tuning of the circuit efficiency. A protein kinase A biosensor was thus generated with a larger dynamic range than its precursors.



Fluorescent Biosensors

M. D. Allen, J. Zhang* 500–502

A Tunable FRET Circuit for Engineering Fluorescent Biosensors



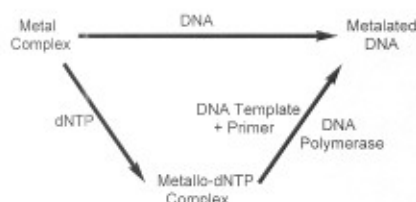
Multiple intervalence-transfer (IT) absorptions (see picture) appear in the near-IR/IR spectra of the mixed-valence complex $[\text{Cl}_3\text{Ru}^{\text{II}}(\text{tppz})\text{Ru}^{\text{III}}(\text{Cl}_3)]^-$ (tppz = tetrakis(2-pyridyl)pyrazine), whose X-ray crystal structure and electronic and vibrational spectroscopic features indicate localized-to-delocalized (Class II–III) behavior.

Mixed Valency

R. C. Rocha,* F. N. Rein, H. Jude, A. P. Shreve, J. J. Concepcion, T. J. Meyer* 503–506

Observation of Three Intervalence-Transfer Bands for a Class II–III Mixed-Valence Complex of Ruthenium





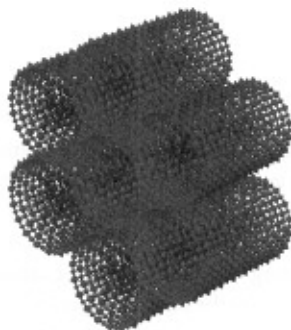
Metal bearing nucleobase: A model DNA polymerase and N7-metalated purine triphosphate nucleotide are used to show that metalated purines can be inserted into DNA during an enzymatic *in vitro* synthetic process (see scheme; dNTP = deoxynucleotide triphosphate). The possibility of site-specific metalation of DNA mediated by DNA polymerase is demonstrated.

Metalated DNA

M. Benedetti, C. Ducani, D. Migoni, D. Antonucci, V. M. Vecchio, A. Ciccarese, A. Romano, T. Verri, G. Ciccarella, F. P. Fanizzi* 507–510

Experimental Evidence That a DNA Polymerase Can Incorporate N7-Platinated Guanines To Give Platinated DNA

Holey Prussian blue, Batman! A family of mesostructured Prussian blue analogues has been developed by a ligand-assisted templating approach in formamide. These new materials are composed of cyanide-linked metal centers organized around alkyl pyrazinium templates with lamellar, hexagonal (see idealized structural model), or cubic periodicity. Evidence for valence delocalization and magnetic interactions in materials formed from $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ is presented.



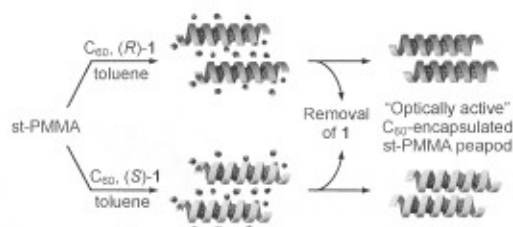
Mesostructures

X. Roy, L. K. Thompson, N. Coombs, M. J. MacLachlan* 511–514

Mesostructured Prussian Blue Analogues

A commodity plastic, syndiotactic poly(methyl methacrylate) (st-PMMA), has been found to fold into a right- or left-handed helix through the assistance of (*R*)- or (*S*)-1-phenylethanol (**1**) and

encapsulates fullerenes within its helical cavity to form a robust, processable, and optically active peapod-like complex whose helicity is retained after removal of the chiral alcohols.



Helical Structures

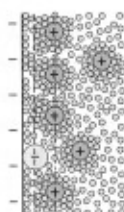
T. Kawauchi,* J. Kumaki,* A. Kitaura, K. Okoshi, H. Kusanagi, K. Kobayashi, T. Sugai, H. Shinohara, E. Yashima* 515–519

Encapsulation of Fullerenes in a Helical PMMA Cavity Leading to a Robust Processable Complex with a Macromolecular Helicity Memory

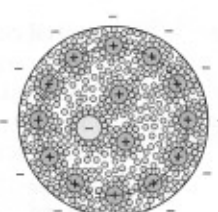
Carbon Materials

J. Huang,* B. G. Sumpter,
V. Meunier — 520–524

 Theoretical Model for Nanoporous Carbon Supercapacitors



EDLC



EDCC



EWCC

Importance of pore curvature: A theoretical model is proposed for nanoporous carbon supercapacitors to replace the commonly used one for an electric double-layer capacitor (EDLC) on the basis of an electric double-cylinder capacitor (EDCC) for mesopores, which

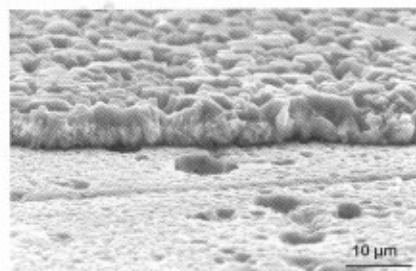
becomes an electric wire-in-cylinder capacitor (EWCC) for micropores (see picture; left to right: decreasing pore size). This model explains the experimental data in various pore ranges, showing the significance of pore curvature.

VIP Zeolite Coatings

R. Cai, M. Sun, Z. Chen, R. Munoz,
C. O'Neill, D. E. Beving,
Y. S. Yan* — 525–528

 Ionothermal Synthesis of Oriented Zeolite AEL Films and Their Application as Corrosion-Resistant Coatings

Does this coat your airplane? Zeolite coatings on aluminum alloys and other metals are a safe alternative to the commonly used, toxic chromate conversion coating. However, zeolite coatings are usually synthesized in aqueous medium under high pressure. Using an ionothermal method, an oriented SAPO-11 coating on an Al alloy was prepared at ambient pressure using microwave radiation. This coating shows exceptional corrosion resistance.

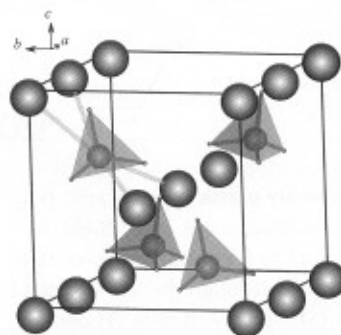


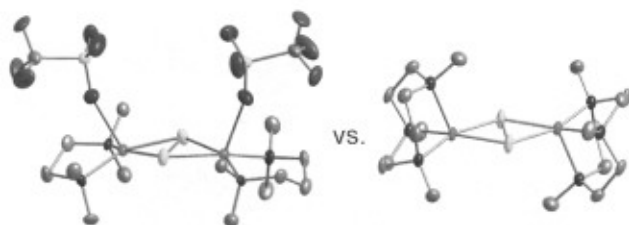
VIP Light-Metal Hydrides

Y. Filinchuk,* D. Chernyshov,
A. Nevidomskyy, V. Dmitriev — 529–532

 High-Pressure Polymorphism as a Step towards Destabilization of LiBH_4

Performing under pressure: The BH_4 group in the high-pressure modification of LiBH_4 has an unprecedented square-planar coordination by four Li atoms (see picture). This structure exhibits a strikingly short $\text{H}\cdots\text{H}$ contact between adjacent BH_4 anions and thus may show completely different hydrogen-storage properties if stabilized by chemical substitution at ambient pressure.





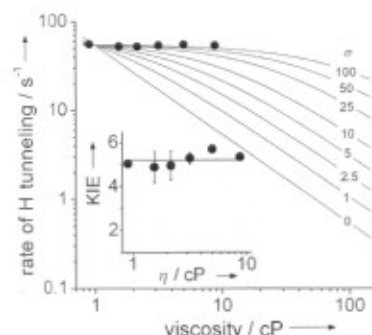
What a difference a ligand makes: A comparison of the reactivity of the two complexes shown (Cu green, S yellow, N blue, O red, F pink, C gray) has revealed new redox processes previously unseen

for copper-sulfur complexes. Furthermore, intriguing supporting-ligand effects on the properties of (disulfido)dicopper cores are uncovered.

Copper-Sulfur Complexes

I. Bar-Nahum, J. T. York, V. G. Young, Jr.,
W. B. Tolman* 533–536

Novel Reactivity of Side-On
(Disulfido)dicopper Complexes
Supported by Bi- and Tridentate Nitrogen
Donors: Impact of Axial Coordination

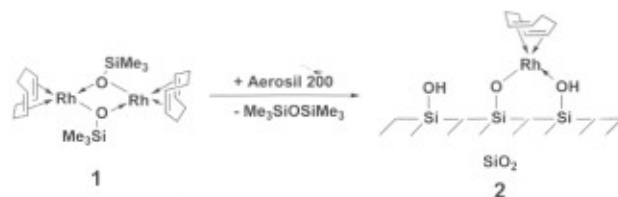


Light at the end of the tunnel? The rate and kinetic isotope effect of an enzymatic H-tunneling reaction are not dependent on solution viscosity (see picture), despite clear evidence that this reaction is coupled to promoting motions within the protein. This finding is in contrast to the viscosity dependence of conformationally gated electron-transfer reactions and suggests that the mechanisms of environmental gating of these reactions are different.

Enzyme Catalysis

S. Hay,* C. R. Pudney, M. J. Sutcliffe,
N. S. Scrutton* 537–540

Are Environmentally Coupled Enzymatic
Hydrogen Tunneling Reactions Influenced
by Changes in Solution Viscosity?



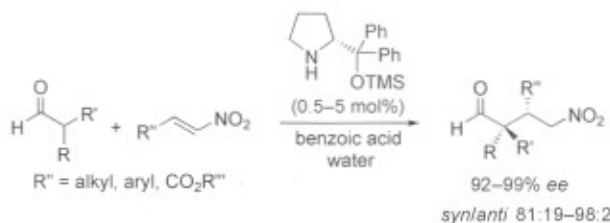
Rhodium siloxide surface complex 2, which was obtained directly by reaction of molecular precursor **1** with aerosil silica and characterized inter alia by solid-state

NMR spectroscopy, is a highly active and stable catalyst for hydrosilylation reactions.

Supported Catalysts

B. Marciniec,* K. Szubert,
M. J. Potrzebowski, I. Kownacki,
K. Łęszczak 541–544

Synthesis, Characterization, and Catalytic
Activity of a Well-Defined Rhodium
Siloxide Complex Immobilized on Silica



Organocatalysis: A highly effective catalytic procedure for the Michael addition of aldehydes to nitroalkenes is achieved by combining the excellent asymmetric induction ability of *o*-TMS-protected

diphenylprolinol compounds, the quick formation of enamines in the presence of benzoic acid, and the highly concentrated organic phase in water (see scheme; TMS = trimethylsilyl).

Nucleophilic Additions

S. Zhu, S. Yu, D. Ma* 545–548

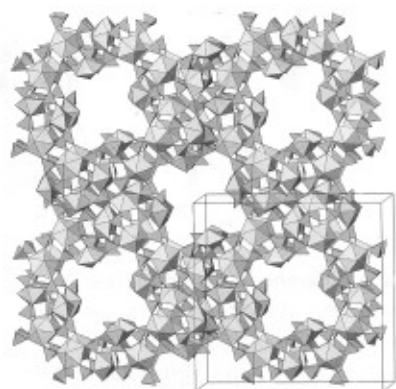
Highly Efficient Catalytic System for
Enantioselective Michael Addition of
Aldehydes to Nitroalkenes in Water

Microporous Frameworks

E. V. Alekseev, S. V. Krivovichev,*
W. Depmeier — 549–551

A Crown Ether as Template for
Microporous and Nanostructured
Uranium Compounds

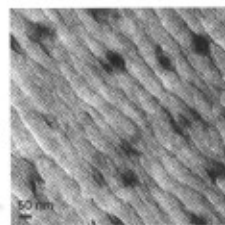
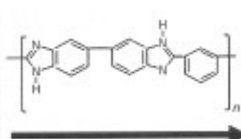
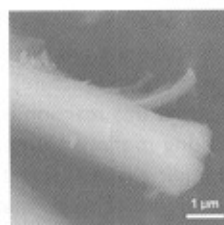
Highly porous uranyl compounds in which SO_4^{2-} or SeO_4^{2-} ions link adjacent U centers were prepared by using a crown ether as template. The uranyl sulfate (see picture; U- and S-centered polyhedra are yellow and green, respectively) has the lowest density so far reported for actinide oxide frameworks, while the uranyl selenate forms tubules that are separated by columns of $[(\text{H}_3\text{O})@([18]\text{crown-6})]^+$ complex cations.



Nanocomposite Membranes

S. Choi, J. Coronas, E. Jordan, W. Oh,
S. Nair, F. Onorato, D. F. Shantz,
M. Tsapatsis* — 552–555

Layered Silicates by Swelling of AMH-3
and Nanocomposite Membranes



Filling in: A new layered silicate material is prepared from a 3D porous silicate framework (AMH-3) by a novel procedure involving ion exchange and sequential intercalation. Layers of swollen AMH-3 are incorporated into a polymer, resulting in a

mixed-matrix nanocomposite (see picture). The room-temperature hydrogen/carbon dioxide ideal selectivity of the swollen nanocomposite membranes is improved by a factor of two compared to the pure polymer.

Ethylene Complexes

H. V. R. Dias,* M. Fianchini, T. R. Cundari,
C. F. Campana — 556–559

Synthesis and Characterization of the
Gold(I) Tris(ethylene) Complex
 $[\text{Au}(\text{C}_2\text{H}_4)_3][\text{SbF}_6]$

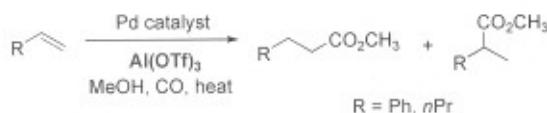
Ethylene el dorado: Gold(I) unusually takes up three ethylene molecules in a spoked-wheel arrangement (see picture). The complex was synthesized as the hexafluoroantimonate salt and structurally characterized.



Methoxycarbonylation

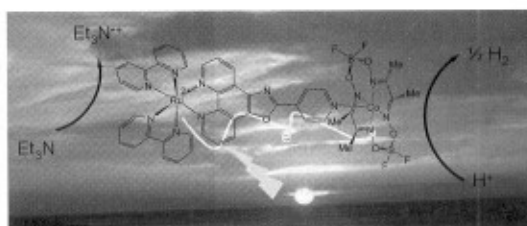
D. B. G. Williams,* M. L. Shaw,
M. J. Green, C. W. Holzapfel — 560–563

Aluminum Triflate as a Highly Active and
Efficient Nonprotic Cocatalyst in the
Palladium-Catalyzed
Methoxycarbonylation Reaction



Lewis does it better: Aluminum triflate readily replaces Brønsted acid cocatalysts in the palladium-catalyzed methoxycarbonylation reaction of styrene and 1-pentene, producing catalysts that are

stable and more active than those using traditional acids. Catalyst loadings of 0.02% allow conversions of up to 100% to be achieved within three hours with no loss of linear/branched ester selectivity.



It is the dawning of the age of supra-molecular photocatalysts for H_2 production using first-row transition-metal catalytic centers. These catalysts consist of a ruthenium tris(diimine) light-harvesting unit covalently linked to various catalytic

cobaloxime centers (see picture). The catalyst stability, Co^{II}/Co^I redox potential, and nucleophilicity of the cobaloxime moiety all affect the photocatalytic properties.

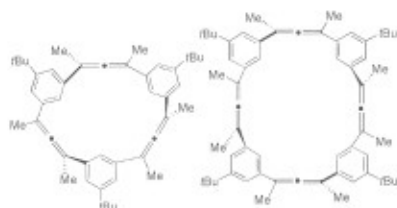
Photocatalysis

A. Fihri, V. Artero,* M. Razavet, C. Baffert, W. Leibl, M. Fontecave — 564–567

Cobaloxime-Based Photocatalytic Devices for Hydrogen Production



Around and around: A strategy based on sequential Pd-catalyzed cross-coupling reactions was applied for the asymmetric synthesis of new macrocyclic *meta*-allenophanes composed of 18- or 24-membered rings (see structures). The chiral components, tertiary propargyl alcohols and allene bridges, were assembled by a general enantioselective protocol, which involved a Sharpless epoxidation, an oxidation, and Sonogashira cross-coupling.



Asymmetric Synthesis

M. Leclère, A. G. Fallis* — 568–572

Asymmetric Allenophanes: Synthesis of a Tris-*meta*-allenophane and Tetrakis-*meta*-allenophane by Sequential Cross-Coupling

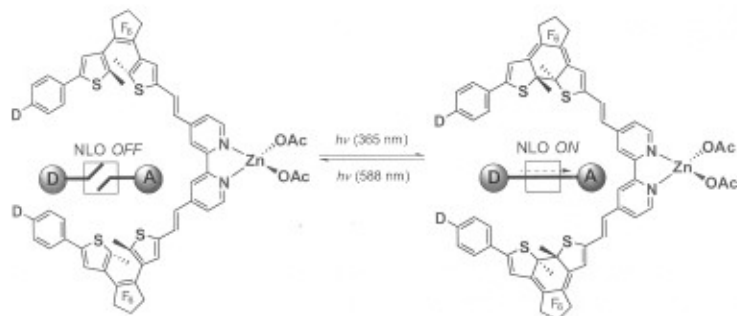
Zinc clusters: The first simple alkylzinc carboxylate provides insights into the previously unexplored oxygenation and sulfuration of alkylzinc complexes supported by carboxylate ligands (see picture).



Oxygen and Sulfur Activation

J. Lewiński,* W. Bury, M. Dutkiewicz, M. Maurin, I. Justyniak, J. Lipkowski — 573–576

Alkylzinc Carboxylates as Efficient Precursors for Zinc Oxocarboxylates and Sulfidocarboxylates



Flipping the switch: A new type of bipyridine-based ligand functionalized by phenyl- and dimethylaminophenyldithienylethene groups allows the preparation

of photochromic dipolar zinc(II) complexes. For the first time, efficient on/off photoswitching of the NLO response of metallochromophores is observed.

Nonlinear Optics

V. Aubert, V. Guerschais, E. Ishow, K. Hoang-Thi, I. Ledoux, K. Nakatani, H. Le Bozec* — 577–580

Efficient Photoswitching of the Nonlinear Optical Properties of Dipolar Photochromic Zinc(II) Complexes

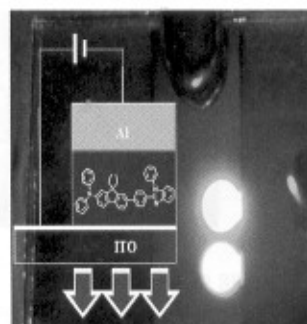


Electroluminescent Materials

M.-Y. Lai, C.-H. Chen, W.-S. Huang,
J. T. Lin,* T.-H. Ke, L.-Y. Chen, M.-H. Tsai,
C.-C. Wu* 581–585

-  Benzimidazole/Amine-Based Compounds Capable of Ambipolar Transport for Application in Single-Layer Blue-Emitting OLEDs and as Hosts for Phosphorescent Emitters

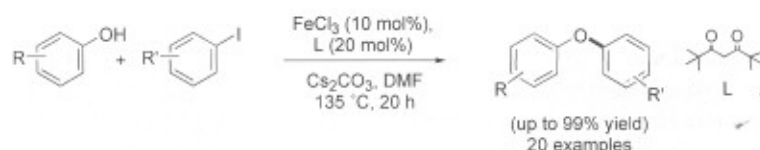
A bolt from the blue? Compounds like that shown containing benzimidazole and arylamine units exhibit intriguing ambipolar carrier-transport properties and can be used to fabricate single-layer blue-emitting electroluminescent devices with very promising performances (see picture, ITO = indium tin oxide).



Cross-Coupling

O. Bistri, A. Correa, C. Bolm* 586–588

-  Iron-Catalyzed C–O Cross-Couplings of Phenols with Aryl Iodides



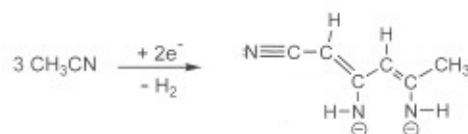
Low-price coupling: A versatile, practical, and cost-efficient iron-catalyzed O-arylation protocol is applied to the synthesis of

a variety of diaryl ethers, which are formed in high yields. Best results were obtained by using FeCl_3 and a β -diketo ligand.

Actinide Chemistry

W. J. Evans,* K. A. Miller,
J. W. Ziller 589–592

-  Reductive Coupling of Acetonitrile by Uranium and Thorium Hydride Complexes To Give Cyanopentadienyl Dianion ($\text{C}_5\text{N}_3\text{H}_7$)^{2−}



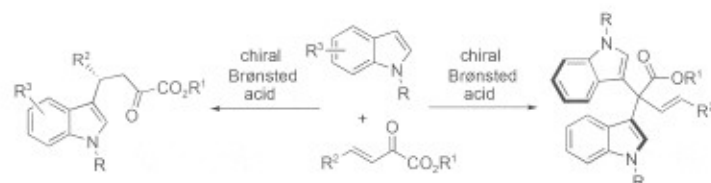
The actinide metallocene hydrides $[(\text{C}_5\text{Me}_5)_2\text{UH}]_2$ and $[(\text{C}_5\text{Me}_5)_2\text{ThH}_2]_2$ convert three equivalents of acetonitrile into a polydentate ligand containing a six

carbon atom chain (see scheme). These reactions show that a Th^{IV} hydride moiety can undergo chemistry similar to U^{III} in a multistep reaction.

Organocatalysis

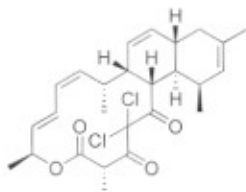
M. Rueping,* B. J. Nachtsheim,
S. A. Moreth, M. Bolte 593–596

-  Asymmetric Brønsted Acid Catalysis: Enantioselective Nucleophilic Substitutions and 1,4-Additions



Executive decision: Depending on the catalyst (both *N*-triflylphosphoramides), the highly enantioselective Brønsted acid catalyzed addition of indoles to α,β -unsaturated carbonyl compounds provides either α -keto esters (up to 92% *ee*,

left side of the scheme), or a novel type of bisindole (right), which displays atropisomerism. The α -keto esters can also be converted into amino acids by a one-pot 1,4-addition-reductive amination reaction.

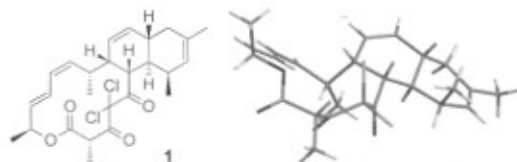


Stacking the deck: The natural product chlorotonil A contains an unprecedented motif in which a CCl_2 unit in a 14-membered macrolide framework is flanked by two carbonyl groups. In the first total synthesis of chlorotonil A a highly selective intramolecular Diels–Alder reaction was employed to generate the decalin system.

Total Synthesis

N. Rahn, M. Kalesse* — 597–599

The Total Synthesis of Chlorotonil A



Previously unknown: *gem*-Dichloro-1,3-diones were unprecedented as natural compounds, but chlorotonil A (**1**) features this functionality in a 14-membered lactone ring. Compound **1** was isolated from

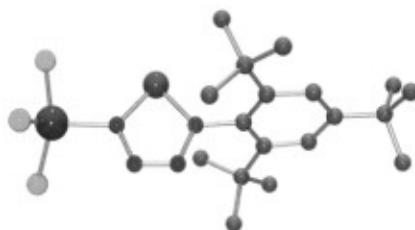
the myxobacterium *Sorangium cellulosum* and its structure elucidated. The poor solubility of **1** in both organic solvents and water again raises the old question of why bacteria create such complex metabolites.

Structure Elucidation

K. Gerth, H. Steinmetz, G. Höfle, R. Jansen* — 600–602

Chlorotonil A, a Macrolide with a Unique *gem*-Dichloro-1,3-dione Functionality from *Sorangium cellulosum*, So ce 1525

Group 15 galore: A new five-membered ring containing only nitrogen and arsenic was synthesized by a GaCl_3 -assisted [3+2] cycloaddition. The novel tetrazarsole was stabilized as the GaCl_3 adduct (see structure; Cl green, Ga purple, N blue, As red, C gray).



Arsenic–Nitrogen Compounds

A. Schulz,* A. Villingner — 603–606

Tetrazarsoles—A New Class of Binary Arsenic–Nitrogen Heterocycles

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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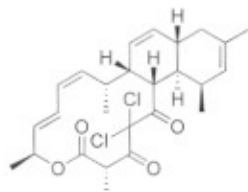
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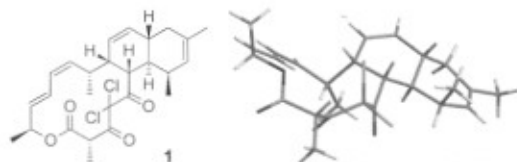


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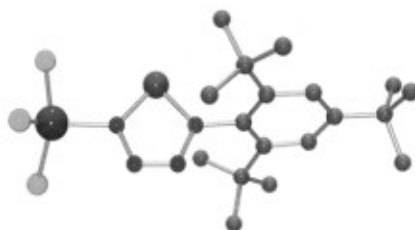
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