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:*

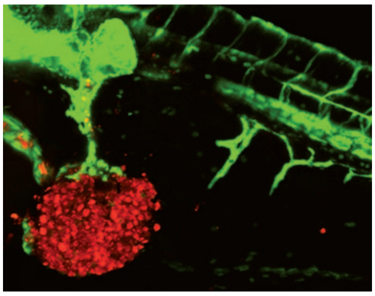
Author Profile

"In my opinion, the word "scientist" means an artist for the future.
If I won the lottery I would buy a winery …"
This and more about Kazunori Kataoka can be found on page 5218.

Books

Meeting Reviews

Highlights



Angiogenesis inhibition: Metal complexes are often overlooked in the development of new drugs. However, rationally designed iridium complexes with bidentate pyridocarbazole ligands have been found to act as selective protein kinase inhibitors. Experiments in zebrafish embryos revealed impressive anti-angiogenic effects for this type of metallodrug. (Picture: tumor-induced angiogenesis in a zebrafish embryo; red: transplanted tumor cells, green: blood vessels).

Bioorganometallic Chemistry

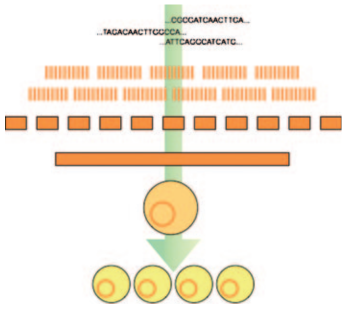
Contents

Intelligent Design?

U. T. Bornscheuer* ________ **5228 – 5230**

The First Artificial Cell—A Revolutionary Step in Synthetic Biology?

It's alive: The creation of an artificial self-replicating microorganism (*Mycobacterium mycoides* JCVIsyn1.0) from a chemically synthesized full-length genome by the team of Craig Venter is without doubt a landmark achievement in synthetic biology. But will this technique revolutionize modern biotechnology and eventually lead to an alternative supply of energy, biofuels, and chemicals?

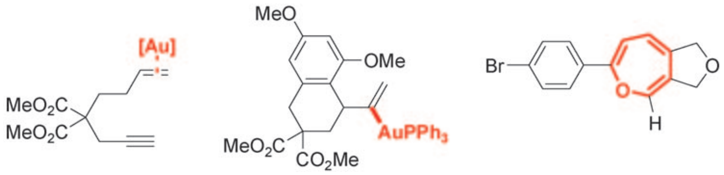


Minireviews

Gold Catalysis

A. S. K. Hashmi* ________ **5232 – 5241**

Homogeneous Gold Catalysis Beyond Assumptions and Proposals—Characterized Intermediates



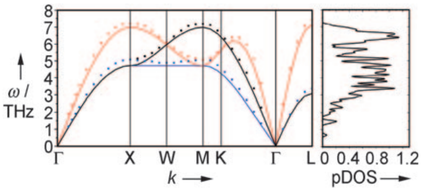
Hard facts: Which intermediates of homogeneous gold-catalyzed conversions have been isolated or detected, and where do we enter the shaky grounds of speculation? The palette of proven intermediates extends from gold π complexes to pure organic cyclization products (see examples).

Reviews

Solid-State Chemistry

R. P. Stoffel, C. Wessel, M.-W. Lumey, R. Dronskowski* ________ **5242 – 5266**

Ab Initio Thermochemistry of Solid-State Materials



The heat of the matter: The quantum-chemical treatment of vibrational modes within crystalline solids is the key towards an ab initio thermochemistry of solid-state materials, which allows classical thermochemistry to be understood atomistically and extended to experimentally inaccessible conditions. Based on Schrödinger's equation, temperature-dependent solid-state chemical problems, such as activation barriers, temperature polymorphs, or free reaction enthalpies, can be tackled computationally.

For the USA and Canada:
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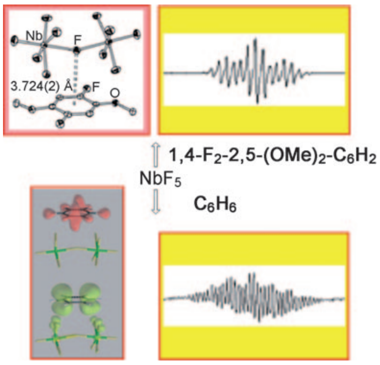
Arene Radical Cations

F. Marchetti, C. Pinzino, S. Zacchini,
G. Pampaloni* ______ 5268 – 5272

Long-Lived Radical Cations of Monocyclic Arenes at Room Temperature Obtained by NbF_5 Acting as an Oxidizing Agent and Counterion Precursor

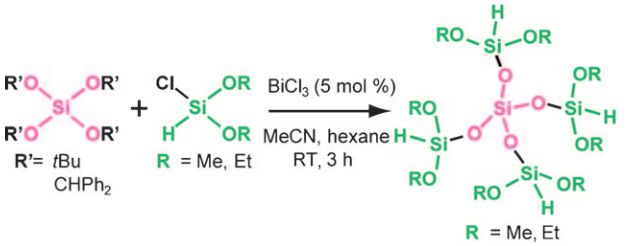


Salt of the earth: Radical cation salts of monocyclic arenes, including benzene, have been obtained in a reaction where niobium pentafluoride behaves both as an oxidizing agent (conversion into NbF_4) and fluoride acceptor (to afford the counterion $[Nb_2F_{11}]^-$, see picture). Anion–π-electron density interactions, as revealed by experimental and computational studies, are crucial in providing unprecedented inertness to the radical cations.

Oligomerization

R. Wakabayashi, K. Kawahara,
K. Kuroda* ______ 5273 – 5277

Nonhydrolytic Synthesis of Branched Alkoxysiloxane Oligomers $Si[OSiH(OR)_2]_4$ (R = Me, Et)

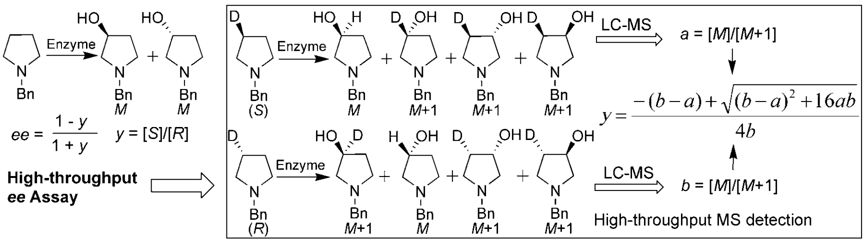


Beyond silanol: A branched siloxane oligomer bearing terminal dialkoxysilyl groups was nonhydrolytically synthesized by direct alkoxysilylation of a tetraalkoxysilane with a chlorodialkoxysilane in the presence of the Lewis acid $BiCl_3$ (see scheme). The reaction proceeds without the formation of intermediate silanol groups, and provides a selective route for siloxane-based oligomers.

Enantioselectivity

Y. Chen, W. L. Tang, J. Mou,
Z. Li* ______ 5278 – 5283

High-Throughput Method for Determining the Enantioselectivity of Enzyme-Catalyzed Hydroxylations Based on Mass Spectrometry

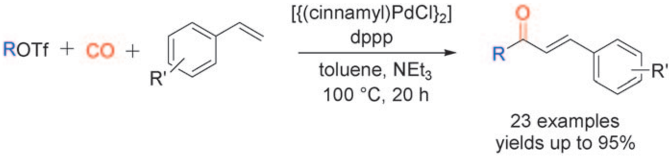


Up to speed: An accurate, sensitive, high-throughput, and simple method for measuring the product *ee* value of enzyme-catalyzed hydroxylations (see scheme) is based on the use of enantiopure or enantioenriched deuterated substrates and mass spectrometric detection.

Palladium Catalysis

X.-F. Wu, H. Neumann,
M. Beller* ______ 5284 – 5288

Palladium-Catalyzed Coupling Reactions: Carbonylative Heck Reactions To Give Chalcones



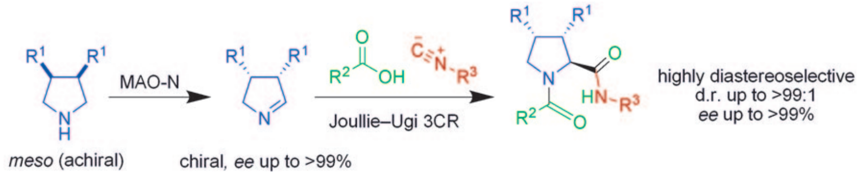
Chalcones made easy: Carbonylative Heck reactions of aryl and alkenyl triflate derivatives with carbon monoxide and aromatic olefins proceed in the presence of palladium catalysts (see scheme; dppp = 1,3-bis(diphenylphosphino)propane, Tf = triflate; R = aryl, vinyl). With this process, the gap between the Suzuki and Sonogashira carbonylative reactions is finally bridged.

Contents

Multicomponent Reactions

A. Znabet, E. Ruijter, F. J. J. de Kanter, V. Köhler, M. Helliwell, N. J. Turner, R. V. A. Orru* ____________ **5289 – 5292**

Highly Stereoselective Synthesis of Substituted Prolyl Peptides Using a Combination of Biocatalytic Desymmetrization and Multicomponent Reactions

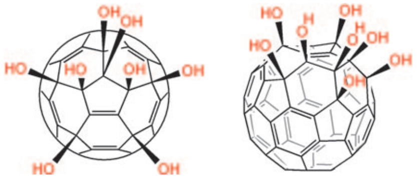


Time and pep-tide wait for no man: Optically pure 3,4-disubstituted 1-pyrrolines, generated from the corresponding *meso*-pyrrolidines by biocatalytic desymmetrization (MAO-N = monoamine oxidase N), react with carboxylic acids and isocyanides in a highly diastereoselective Ugi-type multicomponent reaction to give substituted prolyl peptides of high pharmaceutical relevance.

Fullerenols

G. Zhang, Y. Liu, D. H. Liang,* L. B. Gan,* Y. L. Li ____________ **5293 – 5295**

Facile Synthesis of Isomerically Pure Fullerenols and Formation of Spherical Aggregates from $C_{60}(OH)_8$

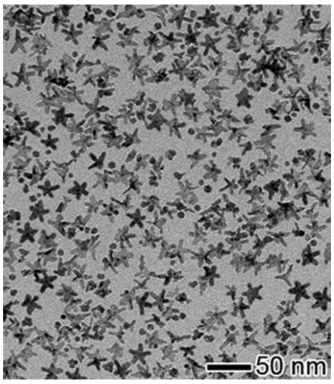


Octahydroxy fullerene $C_{60}(OH)_8$ (see picture) is among the isomerically pure fullerenols with two to eight OH groups that were prepared by selective transformation of *tert*-butylperoxo groups of fullerene mixed peroxides. Since $C_{60}(OH)_8$ has all OH groups on the same hemisphere, it is amphiphilic and forms stable spherical aggregates in water.

Pentapod Nanostructures

H. Zhang,* X. Xia, W. Li, J. Zeng, Y. Dai, D. Yang, Y. Xia* ____________ **5296 – 5300**

Facile Synthesis of Five-fold Twinned, Starfish-like Rhodium Nanocrystals by Eliminating Oxidative Etching with a Chloride-Free Precursor



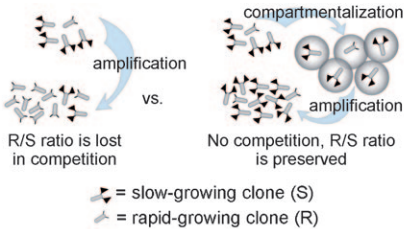
Five-fold twinned, starfish-like Rh nanocrystals consisting of five arms (see TEM) have been synthesized in high yields with the use of $[\{(CF_3COO)_2Rh\}_2]$ as a precursor to completely eliminate oxidative etching from this system. The as-prepared Rh nanocrystals were shown with great performance as a substrate for SERS.

Phage Display

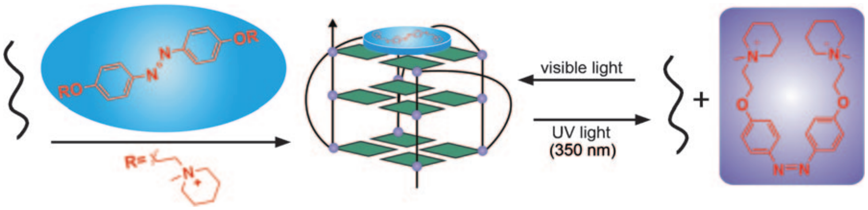
R. Derda,* S. K. Y. Tang, G. M. Whitesides* ____________ **5301 – 5304**

Uniform Amplification of Phage with Different Growth Characteristics in Individual Compartments Consisting of Monodisperse Droplets

Save every clone! In phage display, clones displaying ligands that hinder growth of phage are lost in amplification. Competition of slowly (S) and rapidly (R) growing phage is mitigated in monodisperse emulsions generated by a simple microfluidic device. Separating R and S in ca. 10^7 droplets maintains R/S ratio throughout amplification. Competition-free amplification of phage preserves ligands that are usually lost in phage display screen.

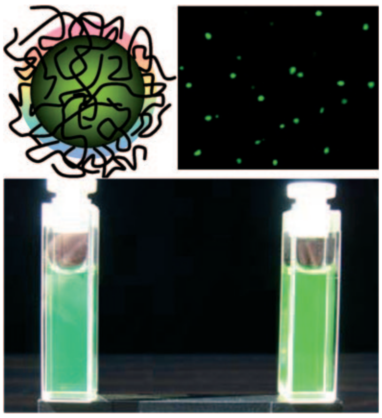


DNA Structures



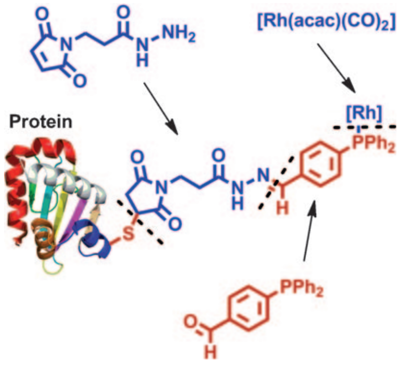
Bend and stretch... bend and stretch... An azobenzene derivative was used to induce reversible stretching and folding of G-quadruplex DNA upon photoirradiation (see picture). The G quadruplex formed in the presence of the *trans* isomer was dissociated by irradiation with UV light, and the resulting open oligomer was refolded into a G quadruplex under visible light. This nanodevice thus converts light directly into mechanical work.

Carbon “Quantum” Dots



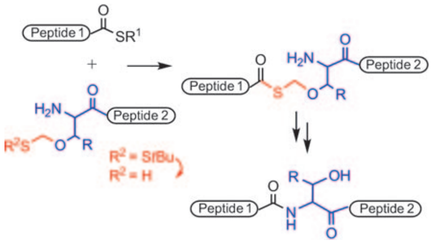
Quantum of solace: Fluorescent carbon dots (surface-passivated carbon nanoparticles) are developed as an alternative to classical semiconductor quantum dots. Gel column chromatography afforded carbon dots with emission yields close to 60%. Their optical properties resemble band-gap transitions found in nanoscale semiconductors, thus suggesting that nanoscale carbon particles acquire essentially semiconductorlike characteristics.

Metalloenzymes



A joint effort: A novel, highly efficient, and selective procedure for phosphane modification of proteins is reported (see scheme). This method involves cysteine modification with a maleimide containing a hydrazide functional group and subsequent hydrazone formation with phosphane aldehydes. Mono- and bidentate phosphane ligands were successfully coupled to several proteins, one of which was coordinated to rhodium to give an artificial metalloenzyme.

Glycopeptide Synthesis



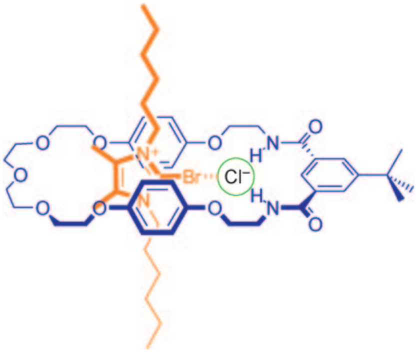
Going native: A mercaptomethyl group on the side-chain hydroxy group of serine and threonine residues facilitates a native chemical ligation reaction at the Xaa-Ser/Thr site (see scheme; R = H or Me). The intermediate thioester is treated to achieve an *S*- to *N*-acyl shift. After ligation, the group is spontaneously removed to obtain the glycopeptide contulakin-G and human calcitonin.

Halogen Bonding

C. J. Serpell, N. L. Kilah, P. J. Costa,
V. Félix, P. D. Beer* ________ **5322 – 5326**

Halogen Bond Anion Templated Assembly of an Imidazolium Pseudorotaxane

Halogen bonding has been exploited in the assembly of an interpenetrated molecular system. The strength of chloride-anion-templated pseudorotaxane formation with a 2-bromo-functionalized imidazolium threading component and an isophthalamide macrocycle (see picture) is significantly enhanced compared to hydrogen-bonded pseudorotaxane analogues.

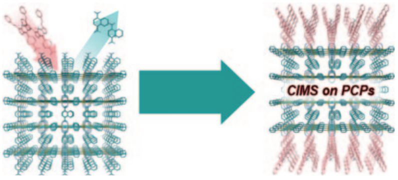


Functional Monolayers

M. Kondo, S. Furukawa,* K. Hirai,
S. Kitagawa* ______________ **5327 – 5330**

Coordinatively Immobilized Monolayers on Porous Coordination Polymer Crystals

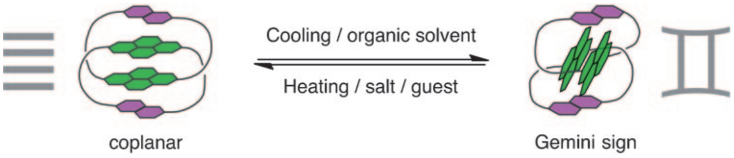
Surface-specific: Coordinatively immobilized monolayers (CIMs) of fluorescent dyes were fabricated on specific single-crystal surfaces of porous coordination polymers (PCPs) (see picture). This approach enables the fabrication of functional PCP crystal surfaces with precisely controlled fluorescent gating and sensing properties.



Catenanes

H. Y. Au-Yeung, G. D. Pantoş,
J. K. M. Sanders* __________ **5331 – 5334**

A Water Soluble Donor–Acceptor [2]Catenane that Can Switch between a Coplanar and a Gemini-Sign Conformation

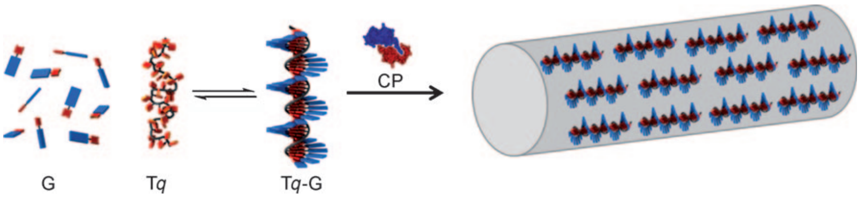


When the moon is in the seventh house: A conformationally switchable donor–acceptor [2]catenane was synthesized from a dynamic combinatorial library in water. The arrangement of the π units in one of the observed conformations features an unprecedented ♊ shape, which is reminiscent of the astrological Gemini sign (see picture). The catenane can be switched between the parallel and non-parallel conformations upon thermal, chemical, or hydrophobic stimuli.

Self-Assembly

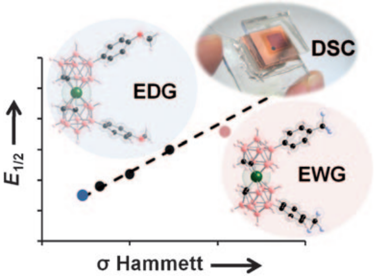
A. de la Escosura,* P. G. A. Janssen,
A. P. H. J. Schenning, R. J. M. Nolte,
J. J. L. M. Cornelissen* _____ **5335 – 5338**

Encapsulation of DNA-Templated Chromophore Assemblies within Virus Protein Nanotubes



A beneficial virus: The hierarchical self-assembly of a three-component system consisting of single-stranded DNA (oligothymines; *Tq*), chromophores (G), and virus coat proteins (CP) leads to the formation of micrometer-long nanotubes (see picture). Tuning the interaction between the three components leads to the formation of structures with different length scales, and the chromophores within the nanotubes maintain the helical arrangement of the *Tq*–G template.

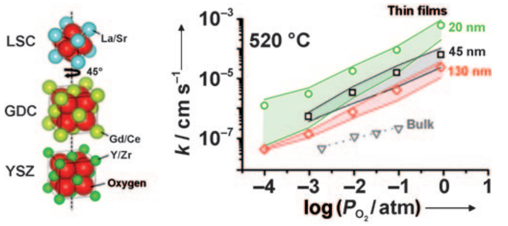
Redox "B"ees: Rational design of a new series of boron-functionalized Ni^{III}/Ni^{IV}–bis(dicarbollide) clusters results in a family of robust and tunable redox shuttles (see diagram; EDG and EWG denote electron-donating and -withdrawing groups, respectively). This offers a means to rationally control the redox properties in dye-sensitized solar cells (DSCs), leading to exceptionally high open-circuit voltages.



Redox Shuttles

A. M. Spokoyny, T. C. Li, O. K. Farha, C. W. Machan, C. She, C. L. Stern, T. J. Marks,* J. T. Hupp,* C. A. Mirkin* **5339 – 5343**

Electronic Tuning of Nickel-Based Bis(dicarbollide) Redox Shuttles in Dye-Sensitized Solar Cells



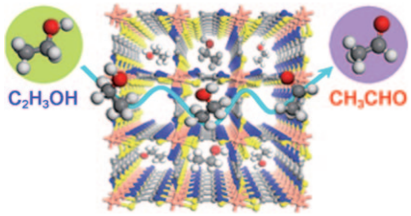
The active ingredient: $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ (LSC) epitaxial thin films are prepared on (001)-oriented yttria-stabilized zirconia (YSZ) single crystals with a gadolinium-doped ceria (GDC) buffer layer (see picture). The LSC epitaxial films exhibit better oxygen reduction kinetics than bulk LSC. The enhanced activity is attributed in part to higher oxygen nonstoichiometry.

Fuel Cells

G. J. la O', S.-J. Ahn, E. Crumlin, Y. Orikasa, M. D. Biegalski, H. M. Christen, Y. Shao-Horn* **5344 – 5347**

Catalytic Activity Enhancement for Oxygen Reduction on Epitaxial Perovskite Thin Films for Solid-Oxide Fuel Cells

No need for nobles: The copper-based metal–organic framework material N,N′-bis(2-hydroxyethyl)dithiooxamidatocopper(II) (see picture, Cu pink, N blue, S yellow, O red, C gray, H white) is an active catalyst for ethanol electrooxidation. The performance of this noble-metal-free material is comparable to those of some reported Pt-based catalysts.

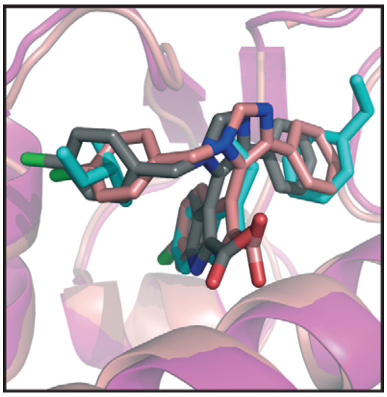


MOF Electrocatalysts

L. Yang, S. Kinoshita, T. Yamada, S. Kanda, H. Kitagawa,* M. Tokunaga, T. Ishimoto, T. Ogura, R. Nagumo, A. Miyamoto, M. Koyama **5348 – 5351**

A Metal–Organic Framework as an Electrocatalyst for Ethanol Oxidation

The parallel discovery of multiple scaffolds useful to antagonize the cancer-relevant protein–protein interaction p53/Hdm2 is described. The new method is based on the tightly interwoven interplay of multicomponent reaction chemistry, structural biology, computational chemistry, and high-content NMR-based screening.



Multicomponent Reactions

A. Czarna, B. Beck, S. Srivastava, G. M. Popowicz, S. Wolf, Y. Huang, M. Bista, T. A. Holak, A. Dömling* **5352 – 5356**

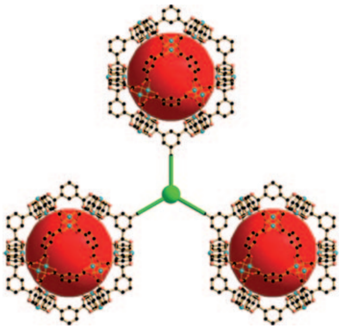
Robust Generation of Lead Compounds for Protein–Protein Interactions by Computational and MCR Chemistry: p53/Hdm2 Antagonists

Metal–Organic Frameworks

D. Yuan, D. Zhao, D. Sun,
H.-C. Zhou* ______ **5357 – 5361**

An Isoreticular Series of Metal–Organic Frameworks with Dendritic Hexacarboxylate Ligands and Exceptionally High Gas-Uptake Capacity

Holding gas: One of the isoreticular metal–organic frameworks (MOFs) that have been synthesized and characterized structurally, PCN-68 (see structure), has a Langmuir surface area of as high as 6033 $m^2 g^{-1}$. The MOFs also display excellent gas (H_2, CH_4, and CO_2) adsorption capacity.

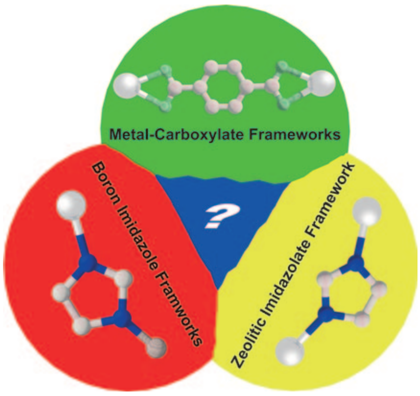


Framework Materials

S. Zheng, T. Wu, J. Zhang, M. Chow,
R. A. Nieto, P. Feng,*
X. Bu* ______ **5362 – 5366**

Porous Metal Carboxylate Boron Imidazolate Frameworks

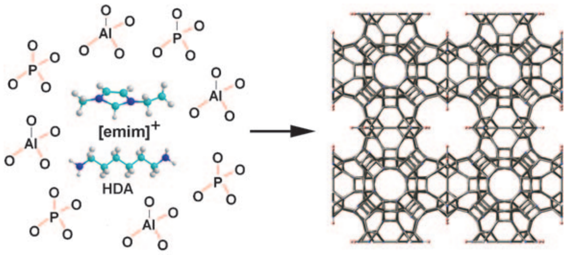
A sponge for carbon: A new family of porous materials with tunable gas sorption properties has been prepared by integrating metal carboxylates and boron imidazolates under hydro- or solvothermal conditions. One hydrothermally synthesized phase exhibits very high volumetric CO_2 storage capacity of 81 $L L^{-1}$ (273 K, 1 atm).



Aluminophosphates

Y. Wei, Z. Tian,* H. Gies, R. Xu, H. Ma,
R. Pei, W. Zhang, Y. Xu, L. Wang, K. Li,
B. Wang, G. Wen, L. Lin ______ **5367 – 5370**

Ionothermal Synthesis of an Aluminophosphate Molecular Sieve with 20-Ring Pore Openings

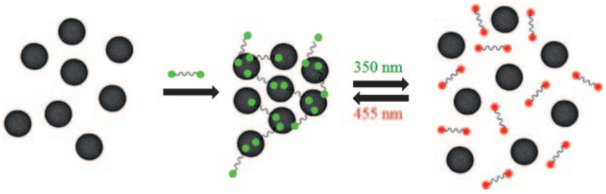


Open for business: The first aluminophosphate molecular sieve with 20-ring pore openings has been synthesized ionothermally using a co-structure-directing agent (see figure; H white, C turquoise, N blue). The new material has a -CLO framework and excellent stability in comparison to the $GaPO_4$ analogue cloverite. These characteristics indicate its potential applications in separation, catalysis, and gas storage.

Photoresponsive Systems

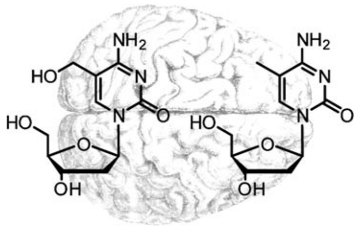
S. K. M. Nalluri,
B. J. Ravoo* ______ **5371 – 5374**

Light-Responsive Molecular Recognition and Adhesion of Vesicles



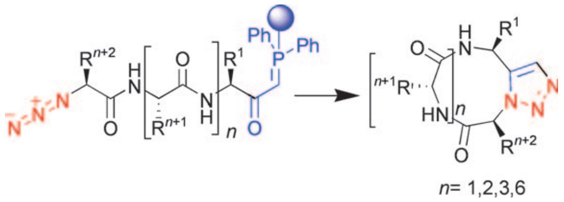
Supramolecular glue: The photoinduced isomerization of difunctional azobenzenes can be used to induce and reverse the molecular recognition and adhesion of bilayer vesicles made up of cyclodextrin (CD) molecules. The molecular basis of this light-responsive supramolecular glue is the *cis–trans* isomerization of the azobenzene (see picture; black circles CD, green *trans*-azobenzene, red *cis*-azobenzene).

Hydroxymethylcytosine



Mind over matter: LC-MS has allowed the amount of the post-replicatively formed DNA base 5-hydroxymethylcytosine (see picture; left) to be quantified in brain tissue. The nucleoside is most abundant in areas that are associated with higher cognitive functions, and its content in mouse hippocampi seems to increase with age. The new method enables hydroxymethylcytosine to be quantified with unprecedented accuracy.

Cyclopeptide Synthesis

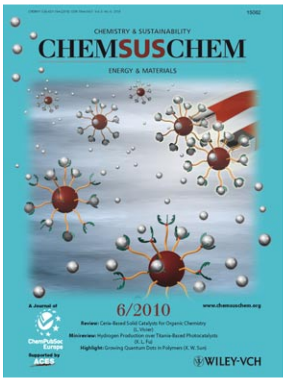


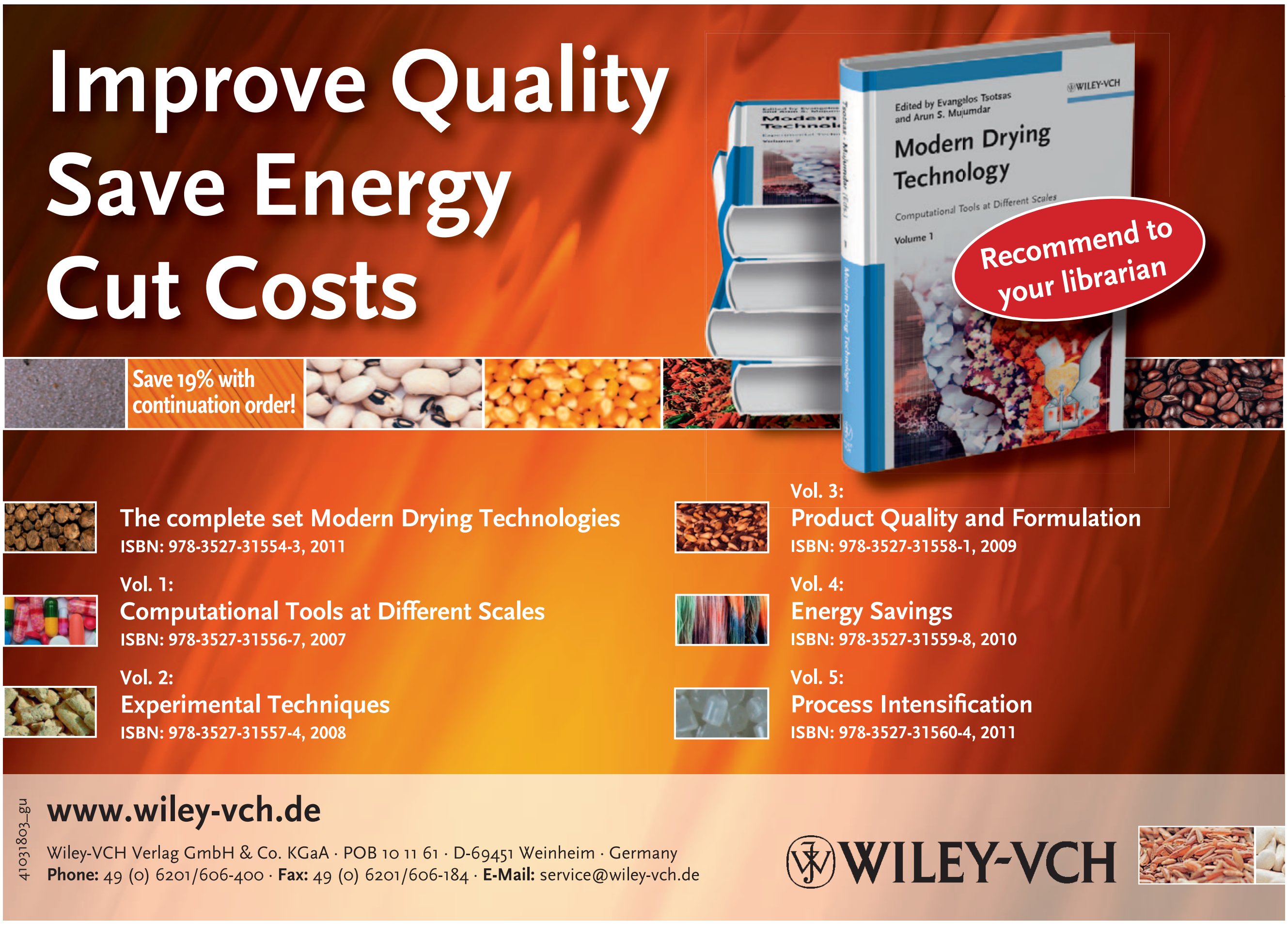
Support and guidance: Azidopeptidyl phosphoranes on a solid support react very efficiently through cyclative cleavage to yield cyclopeptides with an incorporated triazole ring. The solid support is advantageous as cyclization is favored strongly over oligomerization reactions and thus only cyclized products are released.

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).

Service




Edited by Evangelos Tsotsas and Arun S. Mujumdar
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