VIP *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:*

*G. E. Veitch, E. Beckmann, B. J. Burke, A. Boyer, C. Ayats, S. V. Ley**
A New Relay Route for the Synthesis of Azadirachtin

I. Paterson, E. A. Anderson, A. D. Findlay*
Synthesis of an Advanced C10–C32 Spiroacetal Fragment and Assignment of the Absolute Stereochemistry of Spirangien A

*B. L. J. Kindler, P. Spiteller**
Chemical Defence of the Crust Fungus *Aleurodiscus amorphus* by a Tailor-Made Cyanogenic Cyanohydrin Ether

*G. V. Zyryanov, M. A. Palacios, P. Anzenbacher, Jr.**
Rational Design of a Fluorescence Turn-On Sensor Array for Phosphates in Blood Serum

S. Shimizu, T. Kiuchi, N. Pan*
A Teflon-Footed Resorcinarene: Hexameric Capsule in Fluorous Solvents and Fluorophobic Effects on Molecular Encapsulation

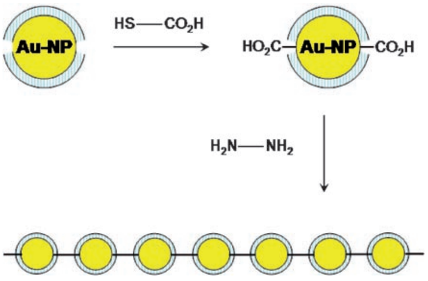
P. Mukhopadhyay, G. Zuber, P. Wipf, D. N. Beratan
Contribution of a Chiral Solvent Imprint of a Solute to Optical Rotation

Obituary

Books

Highlights

Nanostructures



Threading nanobeads: Gold nanoparticles (NPs) coated with functional organic ligands are candidate building blocks for the bottom-up fabrication of nanostructured materials. This Highlight describes a recent approach to achieving bidirectional NP–NP connectivity, which is an essential step in the assembly of NP-based polymers (see scheme) and more complex nanoarchitectures.

Essays

History of Chemistry

A double jubilee: This year marks the 50th anniversary of the discovery of the Asinger reaction—the original version a three-component reaction for the direct synthesis of thiazolines from elemental sulfur, ammonia, and a carbonyl component—and the centennial anniversary of the birth of its eponym, Friedrich Asinger (1907–1999).

Contents

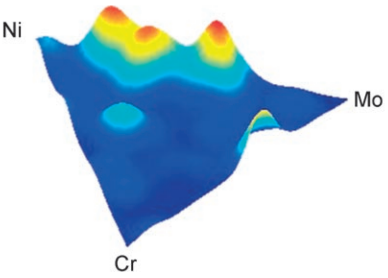
Reviews

Materials Research

W. F. Maier,* K. Stöwe,
S. Sieg _______________ **6016 – 6067**

Combinatorial and High-Throughput Materials Science

Combinatorial discovery: High-throughput techniques are already used routinely for research on complex materials, such as polymers, electronic materials, and catalysts. Remarkable achievements are related to parallel syntheses and analyses, data-mining technologies, modeling approaches, as well as evolutionary strategies for materials development and formulations. The discoveries and success stories document the power of these emerging technologies.



Communications

Polypeptide Synthesis

H. Sun,* J. Zhang, Q. Liu, L. Yu,
J. Zhao _______________ **6068 – 6072**

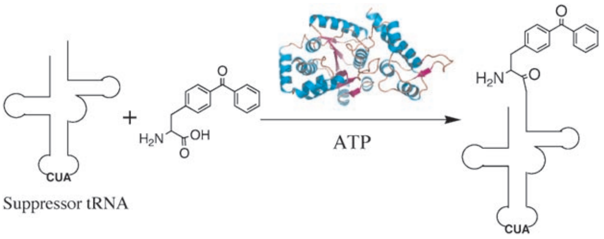
Metal-Catalyzed Copolymerization of Imines and CO: A Non-Amino Acid Route to Polypeptides

The path less taken: Copolymerization of imines and carbon monoxide has long been highly desirable as a route to synthesize polypeptides, but has been difficult to implement because of the lack of appropriate catalysts. This reaction has now been realized for the first time by using a simple cobalt catalyst (see scheme).

Nonnatural Amino Acids

W. Liu, L. Alfonta, A. V. Mack,
P. G. Schultz* _______________ **6073 – 6075**

Structural Basis for the Recognition of *para*-Benzoyl-L-phenylalanine by Evolved Aminoacyl-tRNA Synthetases



Nonnatural interactions: The X-ray crystal structure of a mutant aminoacyl-tRNA synthetase that selectively recognizes *para*-benozyl-L-phenylalanine has been solved. This structure shows that mutations to the enzyme lead to new hydrophobic binding interactions with the unnatural amino acid, and a loss of specific hydrogen-bonding interactions with tyrosine, without a significant change in the polypeptide backbone conformation.

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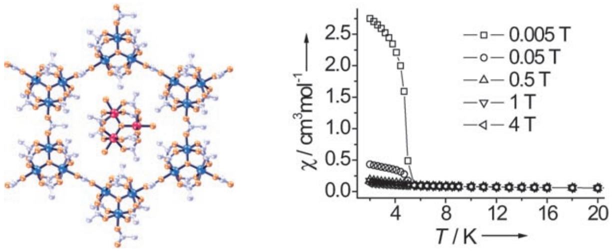
Frustrated Magnets

Y.-Z. Zheng, M.-L. Tong, W. Xue, W.-X. Zhang, X.-M. Chen,* F. Grandjean, G. J. Long* **6076 – 6080**

A "Star" Antiferromagnet: A Polymeric Iron(III) Acetate That Exhibits Both Spin Frustration and Long-Range Magnetic Ordering

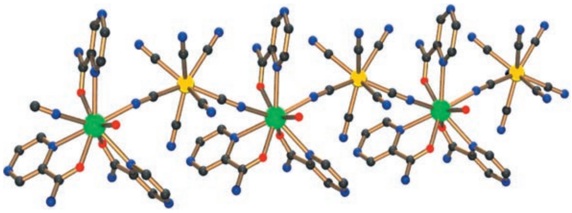


Star formation: Polymeric $[Fe_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6(H_2O)_3][Fe_3(\mu_3\text{-}O)\mu\text{-}OAc)_{7.5}]_2\cdot 7\,H_2O$ is synthesized by linking triangular $\{Fe_3\text{-}(\mu_3\text{-}O)\}$ clusters through *anti-anti* bridging acetate ligands (see picture; red and blue: Fe, orange: O). Spin frustration and long-range magnetic order coexist in this compound below 4.5 K (see graph).

Heterometallic Complexes

F. Prins, E. Pasca, L. J. de Jongh,* H. Kooijman, A. L. Spek, S. Tanase* **6081 – 6084**

Long-Range Magnetic Ordering in a Tb^{III}–Mo^{V} Cyanido-Bridged Quasi-One-Dimensional Complex



One-dimensional polymer $[Tb(pzam)_3(H_2O)Mo(CN)_8]\cdot H_2O$ (see picture, pzam = pyrazine-2-carboxamide; C black, Mo yellow, N blue, O red, Tb green) has been synthesized and characterized. Its magnetic susceptibility data indicate substantial ferromagnetic superexchange between Tb^{III} and Mo^{V} via the cyanido bridge, and the occurrence of long-range magnetic ordering between chains at $T_c \approx 1$ K.

Microreactors

A. Kishimura, A. Koide, K. Osada, Y. Yamasaki, K. Kataoka* **6085 – 6088**

Encapsulation of Myoglobin in PEGylated Polyion Complex Vesicles Made from a Pair of Oppositely Charged Block Ionomers: A Physiologically Available Oxygen Carrier

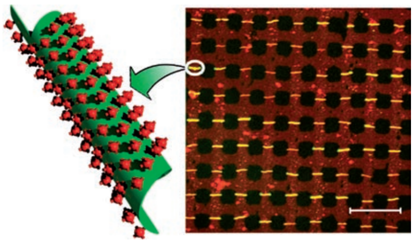
Take your PIC: Biologically active polyion complex vesicles (PICsomes) with encapsulated myoglobin (Mb) can be prepared by the self-assembly of a pair of oppositely charged block ionomers with polyethylene glycol (PEG) segments (see picture; metMb: metmyoglobin). The loaded Mb maintains reversible oxygenation even in the presence of trypsin.

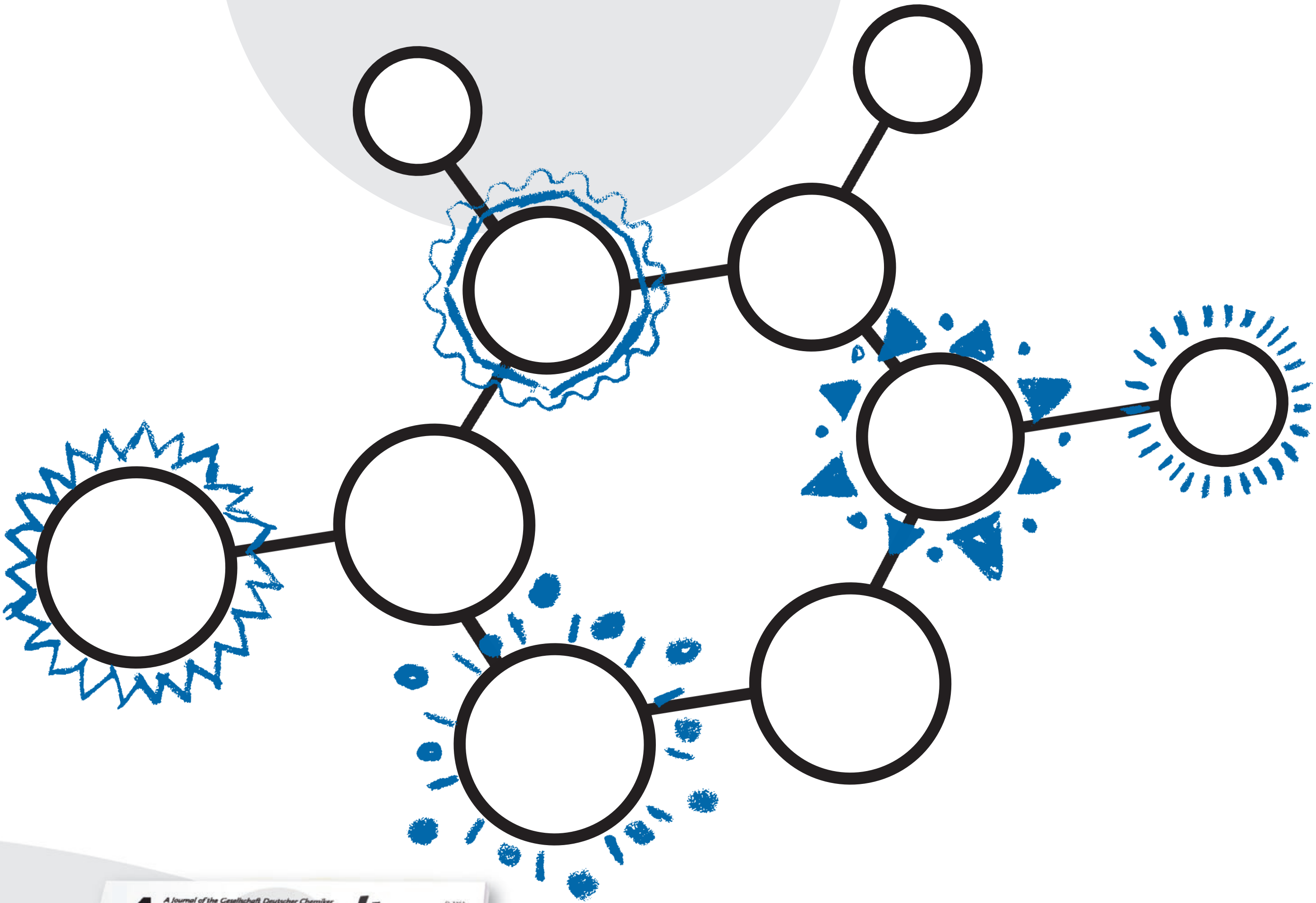
Nanotechnology

C. Lin, Y. Ke, Y. Liu, M. Mertig, J. Gu, H. Yan* **6089 – 6092**

Functional DNA Nanotube Arrays: Bottom-Up Meets Top-Down

Meeting in the middle: Well-organized arrays of self-assembled functional DNA nanotubes can be constructed by combining bottom-up and top-down methods. Such DNA-nanotube arrays allow the construction of arrays of quantum dots, proteins, and DNA targets (see picture; green: DNA nanotube, red: streptavidin–quantum dot conjugate; scale bar: 20 μm).






Angewandte Chemie
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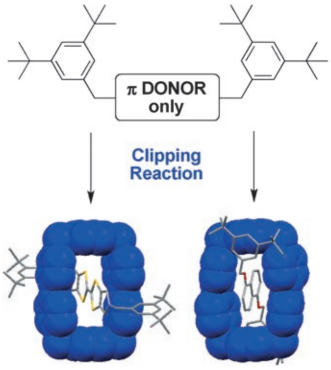
Magnetic
Materials
WILEY-VCH

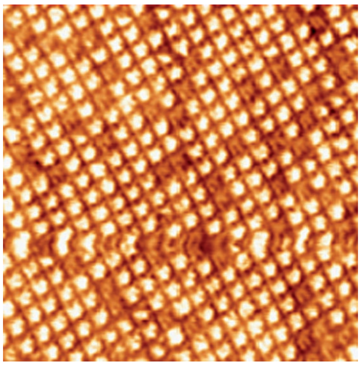


Completely armless: The efficient synthesis of two sterically confined [2]rotaxanes has shown that oligoethylene glycol arms are not requisites for a clipping reaction to form π-donor/acceptor [2]rotaxanes (see scheme). The rigid nature of the [2]rotaxanes forces the tetracationic cyclophane to encapsulate the initially π-electron-rich station, regardless of its oxidation state, thus generating tunable properties and enhanced stabilities.

[2]Rotaxanes

S. Nygaard, B. W. Laursen, T. S. Hansen, A. D. Bond, A. H. Flood, J. O. Jeppesen* ———— **6093 – 6097**

Preparation of Cyclobis(paraquat-*p*-phenylene)-Based [2]Rotaxanes Without Flexible Glycol Chains

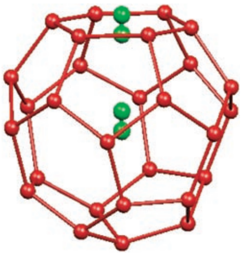


Potential causes: The combination of potential-pulse perturbation and STM has shown that the interfacial oxidation of an adsorbed 5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-porphine (TPyP) monolayer at the Au(111)/0.1 M H_2SO_4 interface is spacially heterogeneous (see STM image; dark spots: oxidized TPyP, light spots: nonoxidized TPyP). The distribution of the oxidized TPyP molecules on the surface depends on the oxidation potential and varies with time.

Electron Transfer

Y. He, E. Borguet* ———— **6098 – 6101**

Dynamics of Porphyrin Electron-Transfer Reactions at the Electrode–Electrolyte Interface at the Molecular Level



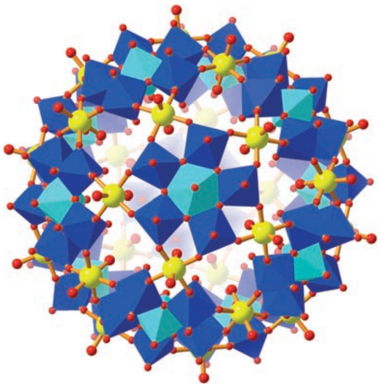
Escape! Electronic-structure calculations have been used to estimate the energy barriers to the migration of H_2 guest molecules from the cages of the structure-II clathrate hydrate (see picture; H green, O red). The escape rates from the cages were calculated using an Arrhenius expression with a tunneling correction.

Electronic-Structure Calculations

S. Alavi,* J. A. Ripmeester — **6102 – 6105**

Hydrogen-Gas Migration through Clathrate Hydrate Cages

Stuck in the middle with you: The spherical cluster $\{(\mathrm{Mo})\mathrm{Mo}_5\}_{12}\mathrm{Cr}_{30}$ (**1**) fills, with its spin, a gap in the series of the analogous Fe ($S=5/2$) and V ($S=1/2$) clusters. This allows a deeper understanding of the magnetic properties of the series members, particularly with reference to geometric frustration, also found in the famous Kagomé lattices. The spherical clusters can be considered as coordination polymers with spherical periodicity which contain unique pentagonal molybdenum oxide based ligands.



Magnetic Properties

A. M. Todea, A. Merca, H. Bögge, J. van Slageren, M. Dressel, L. Engelhardt, M. Luban, T. Glaser, M. Henry, A. Müller* ———— **6106 – 6110**

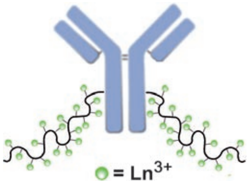
Extending the $\{(\mathrm{Mo})\mathrm{Mo}_5\}_{12}\mathrm{M}_{30}$ Capsule Keplerate Sequence: A $\{\mathrm{Cr}_{30}\}$ Cluster of $S=3/2$ Metal Centers with a $\{\mathrm{Na}(\mathrm{H}_2\mathrm{O})_{12}\}$ Encapsulate

Contents

Bioassays

X. Lou, G. Zhang, I. Herrera, R. Kinach, O. Ornatsky, V. Baranov,* M. Nitz,* M. A. Winnik* ______ **6111–6114**

Polymer-Based Elemental Tags for Sensitive Bioassays

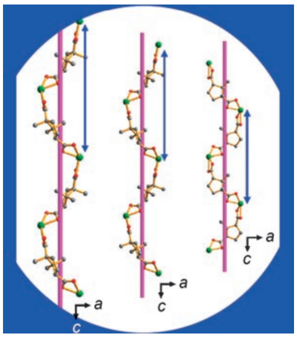


It's elemental: A water-soluble polymer bearing multiple metal-chelating ligands has been used as a tag for bioassays with inductively coupled plasma mass spectrometry. The tag was covalently conjugated to antibodies, and the polymer–antibody constructs were loaded with lanthanide ions (Ln^{3+}) and used for the simultaneous assay of five orthogonally labeled antibodies against cell surface antigens that differ in abundance by more than two orders of magnitude.

Chiral Frameworks

J. Zhang, X. Bu* ______ **6115–6118**

Chiralization of Diamond Nets: Stretchable Helices and Chiral and Achiral Nets with Nearly Identical Unit Cells



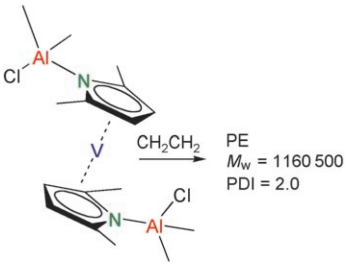
Stretchable diamond nets: Homochiral and achiral diamond nets with nearly identical unit cells have been found in a family of 3D framework materials containing flexible helical substructures (see picture; Cd green, O red, C gray). Such structures raise intriguing prospects for developing general strategies for the direct conversion of achiral four-connected networks into homochiral networks through ligand substitution.

Catalyst Design

A. Jabri, I. Korobkov, S. Gambarotta,* R. Duchateau* ______ **6119–6122**

Single-Site, Single-Component Catalysts for Very High Molecular Weight Polyethylene: A Robust "Ready-To-Go" Vanadium π-Bonded Complex Without a Preformed V–C Bond

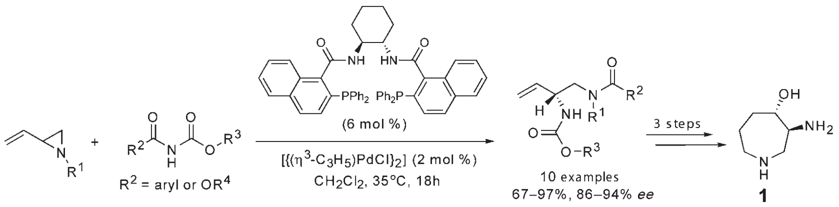
On its own: A vanadium(II) bis(pyrrolide) complex with a vanadocene-type structure is a single-component catalyst for the preparation of ultrahigh molecular weight polyethylene (PE; see scheme; M_w = weight-average molecular weight, PDI = polydispersity index).



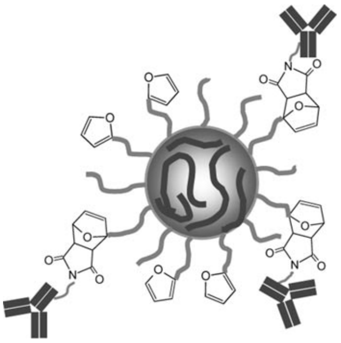
Asymmetric Catalysis

B. M. Trost,* D. R. Fandrick, T. Brodmann, D. T. Stiles ______ **6123–6125**

Dynamic Kinetic Asymmetric Allylic Amination and Acyl Migration of Vinyl Aziridines with Imido Carboxylates



An atom-economical method has been developed for the preparation of chiral vicinal diamines through a dynamic kinetic asymmetric allylic amination and acyl-group migration of vinyl aziridines with imido carboxylates. Application of the asymmetric transformation enabled the concise synthesis of the azepane core **1** of (+)-balanol and its *syn* analogue.



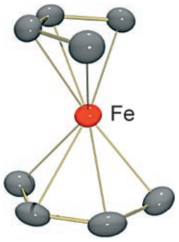
Hitting the target: Self-assembled polymeric nanoparticles from an amphiphilic copolymer were prepared with furan groups on the outer polyethylene glycol corona that were accessible for Diels–Alder reactions with maleimide-functionalized antibodies for the preparation of immuno-nanoparticles (see picture). The simple and clean coupling methodology allows facile modification of nanoparticles for use in targeted delivery to cancer cells.

Bioorganic Chemistry

M. Shi, J. H. Wosnick, K. Ho, A. Keating, M. S. Shoichet* ———— **6126 – 6131**

Immuno-Polymeric Nanoparticles by Diels–Alder Chemistry

Magnetic personalities: $[Fe(\eta^4\text{-}C_{14}H_{10})_2]^-$ is an unprecedented example of an anionic 17-electron homoleptic polyarene transition-metal complex. This species is the first isolable homoleptic polyarene iron complex. It provides "naked" atomic Fe^{-I} in its reaction with 1,3-butadiene to yield the first structurally authenticated homoleptic bis(1,3-butadiene) metal complex, $[Fe(\eta^4\text{-}C_4H_6)_2]^-$ (see structure).



Organometallic Metalate Complexes

W. W. Brennessel, R. E. Jilek, J. E. Ellis* ———— **6132 – 6136**

Bis(1,2,3,4-η^4-anthracene)ferrate(1−): A Paramagnetic Homoleptic Polyarene Transition-Metal Anion

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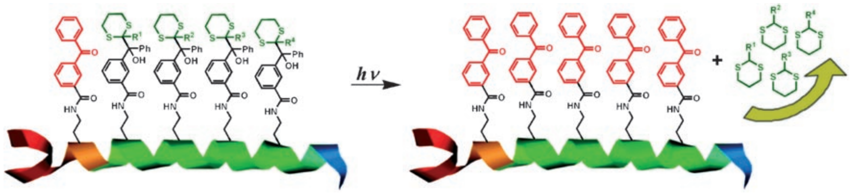

Binary encoding and amplification can be achieved in linear polypeptide-based scaffolds of photoactive dithiane adducts. QA masked sensitizer is tethered to lysine and incorporated in a peptide chain terminated with a sensitizer (see picture). When illuminated, the sensitizer induces fragmentation, thus unmasking more sensitizer and resulting in a linear domino photoamplification effect.

Photoamplification

K. Majjigapu, J. R. R. Majjigapu, A. G. Kutateladze* ———— **6137 – 6140**

Photoamplification and Multiple Tag Release in a Linear Peptide-Based Array of Dithiane Adducts

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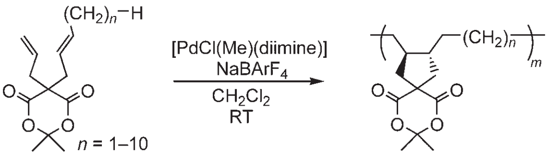


Walk the line: Cyclopolymerization of 1,6-dienes with vinyl and vinylene groups catalyzed by Pd^{II}–diimine complexes causes chain walking of the growing polymer. This isomerization leads to polymers with *trans*-1,2-disubstituted cyclopentane groups located regularly along the linear polymer chain (see scheme). The polymerization is applicable for dienes with various functional groups.

Controlled Polymer-Chain Growth

T. Okada, S. Park, D. Takeuchi, K. Osakada* ———— **6141 – 6143**

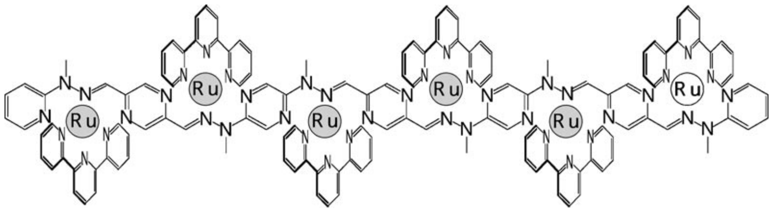
Pd-Catalyzed Polymerization of Dienes that Involves Chain-Walking Isomerization of the Growing Polymer End: Synthesis of Polymers Composed of Polymethylene and Five-Membered-Ring Units

Contents

Supramolecular Chemistry

F. Loiseau, F. Nastasi, A.-M. Stadler,
S. Campagna,* J.-M. Lehn* **6144 – 6147**

Molecular Wire Type Behavior of Polycationic Multinuclear Rack-Type Ru^{II} Complexes of Polytopic Hydrazone-Based Ligands

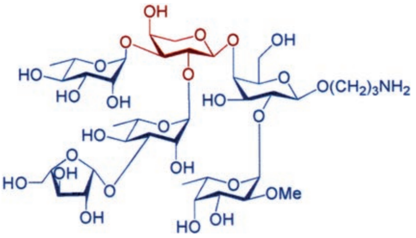


On the rack: Splitting of the peripheral metal-based oxidation, which indicates a large coupling between the redox sites, has been obtained in polymetallic arrays composed of rack-type complexes containing two, three, four, or six Ru^{II} subunits appended to hydrazone-based molecular strands (see picture). The relatively small coupling attenuation parameter calculated for the metal-based, cationic subunit(s) suggests molecular-wire behavior.

Carbohydrate Synthesis

Y. Rao, G.-J. Boons* ______ **6148 – 6151**

A Highly Convergent Chemical Synthesis of Conformational Epitopes of Rhamnogalacturonan II

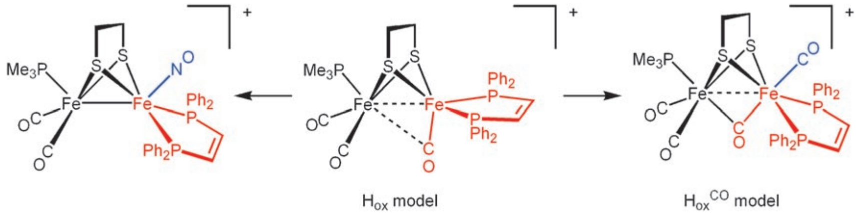


Upon careful tuning of the reactivity of glycosyl donors and acceptors, tetra- and hexasaccharide fragments (see structure) of the B chain of rhamnogalacturonan II (RGII) were prepared in a convergent and stereoselective manner. The conformation of the central arabinopyranosyl ring (red) was found to depend on the saccharide substitution pattern. This conformational epitope may influence the biological functions of RGII.

Hydrogenase Models

A. K. Justice, T. B. Rauchfuss,*
S. R. Wilson ______ **6152 – 6154**

Unsaturated, Mixed-Valence Diiron Dithiolate Model for the H_{ox} State of the [FeFe] Hydrogenase



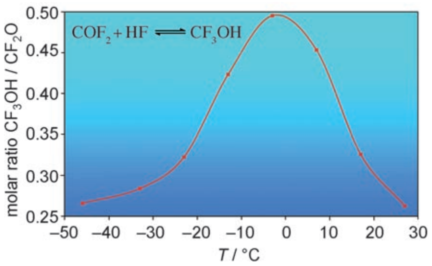
Chemists are closing in on functional and structural models for the [FeFe] hydrogenases. Oxidation of $[Fe_2(S_2C_2H_4)(CO)_3(PMe_3)(dppv)]$ (dppv = *cis*-1,2-$C_2H_2(PPh_2)_2$) by one electron affords a mixed-valence model for the H_{ox} state of the active site of the [FeFe] hydrogenases. Like the enzyme, this model exhibits the "rotated structure" and binds CO (see scheme). The radical character of the model is confirmed by its ready binding of NO.

Perfluorinated Compounds

K. O. Christe,* J. Hegge, B. Hoge,
R. Haiges ______ **6155 – 6158**

Convenient Access to Trifluoromethanol

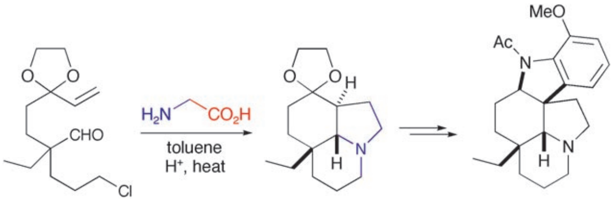
From chimera to useful reagent: Easy access to trifluoromethanol in a one-step reaction from readily available inexpensive bulk chemicals opens the door for CF_3OH to become a useful general reagent in synthetic chemistry and industrial applications.



Alkaloid Synthesis

I. Coldham,* A. J. M. Burrell, L. E. White, H. Adams, N. Oram **6159 – 6162**

Highly Efficient Synthesis of Tricyclic Amines by a Cyclization/Cycloaddition Cascade: Total Syntheses of Aspidospermine, Aspidospermidine, and Quebrachamine

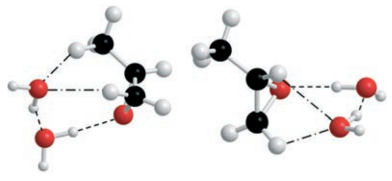


Three in one: Three new rings can be made in one pot with complete control of the regio- and stereochemistry by a tandem cyclization/cycloaddition cascade reaction. Treatment of a chloroaldehyde with an amine gives a cyclic azomethine ylide that undergoes intramolecular cycloaddition onto a tethered alkene. The method was applied to the shortest known synthesis of aspidospermine (see scheme).

Hydration

Z. Su, Y. Xu* **6163 – 6166**

Hydration of a Chiral Molecule: The Propylene Oxide···(Water)$_2$ Cluster in the Gas Phase



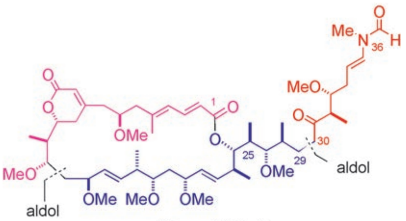
syn PO···$(H_2O)_2$ *anti* PO···$(H_2O)_2$

Bridging the gap between a binary system and a solute in aqueous solution: Conformers of the ternary cluster propylene oxide (PO)···$(H_2O)_2$ were studied using rotational spectroscopy and high-level ab initio calculations. The experimental observation shows that the *anti* conformer is favored over the *syn* conformer, opposite to what was detected for PO···H_2O, but in accord with what was predicted for PO in water.

Natural Product Synthesis

I. Paterson,* K. Ashton, R. Britton, G. Cecere, G. Chouraqui, G. J. Florence, J. Stafford **6167 – 6171**

Total Synthesis of (−)-Reidispongiolide A, an Actin-Targeting Marine Macrolide



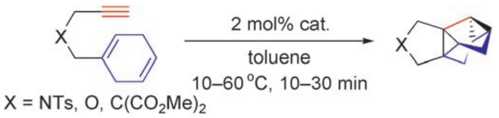
reidispongiolide A

Actin class: A stereoselective synthesis of the microfilament-destabilizing cytotoxic macrolide (−)-reidispongiolide A, isolated from the marine sponge *Reidispongia coerulea*, uses a convergent aldol-based strategy to construct the 26-membered macrolactone, followed by a coupling with an *N*-vinylformamide subunit. This constitutes the first synthesis of any member of the reidispongiolide/sphinxolide family.

Cycloisomerization

S. M. Kim, J. H. Park, S. Y. Choi, Y. K. Chung* **6172 – 6175**

(N-Heterocyclic Carbene)Gold(I)-Catalyzed Cycloisomerization of Cyclohexadienyl Alkynes to Tetracyclo[3.3.0.0^{2,8}.0^{4,6}]octanes



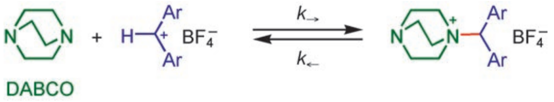
Biscyclopropanation: Dienynes containing a cyclohexadienyl unit can be converted into tetracyclo[3.3.0.0^{2,8}.0^{4,6}]octanes by treatment with an (N-heterocyclic carbene)gold catalyst. When the dienynes bear an open-chain diene instead of cyclohexadiene, open-cage compounds, with two sides missing from the cage, are obtained.

Contents

Organocatalysis

M. Baidya, S. Kobayashi, F. Brotzel,
U. Schmidhammer, E. Riedle,
H. Mayr* ______________ **6176 – 6179**

DABCO and DMAP—Why Are They Different in Organocatalysis?



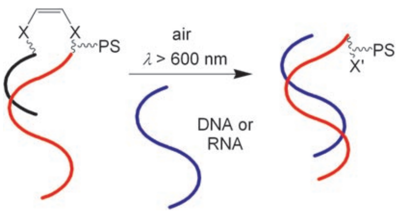
What makes a good organocatalyst? DABCO (1,4-diazabicyclo[2.2.2]octane) is a thousandfold better nucleophile ($k_{\rightarrow}$) and at the same time a million times better leaving group ($k_{\leftarrow}$) than DMAP (4-(dimethylamino)pyridine). This apparent contradiction is resolved by consideration of the intrinsic reaction barriers.

Photoactivatable Compounds

A. Rotaru, A. Mokhir* ______ **6180 – 6183**

Nucleic Acid Binders Activated by Light of Selectable Wavelength

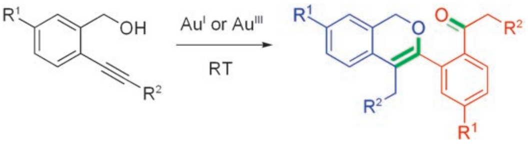
Let loose in the red-light district: "Caged" DNAs are described that can be activated by light of selectable wavelength. This is possible with, for example, red light, which is significantly less damaging than UV light and can permeate deeply into tissues (see scheme).



Gold Catalysis

A. S. K. Hashmi,* S. Schäfer, M. Wölfle,
C. Diez Gil, P. Fischer, A. Laguna,*
M. C. Blanco, M. C. Gimeno **6184 – 6187**

Gold-Catalyzed Benzylic C–H Activation at Room Temperature

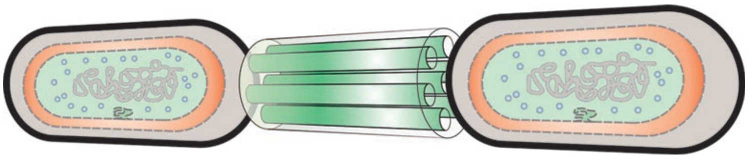


A tale of the unexpected: Coordinating and potentially chelating groups allow gold-catalyzed benzylic C–H activation at room temperature. Substrates with additional nucleophilic substituents undergo unexpected dimerizations, in which eight new bonds are formed (see scheme).

Self-Assembly of Bacteria

Z. Popović, M. Otter, G. Calzaferri,
L. De Cola* ______________ **6188 – 6191**

Self-Assembling Living Systems with Functional Nanomaterials

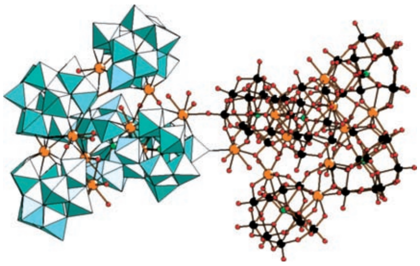


To catch a bug: Self-assembly of bacteria has been achieved by combining *Escherichia coli* and synthetic zeolite L. The assembly can be controlled so that the structure possesses either a 1:1 or 2:1 ratio (see schematic representation) between the bacteria and porous nanocontainers.

Polyoxometalates

B. S. Bassil, M. H. Dickman, I. Römer,
B. von der Kammer,
U. Kortz* ______________ **6192 – 6195**

The Tungstogermanate $[Ce_{20}Ge_{10}W_{100}O_{376}(OH)_4(H_2O)_{30}]^{56-}$: A Polyoxometalate Containing 20 Cerium(III) Atoms

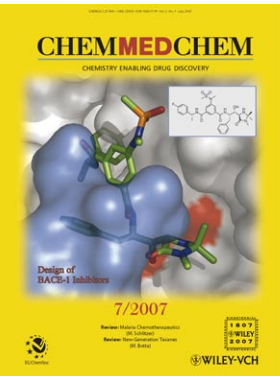


Big W: One of the largest polytungstates, the 20 cerium(III) atom tungstogermanate $[Ce_{20}Ge_{10}W_{100}O_{376}(OH)_4(H_2O)_{30}]^{56-}$ (**1**), has been synthesized from Ce^{III} ions and $[\alpha\text{-}GeW_9O_{34}]^{10-}$ in aqueous acidic medium at pH 5.0. Polyanion **1** represents the first lanthanide-substituted tungstogermanate and can be described as a dimer that is linked through long Ce–O(W) bridges.

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).

Service



Corrigendum

The authors of this Communication wish to correct a remark in their introductory paragraph: "There have been several unsuccessful attempts to generate and characterize gas-phase H_2CO_3 by heating solid H_2CO_3[3] or NH_4HCO_3.[12]" This statement is incorrect and misleading, and the authors apologize for their oversight. The sentence should read: "Although there have been several successful attempts to generate and identify gas-phase H_2CO_3 by heating solid H_2CO_3[3] or NH_4HCO_3,[12] there is still a lack of detailed experimental information on its structural, spectroscopic, and thermochemical properties."

IR Spectra of Protonated Carbonic Acid and Its Isomeric $H_3O^+\cdot CO_2$ Complex

H.-S. Andrei, S. A. Nizkorodov, O. Dopfer* ——— **4754–4756**

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[12] J. K. Terlouw, C. B. Lebrilla, H. Schwarz, *Angew. Chem.* **1987**, *99*, 352; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 354.