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:

*B. L. Merner, L. N. Dawe, G. J. Bodwell**
1,1,8,8-Tetramethyl[8](2,11)teropyrenophane: Half of an Aromatic Belt and a Segment of an (8,8) Single-walled Carbon Nanotube

*B. Brugger, S. Rütten, K.-H. Phan, M. Möller, W. Richtering**
Colloidal Suprastructure of Smart Microgels at Oil/Water Interfaces

*B. Liu, H. Wang, H. Xie, B. Zeng, J. Chen, J. Tao, T. B. Wen, Z. Cao, H. Xia**
Osmapyridine and Osmapyridinium from a Formal [4+2] Cycloaddition Reaction

*J. Tolosa, C. Kub, U. H. F. Bunz**
Hyperbranched: A Universal Conjugated Polymer Platform?

D. Xu, Z. Liu, H. Yang, Q. Liu, J. Zhang, J. Fang, S. Zou,* K. Sun*
Solution-Based Evolution of Monodisperse Pt–Cu Nanocubes and Their Enhanced Methanol Oxidation Activity

*H. Moroder, J. Steger, D. Graber, K. Fauster, K. Trappl, V. Marquez, N. Polacek, D. N. Wilson, R. Micura**
Nonhydrolyzable RNA–Peptide Conjugates: A Powerful Advance in the Synthesis of Mimics for 3'-Peptidyl tRNA Termini

*J. L. Alonso-Gómez, P. Rivera-Fuentes, N. Harada, N. Berova, F. Diederich**
An Enantiomerically Pure Alleno-Acetylenic Macrocycle: Synthesis and Rationalization of Its Outstanding Chiroptical Response

*P. García-García, M. A. Fernández-Rodríguez, E. Aguilar**
Gold-Catalyzed Cycloaromatization of 2,4-Dien-6-yne Carboxylic Acids: Synthesis of 2,3-Disubstituted Phenols and Unsymmetrical Bi- and Terphenyls

*H. Jiang, P. Elsner, K. L. Jensen, A. Falcicchio, V. Marcos, K. A. Jørgensen**
Achieving Molecular Complexity by Organocatalytic One-Pot Strategies: A Fast Entry for the De Novo Synthesis of Sphingoids, Amino Sugars and Polyhydroxylated α-Amino Acids

P. A. Rupar, R. Bandyopadhyay, B. F. T. Cooper, M. R. Stinchcombe, P. J. Ragogna, C. L. B. Macdonald, K. M. Baines**
Cationic Crown Ether Complexes of Germanium(II)

*X. Zeng, H. Beckers, H. Willner**
Difluoro-λ⁵-Phosphinonitrile $F_2P{=}N$: Matrix Isolation and Photoisomerization into FP=NF

*H. Huang, B. Chung, J. Jung, H.-W. Park, T. Chang**
Toroidal Micelles of Uniform Size from Diblock Copolymers

News

Green Chemistry:
G. W. Coates Honored ____ 3730

Polymers:
Prize for B. D. Freeman ____ 3730

Organic Chemistry:
B. M. Stoltz Awarded ____ 3730

G. W. Coates

B. D.Freeman

B. M. Stoltz

Author Profile

M. T. Reetz ____ 3731

"My favorite subject at school was tennis. When I was eighteen I wanted to be a chemist....!"
This and more about Manfred T. Reetz can be found on page 3731.

Contents

Books

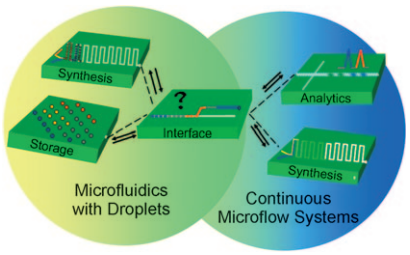
Modified Nucleosides in Biochemistry, Biotechnology and Medicine — Piet Herdewijn — *reviewed by M. K. Lakshman* — 3734

Highlights

Lab on a Chip

D. Belder* — 3736 – 3737

Towards an Integrated Chemical Circuit



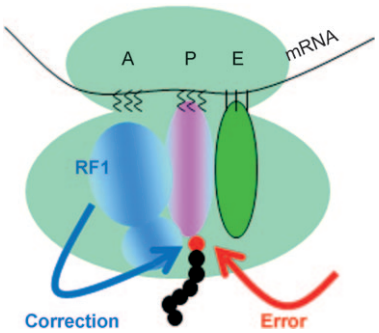
Everything on a chip: Recent developments in microfluidics enable the combination of droplet microfluidics with continuous-flow systems (see picture). This is a promising step towards the development of integrated, complex synthesis and analysis laboratories on chips. For example, a building-block principle could be used to integrate a multistep reaction with purification and analysis.

Protein Biosynthesis

M. Sprinzl* — 3738 – 3739

Correction of Errors during Protein Synthesis

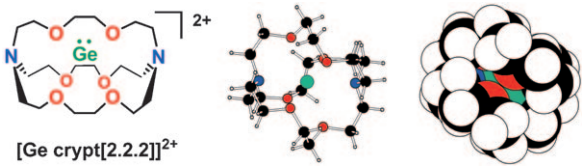
Quality control: The incorporation of a wrong amino acid into a growing polypeptide chain induces a correction step in which the release factor (RF1) hydrolyzes the peptide from the incorrectly matched peptidyl-tRNA (see picture). The nascent erroneous polypeptide is released from the ribosome and degraded.



Germanium(II) Dications

T. Müller* — 3740 – 3742

Splendid Isolation for a Nonmetallic Dication



Confined, but happy: The triflate salt of a germanium(II) dication, an atomic cation of a nonmetal, was isolated by encapsulation in [2.2.2]cryptand (see formula and molecular structure in the crystal). The cryptand satisfies the electron demand of the cation and sterically protects it (see space-filling depiction, right).

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Essays

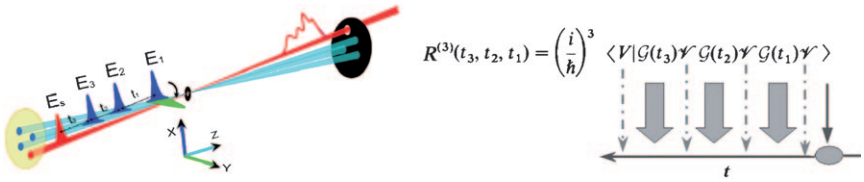
A reputation restored: Eligio Perucca (see photo) first observed the enantioselective adsorption of a racemic mixture to a chiral crystal ($NaClO_3$) in Turin in 1919. However, this milestone in enantioselective chemistry and chiroptics went unnoticed. Identified previously as a coward who refused in 1941 to supervise the research of the budding stereochemist Primo Levi because of the race laws, Perucca was opposed to the fascist regime.

History of Science

B. Kahr,* Y. Bing, W. Kaminsky, D. Viterbo* ——— **3744 – 3748**

Turinese Stereochemistry: Eligio Perucca's Enantioselectivity and Primo Levi's Asymmetry

Reviews



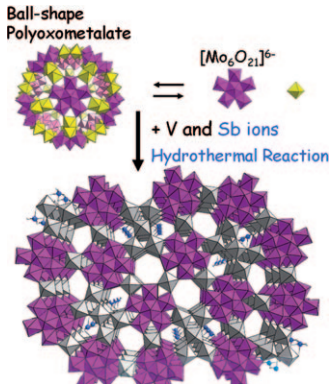
Good vibrations: The vibrational response of complex molecules to sequences of infrared pulses provides novel femtosecond snapshots of their structure and dynamics. This technique, which is the optical analogue of multidimensional NMR spectroscopy, gives correlation plots of motions during controlled time intervals between pulses that are applied to study protein folding, chirality, hydrogen-bonding, phospholipid membranes, and chemical exchange.

Spectroscopic Methods

W. Zhuang, T. Hayashi, S. Mukamel* ——— **3750 – 3781**

Coherent Multidimensional Vibrational Spectroscopy of Biomolecules: Concepts, Simulations, and Challenges

Communications

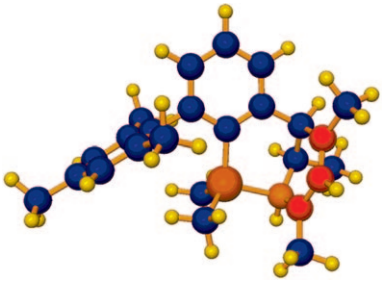


Mix and match: The pentagonal $[Mo_6O_{21}]^{n-}$ polyoxomolybdate building block assembles with other sources of Mo, V, and Sb ions to form an orthorhombic Mo-V-Sb oxide. The first single-crystal X-ray analysis of an orthorhombic Mo–V-based oxide, a promising catalyst for light alkane selective oxidation known as the "M1 phase", revealed the structure of the compound.

Polyoxometalates

M. Sadakane,* K. Yamagata, K. Kodato, K. Endo, K. Toriumi, Y. Ozawa, T. Ozeki, T. Nagai, Y. Matsui, N. Sakaguchi, W. D. Pyrz, D. J. Buttrey, D. A. Blom, T. Vogt, W. Ueda* ——— **3782 – 3786**

Synthesis of Orthorhombic Mo-V-Sb Oxide Species by Assembly of Pentagonal Mo_6O_{21} Polyoxometalate Building Blocks



Sly silyl caught in the act: Protonation of a mesitylene ring by the strongly acidic arenium carborane $[CH_3C_6H_6]$-$[CHB_{11}Me_5Br_6]$ initiates a cascade reaction that results in a stable β-silyl allyl cation (see picture, H yellow, C blue, silyl allyl group red). Remarkably, the driving force in the reaction suffices to disrupt a stable aromatic ring in favor of a cationic reactive intermediate.

Reactive Intermediates

S. Duttwyler, Y. Zhang, D. A. Linden, C. A. Reed,* K. K. Baldridge,* J. S. Siegel* ——— **3787 – 3790**

Synthesis and Crystal Structure of a Silyl-Stabilized Allyl Cation Formed by Disruption of an Arene by a Protonation–Hydrosilylation Sequence

Incredibly

iNcOgnitO

...!

Did you know that Angewandte Chemie is owned by the German Chemical Society (Gesellschaft Deutscher Chemiker, GDCh)? With nearly 30000 members, the GDCh is the largest chemical society in continental Europe and holds complete responsibility over the contents of *Angewandte*. The GDCh appoints the members of *Angewandte's* editorial board and international advisory board; the editor-in-chief is appointed jointly by the GDCh and the publishers. Wiley-VCH has collaborations with over 50 scientific societies and institutions; the parent company John Wiley & Sons collaborates with many more still.

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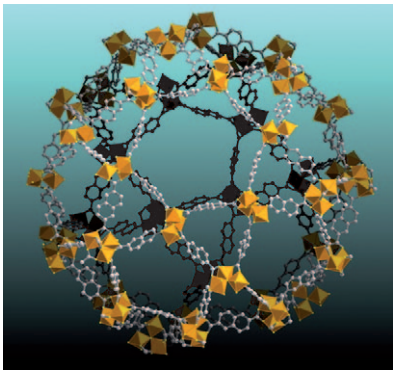
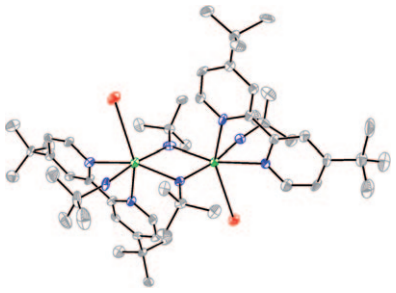


Large, larger, ... Replacement of 1,4-benzenedicarboxylate by 2,6-naphthalenedicarboxylate in the MIL-101 structure leads to an isoreticular mesoporous framework containing cages with diameters of 39 and 46 Å. High-throughput methods are employed to determine appropriate reaction conditions. The microcrystalline compound is characterized by molecular simulation techniques, powder X-ray diffraction, N_2-sorption, and TEM investigations.

Metal–Organic Frameworks

A. Sonnauer, F. Hoffmann, M. Fröba, L. Kienle, V. Duppel, M. Thommes, C. Serre, G. Férey, N. Stock* **3791 – 3794**

Giant Pores in a Chromium 2,6-Naphthalenedicarboxylate Open-Framework Structure with MIL-101 Topology

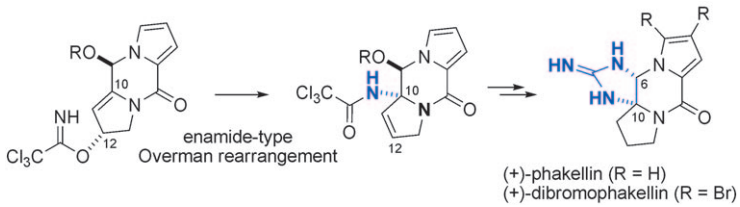


Communication is important: The dimeric bis(imido) uranium complex $[\{U(N\mathit{t}Bu)_2(I)(\mathit{t}Bu_2bpy)\}_2]$ (see picture; U green, N blue, I red) has cation–cation interactions between $[U(NR)_2]^+$ ions. This f^1–f^1 system also displays f orbital communication between uranium(V) centers at low temperatures, and can be oxidized to generate uranium(VI) bis(imido) complexes.

Actinide Chemistry

L. P. Spencer, E. J. Schelter, P. Yang, R. L. Gdula, B. L. Scott, J. D. Thompson, J. L. Kiplinger, E. R. Batista, J. M. Boncella* **3795 – 3798**

Cation–Cation Interactions, Magnetic Communication, and Reactivity of the Pentavalent Uranium Ion $[U(N\mathit{t}Bu)_2]^+$

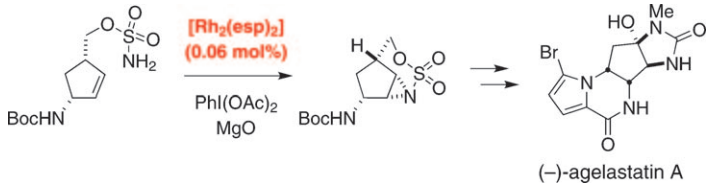


Two members of a family of pyrrole–imidazole marine alkaloids, (+)-dibromophakellin and the nonnatural congener (+)-phakellin, were synthesized enantioselectively from 4-hydroxy-L-proline. The chiral aminal at C10 was constructed efficiently by means of an Overman-type [3,3] sigmatropic rearrangement of an enamide (see scheme).

Guanidine Alkaloids

T. Imaoka, O. Iwamoto, K.-i. Noguchi, K. Nagasawa* **3799 – 3801**

Total Synthesis of (+)-Dibromophakellin



Weaving an intricate web: A stereoselective synthesis of (−)-agelastatin A has been developed, which requires 11 steps from commercially available starting material. The application of a Rh-catalyzed intramolecular olefin aziridination reaction and the subsequent manipulation of the resulting tricyclic intermediate (see scheme) punctuate this study.

Natural Product Synthesis

P. M. Wehn, J. Du Bois* **3802 – 3805**

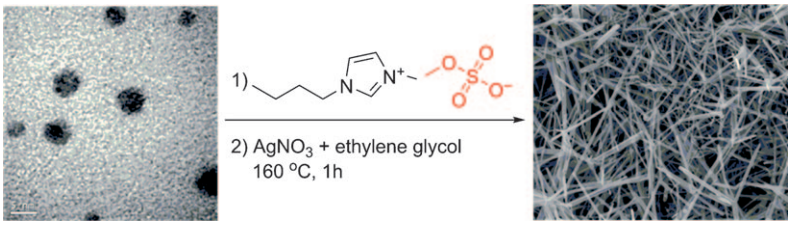
A Stereoselective Synthesis of the Bromopyrrole Natural Product (−)-Agelastatin A

Contents

Nanowires

T. Y. Kim, W. J. Kim, S. H. Hong, J. E. Kim, K. S. Suh* _____ **3806 – 3809**

Ionic-Liquid-Assisted Formation of Silver Nanowires



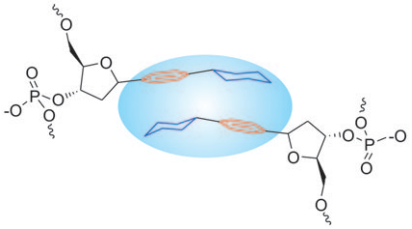
Down to the wire: A simple and effective method to synthesize silver nanowires through an ionic-liquid-assisted polyol process is developed (see scheme; scale bar = 5 nm). The ionic liquids are tuned to provide the anisotropic growth of silver nanoparticles into nanowires.

DNA Recognition

M. Kaufmann, M. Gisler, C. J. Leumann* _____ **3810 – 3813**

Stable Cyclohexyl–Phenyl Recognition in the Center of a DNA Duplex

Even saturated carbocycles are compatible with Watson–Crick pairing, as shown by the incorporation of phenylcyclohexyl-C-nucleoside pairs into the center of a DNA double helix (see picture). The increase in duplex stability arises from cyclohexyl/phenyl CH/π interactions. This makes the system an interesting scaffold for studying hydrophobic interactions and allows for the incorporation of additional molecular entities into the double helix.

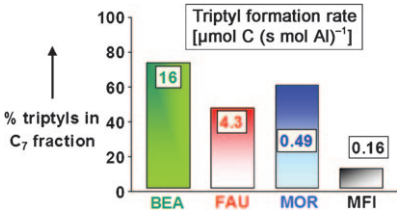


Heterogeneous Catalysis

J. H. Ahn, B. Temel, E. Iglesia* _____ **3814 – 3816**

Selective Homologation Routes to 2,2,3-Trimethylbutane on Solid Acids

Sailing the seven 'C's: 2,2,3-Trimethylbutane (triptane) selectively forms from dimethyl ether at low temperatures on acid zeolites. Selective methylation at less-substituted carbons, relative rates of methylation to hydrogen transfer as a function of chain size, slow skeletal isomerization, and β-scission cracking of triptyl chains and their precursors are intrinsic properties of carbenium ions and account for the remarkable triptane selectivities within C_7.

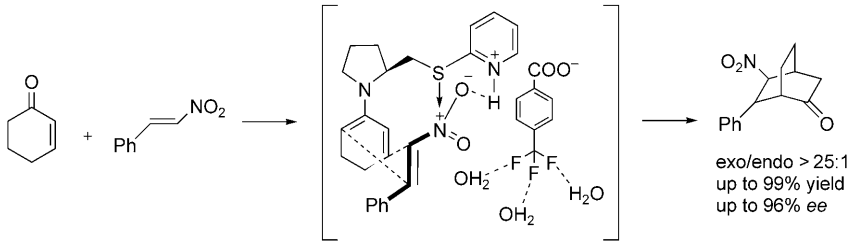


Iron Catalysis

Y.-Z. Li, B.-J. Li, X.-Y. Lu, S. Lin, Z.-J. Shi* _____ **3817 – 3820**

Cross Dehydrogenative Arylation (CDA) of a Benzylic C–H Bond with Arenes by Iron Catalysis

Hooking up: $FeCl_2$ catalyzes the efficient cross dehydrogenative arylation of substrates having benzylic C–H bonds (see scheme). High regioselectivity was observed during the cross-coupling between compounds containing aromatic $C(sp^2)$–H bonds and benzylic $C(sp^3)$–H bonds. This process is proposed to proceed by single-electron-transfer oxidation and Friedel–Crafts alkylation.

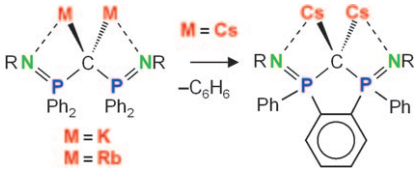


Deep-sea Diels–Alder: The asymmetric organocatalytic Diels–Alder reaction of cyclohexenones with aromatic nitroolefins can be carried out in seawater and brine. The reaction proceeds by an in situ enamine activation involving a one-step concerted addition pathway (see scheme).

Asymmetric Catalysis

D.-Q. Xu, A.-B. Xia, S.-P. Luo, J. Tang, S. Zhang, J.-R. Jiang
Z.-Y. Xu* ——— **3821 – 3824**

In Situ Enamine Activation in Aqueous Salt Solutions: Highly Efficient Asymmetric Organocatalytic Diels–Alder Reaction of Cyclohexenones with Nitroolefins



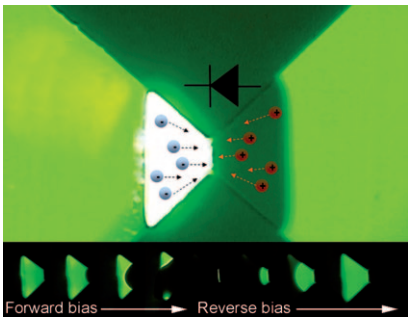
Size does matter: Whereas geminal bimetallic bis(amidophosphorano)methandiide complexes of the heavy alkali metals K and Rb are relatively stable, that of Cs, the largest and most electropositive of the alkali metals, decomposes to form a cyclic product, which cocrystallizes with benzylcesium.

Alkali-Metal Complexes

L. Orzechowski, G. Jansen, S. Harder* ——— **3825 – 3829**

Methandiide Complexes (R_2CM_2) of the Heavier Alkali Metals (M = Potassium, Rubidium, Cesium): Reaching the Limit?

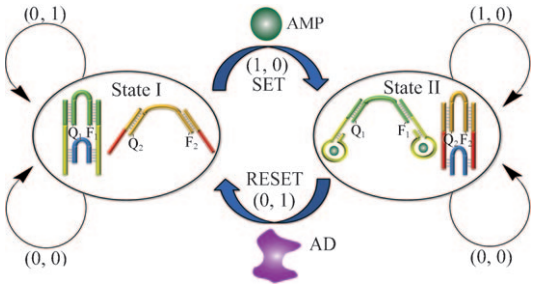
Green means go: A polyelectrolyte diode on a microchip exhibits well-defined nonlinear rectifying behavior. This system visualizes the dynamic distribution of ions in a charged polymer phase under an electric field on a real-time basis using fluorescence images (see picture). Multiple polyelectrolyte diodes are integrated on a microchip to produce a variety of logic gates based on ionic circuits.



Ionic Circuits

J.-H. Han, K. B. Kim, H. C. Kim, T. D. Chung* ——— **3830 – 3833**

Ionic Circuits Based on Polyelectrolyte Diodes on a Microchip



Open sesame: Aptamer–substrate complexes activate the coherent operation of two tweezers that act as a "SET–RESET" logic system. Each tweezer cycles between a fluorescent open state and a closed quenched state (Q = quencher, F = fluorophore) when triggered by adenosine monophosphate (AMP) and adenosine deaminase (AD).

Molecular Devices

J. Elbaz, M. Moshe, I. Willner* ——— **3834 – 3837**

Coherent Activation of DNA Tweezers: A "SET–RESET" Logic System

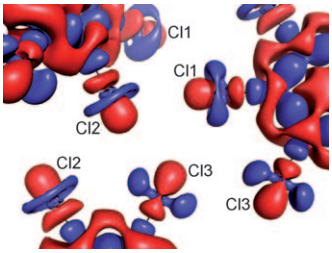
Contents

Halogen Interactions

T. T. T. Bui, S. Dahaoui, C. Lecomte, G. R. Desiraju, E. Espinosa* **3838 – 3841**

The Nature of Halogen···Halogen Interactions: A Model Derived from Experimental Charge-Density Analysis

Slightly attractive: The attractive and anisotropic nature of the Cl···Cl interaction in C_6Cl_6 is experimentally demonstrated from an expansion of the electron density $\rho(\mathbf{r})$ around the chlorine nuclei. The interaction is explained in a model in which there is a bonding attraction involving electron-deficient (see picture, blue) and electron-rich (red) regions of adjacent Cl atoms.

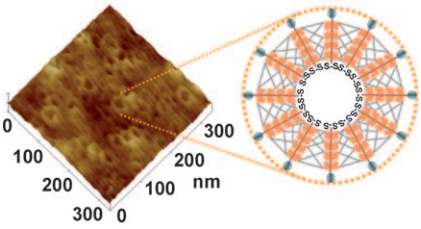


Nanostructures

Y.-L. Wu, J. Li* **3842 – 3845**

Synthesis of Supramolecular Nanocapsules Based on Threading of Multiple Cyclodextrins over Polymers on Gold Nanoparticles

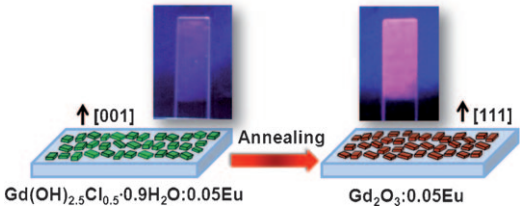
The CD's stuck: Poly(ethylene glycol) chains anchored onto gold nanoparticles (AuNPs) are threaded by multiple α-cyclodextrin (α-CD) rings to form a supramolecular outer layer composed of pseudopolyrotaxane columns perpendicular to the nanoparticle surface. Capping the polymer ends confines α-CD on the nanoparticle surface, cross-linking the α-CD rings and then removing the AuNP cores produces supramolecular nanocapsules.



Photoluminescence

L. Hu, R. Ma, T. C. Ozawa, T. Sasaki* **3846 – 3849**

Oriented Monolayer Film of Gd_2O_3:0.05 Eu Crystallites: Quasi-Topotactic Transformation of the Hydroxide Film and Drastic Enhancement of Photoluminescence Properties

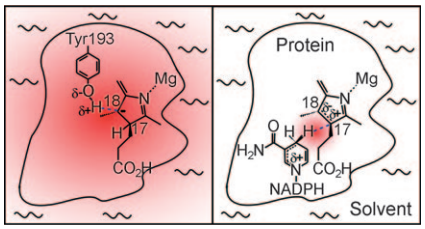


Caught on film: A semitransparent and intensely luminescent monolayer film of oriented Gd_2O_3:0.05 Eu platelet crystallites is fabricated by annealing the precursor hydroxide film (see scheme). The photoluminescence properties of the as-transformed film are greatly improved over those of the hydroxide film, and are much more pronounced than those of the corresponding Gd_2O_3:0.05 Eu powder.

Enzyme Catalysis

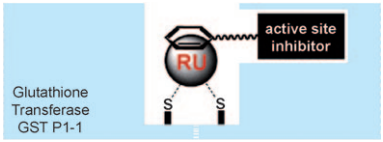
D. J. Heyes,* M. Sakuma, N. S. Scrutton* **3850 – 3853**

Solvent-Slaved Protein Motions Accompany Proton but Not Hydride Tunneling in Light-Activated Protochlorophyllide Oxidoreductase



H^+ but not H^-: The reduction reaction of protochlorophyllide catalyzed by protochlorophyllide oxidoreductase features solvent-slaved motions that control the proton- but not the hydride-tunneling mechanism. These motions imply a long-range dynamic network from the solvent to the enzyme active site that facilitate proton transfer (see picture, left). Motions for hydride transfer are more localized and are not slaved by the solvent (see picture, right).

Double trouble: A hybrid organic–inorganic (organometallic) inhibitor was designed to target glutathione transferases. The metal center is used to direct protein binding, while the organic moiety acts as the active-site inhibitor (see picture). The mechanism of inhibition was studied using a range of biophysical and biochemical methods.

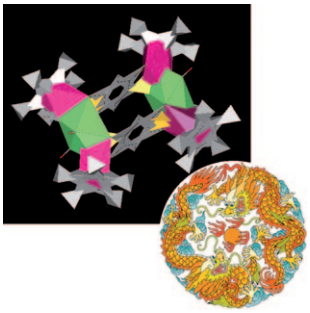


Enzyme Inhibition

W. H. Ang, L. J. Parker, A. De Luca, L. Juillerat-Jeanneret, C. J. Morton, M. Lo Bello, M. W. Parker, P. J. Dyson* ——— **3854 – 3857**

Rational Design of an Organometallic Glutathione Transferase Inhibitor

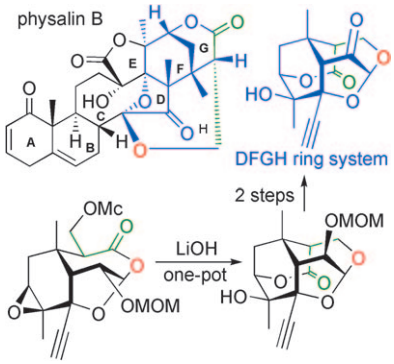
Two dragons playing ball: Direct metal–metal bond formation using a π-conjugated dinuclear metalladithiolene complex with two electron-deficient metal centers as building blocks led to a cyclic double trinuclear heterometalladithiolene cluster with two parallel plane bridges (see structure; Rh pink, Mo green, S yellow, C gray, O red).



Cluster Compounds

B.-H. Zhu, Y. Shibata, S. Muratsugu, Y. Yamanoi, H. Nishihara* — **3858 – 3861**

A Cyclic Hexanuclear Heterometalladithiolene Cluster $[\{(Cp^*Rh)_2Mo(\mu\text{-}CO)_2(CO)\}_2(S_2C_6H_2S_2)_2]$ with Two π-Conjugated $S_2C_6S_2$ Bridges: Synthesis, Crystal Structure, and Properties

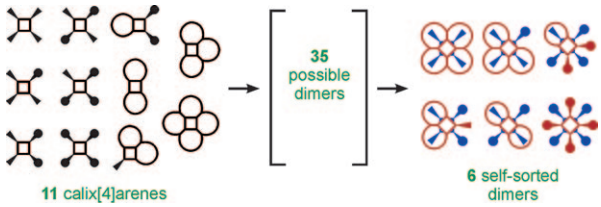


Let the dominos fall: Synthesis of the complex DFGH ring system of the title compounds has been accomplished. The approach features simple treatment of the key intermediate with a Brønsted base to afford the tetracyclic cage-shaped target in one pot through a four-step domino transformation (see scheme; Mc = monochloromesylate, MOM = methoxymethyl).

Natural Products

M. Ohkubo, G. Hirai, M. Sodeoka* ——— **3862 – 3866**

Synthesis of the DFGH ring system of Type B Physalins: Highly Oxygenated, Cage-Shaped Molecules



Size and shape do matter: When dimerized in nonpolar solvents, an equimolar mixture of eleven tetra-urea calix[4]arenes with different wide-rim substituents self-sorts into only six out of 35 different homo- and heterodimers (see picture).

Since the calixarene scaffold and the four urea units are the same in all cases, the self-sorting process is driven only by the cooperative action of steric requirements and stoichiometry.

Self Assembly

Y. Rudzevich, V. Rudzevich, F. Klautzsch, C. A. Schalley,* V. Böhmer* **3867 – 3871**

A Self-Sorting Scheme Based on Tetra-Urea Calix[4]arenes

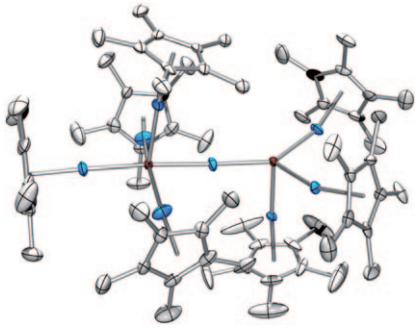
Contents

Gallium Ligands

T. Cadenbach, C. Gemel, R. Schmid, M. Halbherr, K. Yusenko, M. Cokoja, R. A. Fischer* ——— **3872 – 3876**

Substituent-Free Gallium by Hydrogenolysis of Coordinated GaCp*: Synthesis and Structure of Highly Fluxional $[Ru_2(Ga)(GaCp^*)_7(H)_3]$

All change: Complete ligand exchange through the hydrogenation of $[Ru(\eta^4\text{-cod})(\eta^6\text{-cot})]$ in the presence of GaCp* under mild conditions leads to the title complex featuring a "naked" gallium atom bridging two ruthenium centers (see structure: C white, Ga blue, Ru red). This cluster can be considered as a trapped intermediate on the way to mixed-metal nanoparticles; cot = 1,3,5-cyclooctatriene; cod = 1,5-cyclooctadiene, Cp* = C_5Me_5.



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