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.-Y. Yu, Q.-F. Sun, T. K.-M. Lee, E. C.-C. Cheng, Y.-Z. Li,* V. W.-W. Yam**
Au_{36} Crown: Macrocyclization Directed by Metal–Metal Bonding Interactions

A. Fürstner, L. Morency*
The Nature of the Reactive Intermediates in Gold-Catalyzed Cycloisomerization Reactions

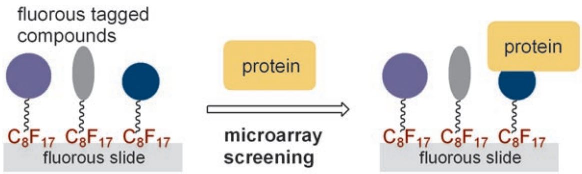
*G. Pasparakis, C. Alexander**
Sweet-Talking Double Hydrophilic Block Copolymer Vesicles

*H. Falsig, B. Hvolbæk, I. S. Kristensen, T. Jiang, T. Bligaard, C. H. Christensen, J. K. Nørskov**
Trends in the Catalytic CO Oxidation Activity of Nanoparticles

Books

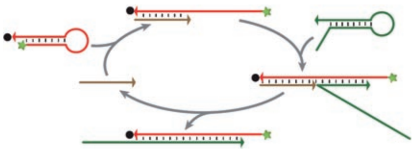
Highlights

Microarrays



Tag team: Not only hydrophilic carbohydrates but also hydrophobic compounds such as histone deacetylase inhibitors and biotin can be incorporated into fluorous-based small-molecule microarrays. A range of fluorous-tagged molecules can be patterned and screened for bioactivity on a fluorous surface with hit rates comparable to those seen by solution-based and surface plasmon resonance-based bioassays.

Nanobiotechnology



Opening time: A method for the systematic and automatable design of DNA hybridization networks was recently introduced, which was based on the catalytic opening of metastable hairpin loops (see scheme). This technique has various applications in nanobiotechnology, such as the stepwise self-assembly of DNA scaffolds and the engineering of dynamic DNA devices.

Contents

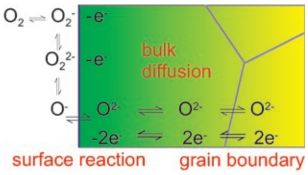
Reviews

Solid-State Reactions

R. Merkle,* J. Maier ______ **3874 – 3894**

How Is Oxygen Incorporated into Oxides? A Comprehensive Kinetic Study of a Simple Solid-State Reaction with $SrTiO_3$ as a Model Material

O, how does it go? Equilibration of an oxide with the surrounding oxygen partial pressure is one of the simplest gas–solid reactions. Nevertheless, it is a complex process comprising a (multistep) surface reaction, chemical bulk diffusion, and transport across or along grain boundaries. This Review gives a detailed phenomenological as well as mechanistic description of these processes for the model perovskite oxide $SrTiO_3$ emphasizing their relevance for electrochemical devices.

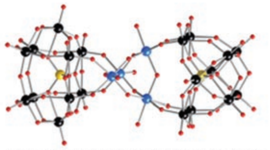


Communications

Oxygen Generation

Y. V. Geletii, B. Botar,* P. Kögerler, D. A. Hillesheim, D. G. Musaev, C. L. Hill* ______ **3896 – 3899**

An All-Inorganic, Stable, and Highly Active Tetraruthenium Homogeneous Catalyst for Water Oxidation



$$4[Ru(bpy)_3]^{3+} + 2\,H_2O \xrightarrow{[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}} 4[Ru(bpy)_3]^{2+} + O_2 + 4\,H^+$$

Oxidation without organics: A tetraruthenium polyoxometalate (see picture; Ru blue, O red, Si yellow, W black) catalyzes the rapid oxidation of H_2O to O_2 in water at ambient temperature, and shows considerable stability under turnover conditions. The complex was characterized by several methods, including X-ray crystallography and cyclic voltammetry.

Lab on a Chip

J. Pipper,* Y. Zhang, P. Neuzil, T.-M. Hsieh ______ **3900 – 3904**

Clockwork PCR Including Sample Preparation

For whom the bell tolls: Surface-functionalized superparamagnetic particles emulsified in mineral oil turn a free-standing droplet into a flexible virtual laboratory with (sub)microliter volumes. By using magnetic forces, rare acute monocytic leukaemia cells are extracted from blood, preconcentrated, purified, lysed, and subjected to a real-time PCR in minutes. The PCR works like a clockwork by rotating the droplet over different temperature zones.

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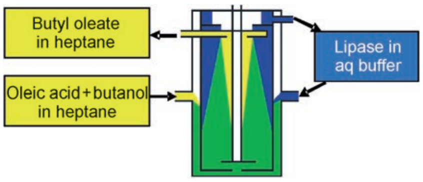


A new spin on catalysis: A table-top centrifugal contact separator allows for fast continuous two-phase reactions to be performed by intimately mixing two immiscible phases and then separating them. Such a device has been used to produce biodiesel from sunflower oil and MeOH/NaOMe. A lipase-catalyzed esterification of oleic acid with *n*BuOH (see picture) also proceeds with high conversion and can be run for up to 13 h.

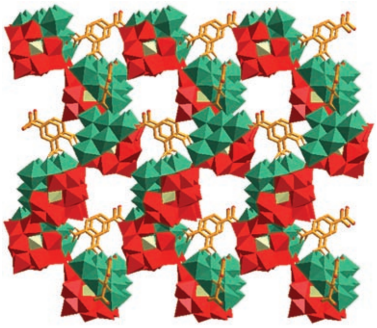
Process Intensification

G. N. Kraai, F. van Zwol, B. Schuur, H. J. Heeres,* J. G. de Vries* ______ **3905–3908**

Two-Phase (Bio)Catalytic Reactions in a Table-Top Centrifugal Contact Separator

---

Directed combination of $\{Ni_6PW_9\}$ building blocks with various rigid carboxylate linkers under hydrothermal conditions yields a series of unprecedented polyoxometalate–organic frameworks (POMOFs) with remarkable structural diversity including 1D, 2D, and 3D structures based on monomers, dimers, or infinite helical chains (see picture for 3D structure: WO_6: red; NiO_6: green; PO_4: yellow; 1,2,4-benzenetricarboxylate: gold).



POM–Organic Frameworks

S.-T. Zheng, J. Zhang, G.-Y. Yang* ______ **3909–3913**

Designed Synthesis of POM–Organic Frameworks from $\{Ni_6PW_9\}$ Building Blocks under Hydrothermal Conditions

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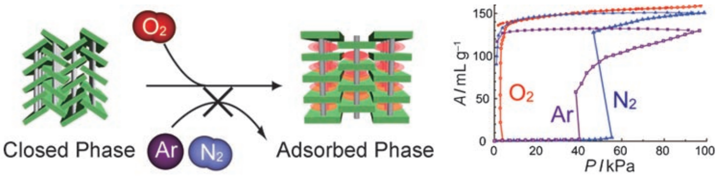

Open the gate! A porous coordination polymer shows abrupt changes in its adsorption isotherm with guest-dependent gate-opening pressure (see picture). Kinetic analysis reveals that adsorption with structure transformation follows a gate-opening model, in which adsorption proceeds through the formation of an intermediate by a gate-opening process. This process provides a significant difference in onset pressure between similar gas molecules.

Coordination Polymers

D. Tanaka, K. Nakagawa, M. Higuchi, S. Horike, Y. Kubota, T. C. Kobayashi, M. Takata, S. Kitagawa* ______ **3914–3918**

Kinetic Gate-Opening Process in a Flexible Porous Coordination Polymer

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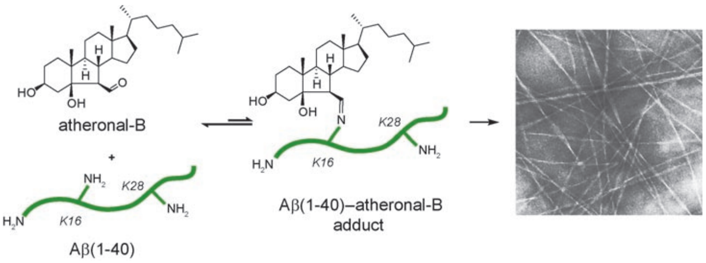
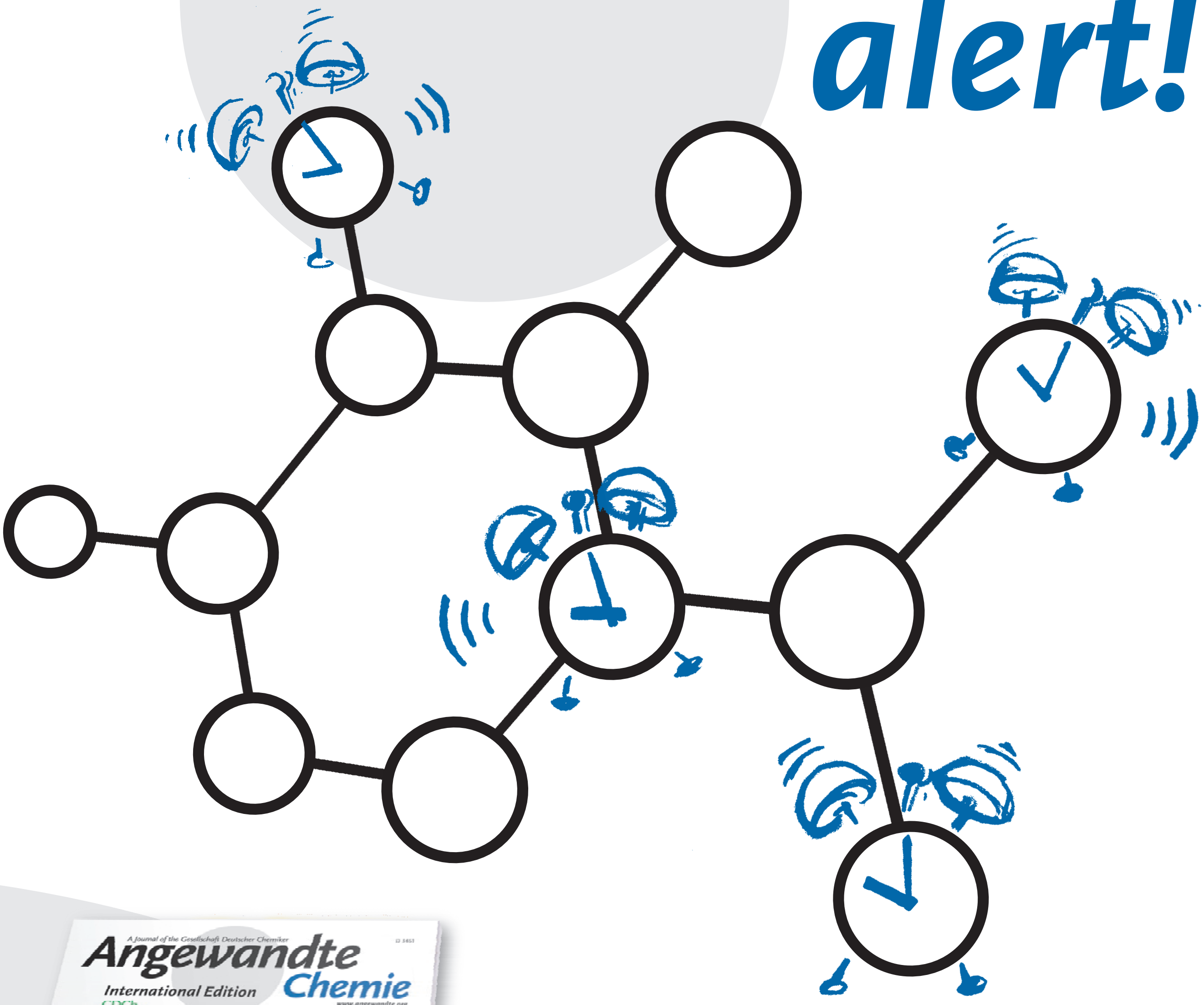


Hot spot on amyloid-β? Atheronal-B-induced aggregation of amyloid-β (Aβ) involves a site-specific adduction of the aldehyde to the ε-amino group of Lys 16, suggesting that Lys 16 is a hot spot for atheronal-induced fibrillization of Aβ (see scheme). This process can be inhibited by molecules like cholesterol that compete for the central hydrophobic cluster binding domain.

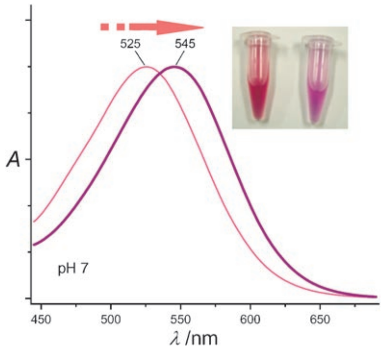
Alzheimer's Disease

J. C. Scheinost, H. Wang, G. E. Boldt, J. Offer, P. Wentworth, Jr.* ______ **3919–3922**

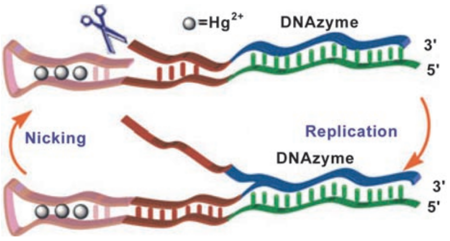
Cholesterol *seco*-Sterol-Induced Aggregation of Methylated Amyloid-β Peptides—Insights into Aldehyde-Initiated Fibrillization of Amyloid-β



Switching from red to pink: It has been believed that only the amino acids near the retinal chromophore are responsible for the color tuning of rhodopsins. Herein is reported a color change of proteorhodopsin, an archaeal-type rhodopsin in marine bacteria, by mutation of Ala178 to Arg at the E–F loop. The red shift at a neutral pH value amounts to 20 nm (see graph).

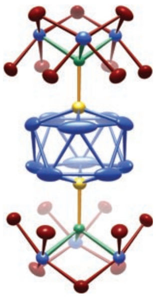


Chromophores



Strand and deliver: Two different optical methods to analyze Hg^{2+} ions based on the formation of thymine–Hg^{2+} complexes are developed. These methods include the analysis of Hg^{2+} ions by using aggregated gold nanoparticles and by using a DNA-based machine (see scheme).

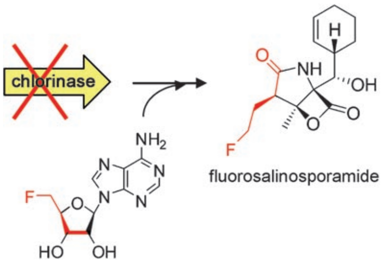
Ion Sensors



A multitude of new binding modes: A $[Bi_{10}Au_2]^{6+}$ heteroicosahedron and two $(SbBi_3Br_9)^{3-}$ hemispheres form molecular cluster $[Bi_{10}Au_2](SbBi_3Br_9)_2$ (see picture: Bi blue, Au yellow, Sb green, Br dark red). The $[Bi_{10}Au_2]^{6+}$ polycation involves significant bismuth–gold interactions. The molecule also exhibits a rare interpnicogen covalent bond between bismuth and antimony and a complex donor–acceptor bond between the anionic caps and the polycation.

Cluster Compounds

A knockout result: Fluorine substituents give drugs beneficial properties. By using a rational combination of genetic engineering and precursor-directed biosynthesis, fluorosalinosporamide (see scheme) was generated in a fermentation-based approach. The anticancer lead compound and marine natural product salinosporamide A is chlorinated. A comparison of the biological activity of these proteasome inhibitors is presented.

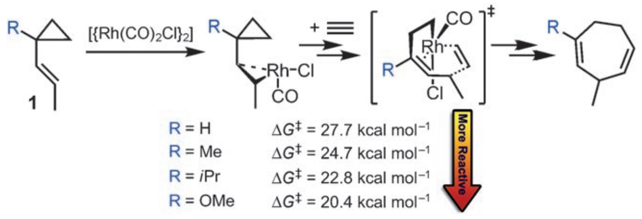


Halogenation

(5+2) Cycloadditions

P. Liu, P. H.-Y. Cheong, Z.-X. Yu,
P. A. Wender, K. N. Houk* _ **3939 – 3941**

Substituent Effects, Reactant Preorganization, and Ligand Exchange Control the Reactivity in Rh$^{\mathrm{I}}$-Catalyzed (5+2) Cycloadditions between Vinylcyclopropanes and Alkynes

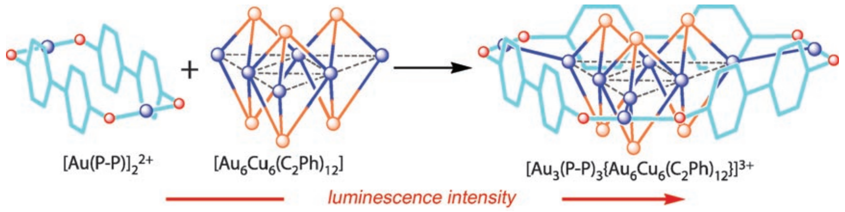


Heteroatom and bulky alkyl substituents dramatically increase the rate of Rh$^{\mathrm{I}}$-catalyzed (5+2) cycloadditions of **1**. This fact could be attributed to steric effects which ease the reactant preorganization, and to the stabilization of the allyl intermediate by (hyper)conjugation with the substituents. The methoxy- and isopropyl-substituted **1** have an activation energy 5 and 7 kcal mol^{-1}, respectively, lower than the unsubstituted vinylcyclopropane.

Cluster Compounds

I. O. Koshevoy,* L. Koskinen, M. Haukka,
S. P. Tunik,* P. Y. Serdobintsev,
A. S. Melnikov,
T. A. Pakkanen* ____________ **3942 – 3945**

Self-Assembly of Supramolecular Luminescent Au$^{\mathrm{I}}$–Cu$^{\mathrm{I}}$ Complexes: “Wrapping” an Au$_6$Cu$_6$ Cluster in a [Au$_3$(diphosphine)$_3$]$^{3+}$ “Belt”

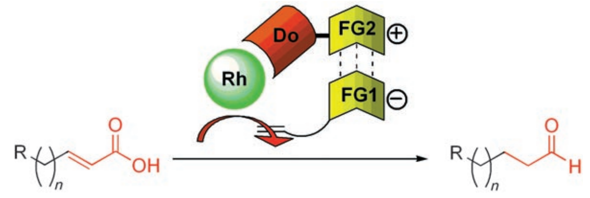


Belt and suspenders: A supramolecular gold–copper cluster has been synthesized by Cu$^+$-assisted self-assembly of [Au(C$_2$Ph)$_2$] rods and a gold–diphosphine belt, which is suspended from the Au$_6$Cu$_6$ core by Au–Au bonds (see picture). The cluster displays strong orange luminescence on excitation at 308 nm which is more intense than that of either of its structural fragments, which were isolated and studied independently. P-P = Ph$_2$PC$_6$H$_4$C$_6$H$_4$PPh$_2$.

Supramolecular Catalysis

T. Šmejkal, B. Breit* ______ **3946 – 3949**

A Supramolecular Catalyst for the Decarboxylative Hydroformylation of α,β-Unsaturated Carboxylic Acids

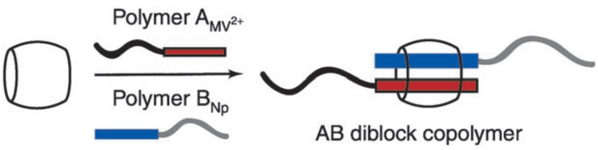


Head ’em up, move ’em out, aldehyde! A catalytic transformation of α,β-unsaturated carboxylic acids into aldehydes through a hydroformylation–decarboxylation process has been developed (see scheme; Do = donor ligand, FG1 and FG2 = complementary functional groups). The reaction proceeds at mild conditions, tolerates many functional groups, and liberates CO$_2$ as the only stoichiometric by-product.

Polymer Architectures

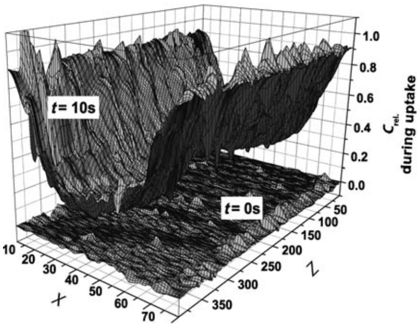
U. Rauwald,
O. A. Scherman* __________ **3950 – 3953**

Supramolecular Block Copolymers with Cucurbit[8]uril in Water



Be my guest! A supramolecular amphiphilic diblock copolymer was prepared with a cucurbit[8]uril molecular “handcuff” (see picture). It subsequently undergoes a hierarchical self-assembly process, resulting in the formation of a tertiary, compartmentalized nanostructure.

The persistence of resistance: In the zeolite silicalite-1, the influence of transport barrier on the surface and between crystal segments, are negligibly small in comparison to the transport resistance of the intracrystalline pore system. Diffusion experiments are conducted with these zeolite crystals and intracrystalline diffusion coefficients of guest molecules determined.



Diffusion in Zeolites

D. Tzoulaki, L. Heinke, W. Schmidt, U. Wilczok, J. Kärger* **3954 – 3957**

Exploring Crystal Morphology of Nanoporous Hosts from Time-Dependent Guest Profiles

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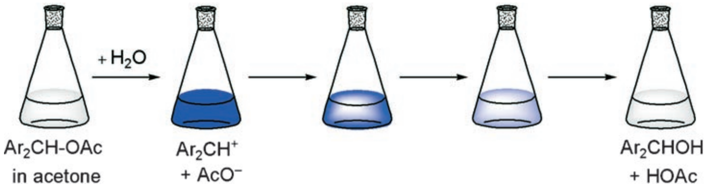
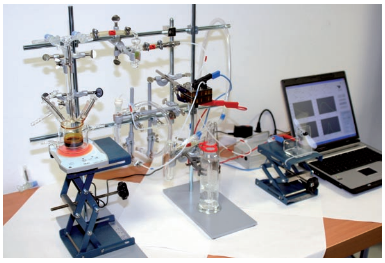


The missing link between conventional S_N1 reactions and the chemistry of stable carbocations has been found. When water is added to the colorless solution of the covalent compound Ar_2CH-OAc (Ar = morpholinophenyl) in acetone, the appearance and disappearance of the intermediate carbocation $ArCH^+$ can be observed with the naked eye!

Carbocations

H. F. Schaller, H. Mayr* **3958 – 3961**

"Carbocation Watching" in Solvolysis Reactions



Forever blowing bubbles: Hydrogen is generated from formic acid amine adducts at room temperature used directly in fuel cells (see picture for apparatus). Ruthenium phosphine systems act as catalysts in this transformation.

Hydrogen Storage

B. Loges, A. Boddien, H. Junge, M. Beller* **3962 – 3965**

Controlled Generation of Hydrogen from Formic Acid Amine Adducts at Room Temperature and Application in H_2/O_2 Fuel Cells

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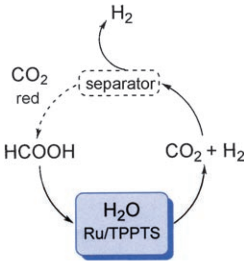


The use of formic acid as a hydrogen-storage material has become more feasible thanks to the development of a homogeneous catalytic system of ruthenium water-soluble complexes (Ru/TPPTS; TPPTS = *meta*-trisulfonated triphenylphosphine) that selectively decomposes HCOOH into H_2 and CO_2. Continuous generation of H_2 of very high purity, over a wide range of pressures, and under mild conditions was achieved.

Hydrogen Storage

C. Fellay, P. J. Dyson, G. Laurenczy* **3966 – 3968**

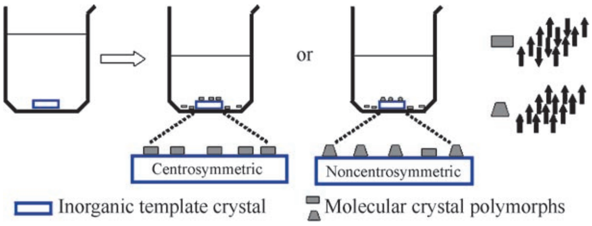
A Viable Hydrogen-Storage System Based On Selective Formic Acid Decomposition with a Ruthenium Catalyst

Contents

Crystal Engineering

M. Jaya Prakash, P. Raghavaiah,
Y. S. R. Krishna,
T. P. Radhakrishnan* ______ **3969–3972**

Growing Molecular Crystals on Inorganic Crystals: Polar Structure Induced by Noncentrosymmetric Templates



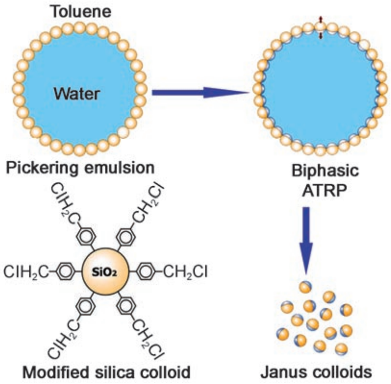
Like promotes like: The templating effect of inorganic crystals is exploited to promote the growth of the polar structure of a molecular crystal of a dipolar zinc(II) complex (see picture). It is likely that the polar nature of the noncentrosymmetric template crystal lattice, and its associated electrostatic field, facilitates the oriented assembly of the dipolar molecules.

Janus Colloids

B. Liu, W. Wei, X. Qu,
Z. Yang* ______ **3973–3975**

Janus Colloids Formed by Biphasic Grafting at a Pickering Emulsion Interface

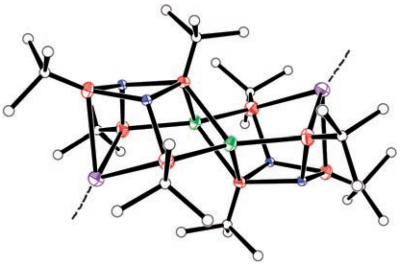
A two-faced synthesis: Biphasic grafting at a Pickering emulsion interface leads to the formation of Janus colloids (see scheme; ATRP: atom transfer radical polymerization), which form Janus composite colloids by the preferential growth of desired materials in specific regions of the original colloids. This approach is general and can be extended to the synthesis of a huge family of such colloids.



Heterotrimetallic Butoxides

X.-H. Wei,* Q.-C. Dong, H.-B. Tong,
J.-B. Chao, D.-S. Liu,*
M. F. Lappert* ______ **3976–3978**

Heterotrimetallic Salts: Synthesis, Structures, and Superbase Reactivity of Crystalline *tert*-Butoxides $[Li_4Na_2K_2(OtBu)_8(\mu\text{-}L)]_n$



Line them up! Crystalline, polymeric arrays of heterotrimetallic ($Li_4Na_2K_2$) *tert*-butoxides of definite composition have been obtained by mixing the individual Li, Na, and K alkoxides. In the crystal, $[Li_4Na_2K_2(\mu_3\text{-}OtBu)_6(\mu_4\text{-}OtBu)_2]$ units (see picture: Li blue, Na green, K purple, C white, O red) are joined through their terminal K ions by $\eta^6{:}\eta^6\text{-}C_6H_6$ or *N*,*N*′-tetramethylethylenediamine bridges.

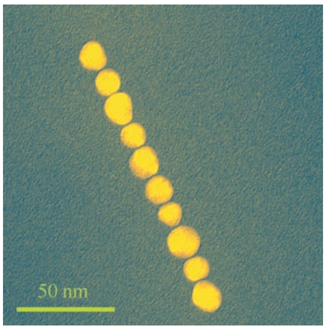
β-Amino Acids

C. M. Byrne, T. L. Church, J. W. Kramer,
G. W. Coates* ______ **3979–3983**

Catalytic Synthesis of β³-Amino Acid Derivatives from α-Amino Acids

α goes to β! The catalytic ring-expansive carbonylation of oxazolines, easily derived from α-amino acids, to yield β-amino acid derivatives is described. The catalyst is $[HCo(CO)_4]$; high yields are observed for most substrates, and enantiopure oxazolines are carbonylated with predictable stereochemistry to the corresponding enantiopure oxazinones.

An electrostatic tuner: Long-range isotropic electrostatic repulsion between identically charged nanoparticles can become anisotropic in the presence of short-range anisotropic dipolar interactions, thus endorsing anisotropic self-assembly of the nanoparticles into chains. The length of these particle chains can be tuned by controlling the interparticle electrostatic repulsion (see image).



Nanoparticle Self-Assembly

H. Zhang, D. Wang* ——— **3984 – 3987**

Controlling the Growth of Charged-Nanoparticle Chains through Interparticle Electrostatic Repulsion

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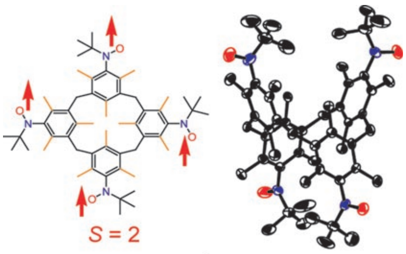
A spin quintet: The electronic and molecular structure of the metacyclophane-based spin-quintet tetraradical **1** with a sterically controlled rigid structure and small fine-structure parameters is characterized. Pulse-ESR based 2D electron spin nutation spectroscopy allows the spin multiplicity of **1** to be unequivocally identified, providing its fine-structure parameters and *g*-values.



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Macrocyclic High-Spin Molecule

T. Sawai, K. Sato,* T. Ise, D. Shiomi,
K. Toyota, Y. Morita,
T. Takui* ——— **3988 – 3990**

Macrocyclic High-Spin ($S=2$) Molecule: Spin Identification of a Sterically Rigid Metacyclophane-Based Nitroxide Tetraradical by Two-Dimensional Electron Spin Transient Nutation Spectroscopy

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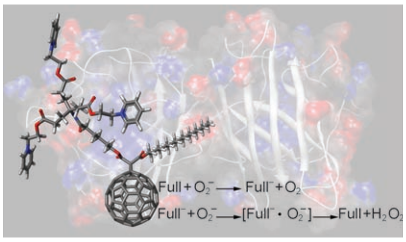


Fullerene antioxidants: A direct correlation between the redox and structural properties of water-soluble fullerenes (see picture) and their reactivity towards superoxide is demonstrated. Some of the C_{60} monoadducts examined act as superoxide dismutase mimetics. The findings establish a guide for designing fullerene derivatives to catalytically decompose the superoxide radical anion.

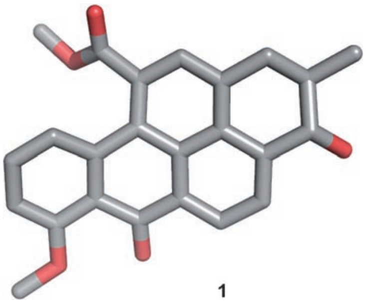
Fullerene Dendrimers

G.-F. Liu, M. Filipović,
I. Ivanović-Burmazović,* F. Beuerle,
P. Witte, A. Hirsch* ——— **3991 – 3994**

High Catalytic Activity of Dendritic C_{60} Monoadducts in Metal-Free Superoxide Dismutation

---

A natural benzopyren: The title compound **1** was discovered by chemical metabolite profiling of a large-scale fermentation of *Streptomyces lavendulae*. Biological evaluation of the *peri*-fused pentacyclic compound revealed antitumor activity against several cell lines. The co-occurrence of an angucyclic polyketide with an identical ring-substitution pattern suggests that **1** is biosynthesized from an angular decaketide and a C_3 building block.



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Natural Products

X. Huang, J. He, X. Niu, K.-D. Menzel,
H.-M. Dahse, S. Grabley, H.-P. Fiedler,
I. Sattler,* C. Hertweck* ——— **3995 – 3998**

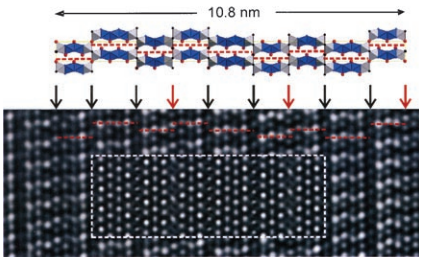
Benzopyrenomycin, a Cytotoxic Bacterial Polyketide Metabolite with a Benzo[*a*]pyrene-Type Carbocyclic Ring System

Contents

Intermetallic Compounds

S. Ponou, T. F. Fässler,*
L. Kienle ______________ **3999 – 4004**

Structural Complexity in Intermetallic Alloys: Long-Periodic Order beyond 10 nm in the System $BaSn_3/BaBi_3$

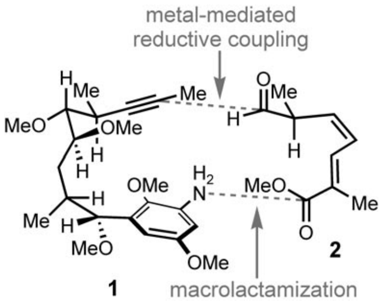


Nanosized long-periodic stacking sequences are formed by polytypic transformations that are initiated by partially substituting Bi for Sn in the close-packed structure of $BaSn_3$. Single-crystal X-ray diffraction and TEM investigations show that temperature-dependent interlayer-ordering processes lead to repeat units beyond 10 nm (see TEM image).

Natural Product Synthesis

J. K. Belardi,
G. C. Micalizio* ______________ **4005 – 4008**

Total Synthesis of Macbecin I



Beyond the bounds of biosynthesis: In a step towards the goal of developing a synthetic pathway for the production of collections of complex molecules related to the benzoquinone ansamycin antibiotics, a natural member of this class was synthesized in a convergent manner through the mild titanium alkoxide mediated coupling of the highly functionalized aniline-containing alkyne **1** with the sensitive polyunsaturated aldehyde **2**.

Natural Products

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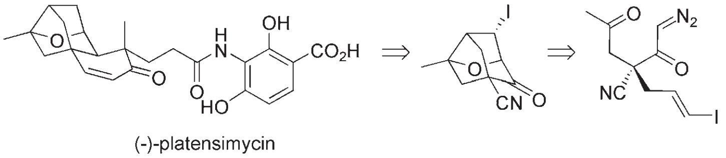
Y. K. Chung, E. Lee* ______________ **4009 – 4011**

A Carbonyl Ylide Cycloaddition Approach to Platensimycin

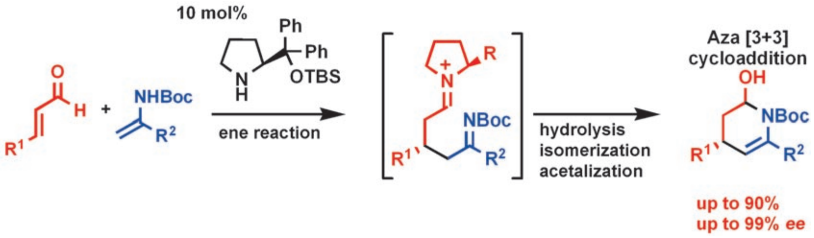


Short and to the point: A formal synthesis of platensimycin has been accomplished by employing a carbonyl ylide [3+2] cycloaddition reaction (see scheme). This short and facile enantioselective synthesis of the pivotal tetracyclic precursor requires 11 steps and proceeds in 20% overall yield from isopropyl cyanoacetate.

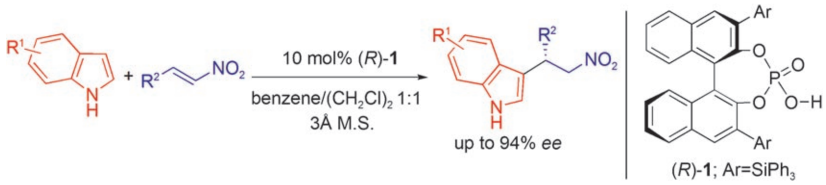
Organocatalysis

Y. Hayashi,* H. Gotoh, R. Masui,
H. Ishikawa ______________ **4012 – 4015**

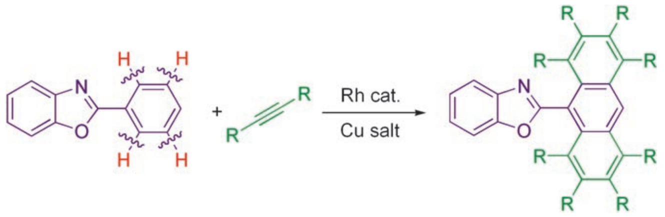
Diphenylprolinol Silyl Ether as a Catalyst in an Enantioselective, Catalytic, Formal Aza [3+3] Cycloaddition Reaction for the Formation of Enantioenriched Piperidines



Aza-ene reaction: Diphenylprolinol silyl ether was found to be an effective organocatalyst for the formal aza [3+3] cycloaddition reaction of α,β-unsaturated aldehydes and enecarbamates (see scheme). The reaction proceeds through an asymmetric catalytic ene reaction, isomerization, hydrolysis, and cyclization to afford piperidine derivatives in good yields and excellent enantioselectivities.



Crafty catalysts: Friedel–Crafts alkylation of indoles with nitroalkenes proceeded in the presence of phosphoric acid **1** and 3 Å molecular sieves to give Friedel–Crafts adducts with excellent enantioselectivities (see scheme).



Bright light rings: The direct coupling of phenylazoles with an internal alkyne proceeds efficiently in the presence of a rhodium catalyst and a copper oxidant to selectively give either the 1-naphthyl- or 1-anthrylazole derivatives through the cleavage of multiple C–H bonds (see scheme; 1-naphthylazole derivative not shown). Some of the products exhibit intense fluorescence in the solid state.

Supporting information is available on www.angewandte.org (see article for access details).

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

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Issue 17: April 8. · Issue 18: April 15. · Issue 19: April 21. · Issue 20: April 28

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