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

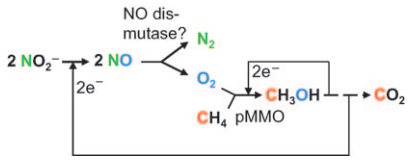
"My favorite subjects at school were scientific subjects such as chemistry, biology, mathematics, and physics. I also liked philosophy.
The biggest problem that scientists face is financial support (and the time invested in getting it). …"
This and more about Ramón Martínez-Máñez can be found on page 6708.

Books

Modern Molecular Photochemistry of Organic Molecules — Nicholas J. Turro, V. Ramamurthy, Juan C. Scaiano

Highlights

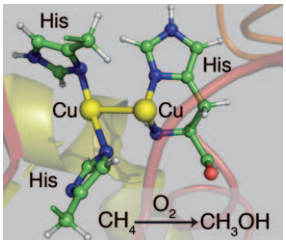
More than one way to skin a cat: Some strictly anaerobic bacteria grow in the presence of methane and nitrite, forming CO_2 and N_2. Recently published experimental evidence suggests the involvement of a NO dismutase and of a particulate methane monooxygenase (pMMO) in the process. Both enzymes are lacking in microorganisms that catalyze anaerobic methane oxidation with sulfate. There are thus at least two pathways that enable anaerobes to use methane as fuel.



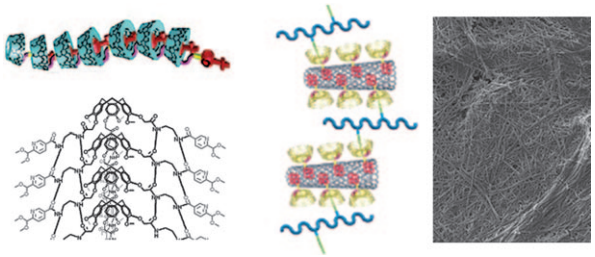
Methane Oxidation

Contents

What/where is the active site? The determination of the metal ion content and makeup of the bacterial membrane protein methane monooxygenase (pMMO) has an enigmatic research history, despite protein X-ray structures. A new study appears to settle the issue; the dicopper center facilitates oxidation of methane to methanol. However, the unusual active-site environment leaves many questions for future investigations on the relevant copper-dioxygen chemistry and biochemistry.



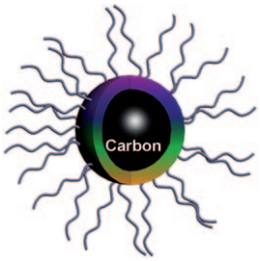
Minireviews



Through the incorporation of cavities into supramolecular gelators, the well-established host–guest chemistry of cavitands can be utilized to build up and break down gel structures, introduce responsive functionalities, and enhance selectivity in applications such as catalysis and extraction.

Reviews

A glowing review: Carbon nanodots have recently emerged as intriguing, cheap, sustainable, and low-toxicity nanoemitters that hold immense promise in energy conversion, bioimaging, diagnostics, and novel composites. This Review summarizes recent advances in the synthesis, understanding, and exploitation of carbon-based quantum dots as nascent biolabels, while pointing to potential new directions for this fascinating class of nanocarbon.



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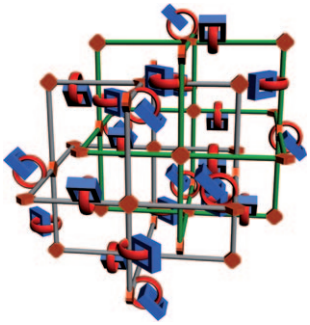
Communications

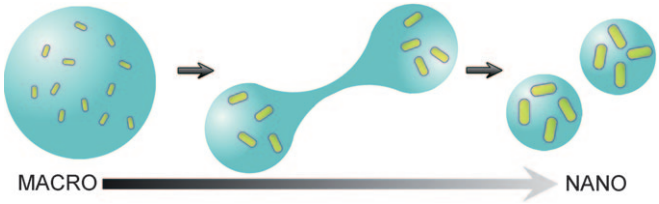
Two-in-one: The integration of two salen/Ti=O units into one molecule allows the enantioselective cyanation of aldehydes to afford the enantioenriched natural or nonnatural cyanohydrin derivatives with turnover numbers of 1960–172000 and *ee* values up to 97% (see scheme). Some of the cyanohydrin derivatives are key intermediates for the synthesis of chiral pharmaceuticals or agrochemicals.

Synthetic Methods



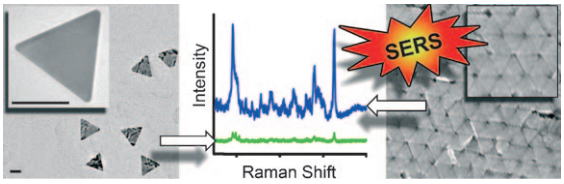
MIMs meet MOFs: Mechanically interlocked molecules (MIMs), in the form of donor–acceptor [2]catenane-containing struts of exceptional length, have been incorporated into a three-dimensional catenated metal–organic framework (MOF) at precise locations and with uniform relative orientations. Catenation is expressed simultaneously within the struts and the framework.

Metal–Organic Frameworks



Divide yourselves! An interfacial reaction drives the spontaneous and sequential division of macroscopic droplets all the way into nanoscopic emulsions (see picture). The sizes of the divided droplets depend on the pH of the solution and the division process is governed by the interplay between surface tension and electrostatic effects. When the dividing droplets contain nanoscopic cargo (e.g., nanorods), they partition it equally into progeny micelles.

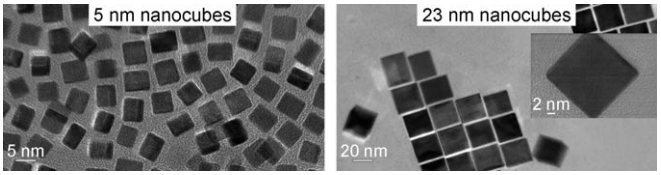
Micelles



SERSly good! Crystallization of triangular gold nanoprisms into close-packed mono- and multilayers is facilitated by electrostatic repulsions. The ordering of the nanotriangles causes an order-of-magnitude increase in surface-enhanced Raman spectroscopy (SERS) enhancement relative to that of disordered assemblies.

Crystal Engineering

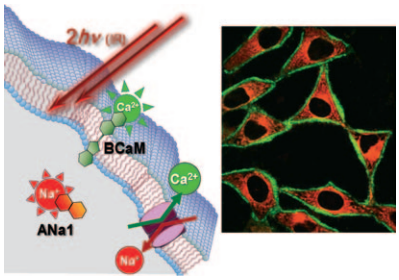
Contents



Precision preparation: A facile, one-step, polyol protocol has been developed to prepare monodisperse, single-crystalline Au–Cu bimetallic nanocubes. Through the careful adjustment of the reaction parameters, both the dimensions of the nanocubes (two examples with edge lengths of 23 and 5 nm are shown) and their gold and copper stoichiometry can be controlled.

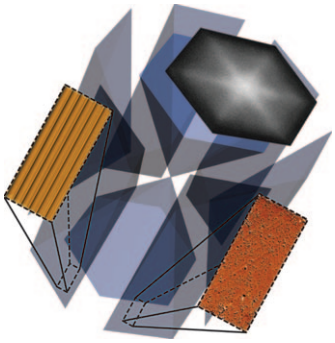
Nanostructures

A two-photon probe (BCaM) shows 14-fold enhancement in two-photon emission fluorescence in response to Ca^{2+} and shows high sensitivity and selectivity for near-membrane Ca^{2+} ions (see picture). Combined with the known Na^+ two-photon probe ANa1, BCaM allows simultaneous dual-color imaging of Ca^{2+}/Na^+ activities within live cells and in tissues at more than 100 μm depth for long time periods without photobleaching.

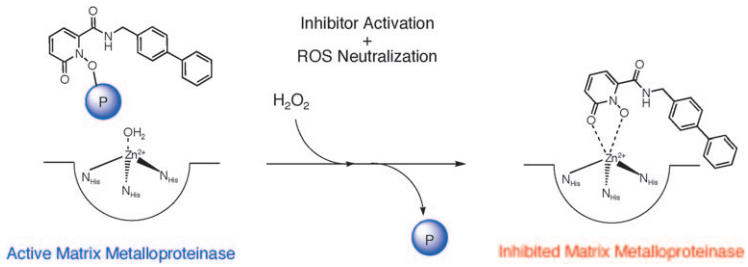


Two-Photon Fluorescent Probes

Starless molecular sieves: The starlike appearance of confocal fluorescence microscopy (CFM) images of large crystals of the AlPO-5 family of microporous materials is due to the presence of barriers to molecular diffusion in the internal crystal architecture (see picture) rather than a star-shaped subcrystal according to studies by CFM, focused ion beam milling, electron backscatter diffraction, and atomic force microscopy.



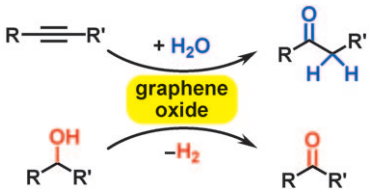
Molecular Sieves



Doing double duty: A metalloproteinase inhibitor that can be activated by reactive oxygen species (ROS) has been designed to protect the blood-brain barrier (BBB) in ischemic reperfusion injury. By both neutralizing damaging ROS and inhibiting degradative metalloproteinases, a single compound can eliminate both threats to the BBB upon activation.

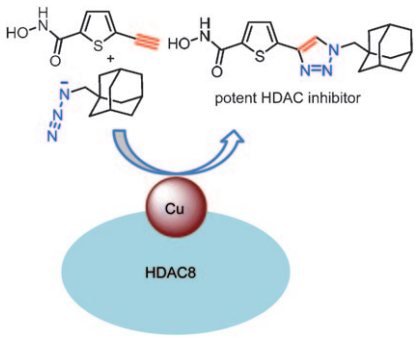
Metalloprotein Proinhibitors

Contents



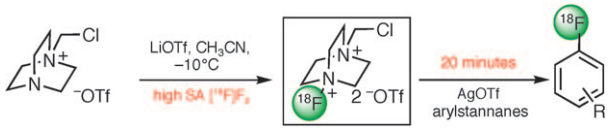
Do not pass GO: Graphene oxide (GO) catalyzes the oxidation of various alcohols and alkenes, and the hydration of various alkynes into their respective aldehydes and ketones in good to excellent yields. The reactions proceed under relatively mild conditions and simple filtration was shown to be a convenient and effective method of catalyst recovery.

Carbocatalysis



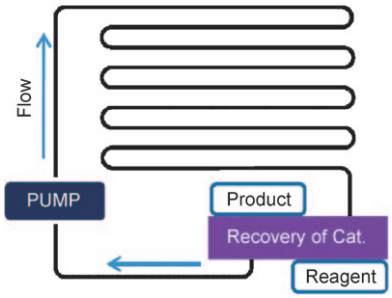
It all happened with a click: In a search for histone deacetylase (HDAC) inhibitors using in situ click chemistry, the first example of protein–Cu acceleration of the azide–alkyne cycloaddition reaction was uncovered. The copper center in the protein target HDAC8 catalyzed triazole formation between one azide–alkyne pair among 30 possibilities. These results provide a new route to HDAC inhibitors and a precedent for new types of protein-based catalysts for click chemistry.

Click Chemistry



Selectfluor, one of the most reactive and commonly used electrophilic fluorinating N–F reagents, has been radiolabeled with ^{18}F. The resulting new [^{18}F]-labeled N–F reagent is safe, nontoxic, and easy to handle. The combined use of [^{18}F]Selectfluor bis(triflate) and AgOTf allows for the preparation of electron-rich ^{18}F-aromatic compounds through a simple "shake and mix" protocol at room temperature (see scheme; SA = specific activtiy).

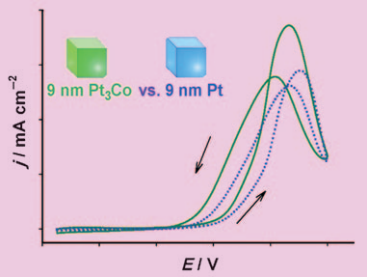
Radiochemistry



Keep on running: A microchemical system for continuous flow catalytic reactions with a magnetic catalyst is presented (see picture). It enables the automatic separation and recirculation of catalyst particles and is applicable to various catalytic reactions.

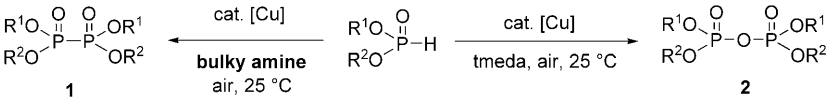
Microreactors

Contents



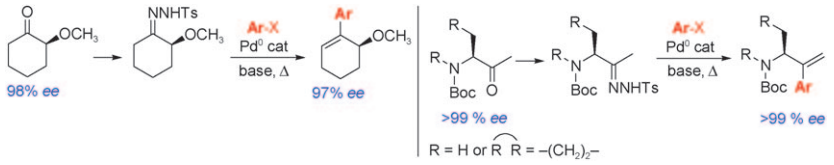
Loaded dice: High-quality and similarly sized Pt_3Co and Pt nanocubes were prepared by gradually reducing metal precursors at high temperatures. Cyclic voltammetric and chronoamperometric results show a much higher methanol oxidation current density on Pt_3Co nanocubes (see picture). The enhanced catalytic activity was explained by the slower and weaker adsorption of CO onto Pt_3Co.

Shape-Controlled Catalysts



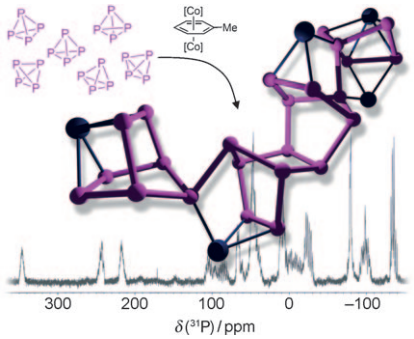
Different copper complexes selectively catalyze the aerobic oxidative coupling of H-phosphonates to afford either hypophosphates and pyrophosphates in high yields with high selectivity (see scheme; tmeda = *N,N,N′,N′*-tetramethylethylenediamine).

Coupling Reactions



Papa was a rollin' ketone: Arylation of ketones with preservation of the chirality in configurationally unstable α-chiral ketones has been achieved by the palladium-catalyzed cross-coupling reaction between tosylhydrazones and aryl halides (see scheme; Boc = *tert*-butoxycarbonyl, Ts = 4-toluenesulfonyl). The regioselectivity in the β-hydride elimination step is key for the retention of configuration.

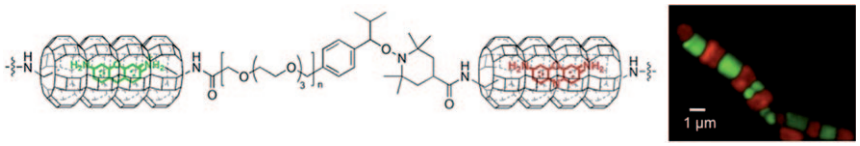
Cross-Coupling



Under control: Controlled self-aggregation of P_4 to extended neutral polyphosphorus cages was achieved in the presence of cobalt complex fragments. X-ray structure analyses of P_{12}, P_{16}, and P_{24} ligand complexes give insights into the formation of aggregated allotropes of phosphorus from elemental P_4.

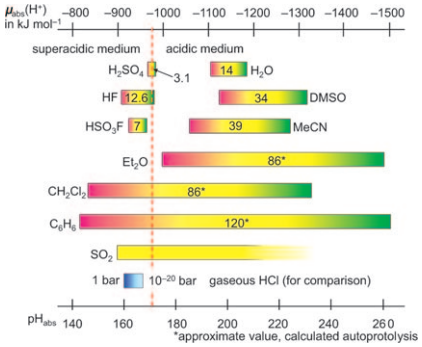
Phosphorus Cages

Contents



Surface Chemistry

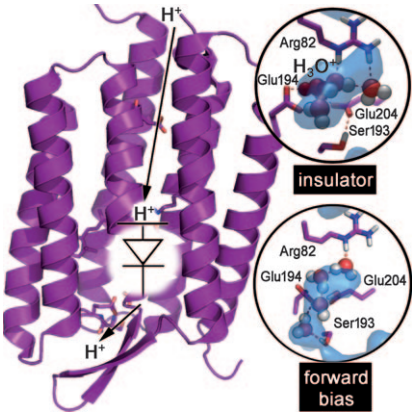
Sticking together: The pore entrances of dye-loaded green or red zeolite L crystals can be site-specifically modified with either alkoxyamines or nitroxide radicals. Mild radical nitroxide exchange reactions of alkoxyamine-terminated "green" zeolite crystals with nitroxide-terminated "red" crystals leads to highly regular crystal chains that contain up to 15 covalently connected crystals with strictly alternating colors.



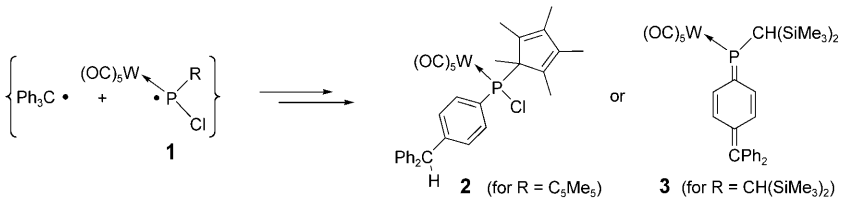
Acidity

One for all! On the basis of the absolute chemical potential of the proton, a unified absolute pH scale is introduced that is universally applicable in the gas phase, in solution, and in the solid state. With this scale, it is possible to directly compare acidities in different media, and to give a thermodynamically meaningful definition of superacidity. This scale can be used in all areas with variable proton activity.

While proton transfer in liquid water is random, membrane proteins creating the proton gradient for ATP synthesis perform a directional proton transfer via protein-bound protonated water molecules. This was shown in bacteriorhodopsin by a combination of time-resolved FTIR spectroscopy, X-ray crystallography, and molecular dynamics simulations.



Structural Biology

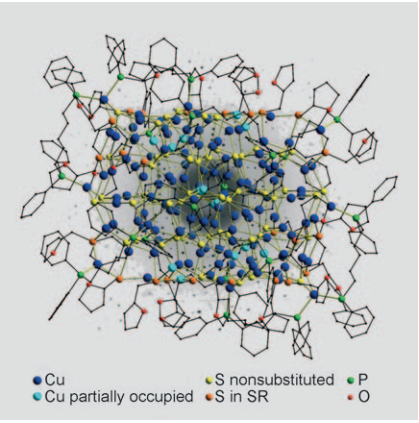


Functionalized Phosphanyl Complexes

C–P or C=P? One-electron oxidation of Li/Cl phosphinidenoid complexes led to the discovery of transient *P*-chlorophosphanyl complexes **1**. Subsequent cross-coupling and rearrangement or elimination reactions yielded **2** and **3**; the latter is the first structurally characterized phosphaquinomethane complex. ESR spectroscopy and DFT calculations support the existence of short-lived P-centered radicals.

Contents

Between molecule and bulk phase: The three title compounds are examples of ligand-stabilized clusters having significant structural features of the corresponding binary copper(I) chalcogenides. The cluster shown, $[Cu_{136}S_{56}(SR)_{24}(dpppt)_{10}]$, can be seen as an approximate $1.2 \times 1.4 \times 1.9$ nm^3 section of a cubic phase of Cu_2S. The background shows a typical X-ray diffraction image of a single crystal of the cluster.



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

Corrigendum

Metal–Silicon Triple Bonds: The Molybdenum Silylidyne Complex $[Cp(CO)_2Mo{\equiv}Si\text{-}R]$

A. C. Filippou,* O. Chernov, K. W. Stumpf, G. Schnakenburg _____ **3296–3300**

Angew. Chem. **2010**, *49*

DOI 10.1002/anie.201000837

In the table of contents entry for this Communication the formula of the title compound was printed with a double bond instead of a triple bond. The correct formula is $[Cp(CO)_2Mo{\equiv}Si\text{-}R]$.