



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. W. Hong, M. Byun, Z. Lin*

Robust Self-Assembly of Highly Ordered Complex Structures by Controlled Evaporation of Confined Microfluids

W. M. Czaplik, M. Mayer, A. Jacobi von Wangelin*

Domino Iron Catalysis: Direct Aryl–Alkyl Cross-Coupling

Z. You, A. H. Hoveyda,* M. L. Snapper*

Catalytic Enantioselective Silylation of Acyclic and Cyclic Triols and Application to Total Syntheses of Cleroindinins D, F, and C

K. Tedsree, A. T. Kong, S. C. Tsang*

Formate as a Surface Probe for Ru Nanoparticles in Liquid ^{13}C NMR Spectroscopy

A. Asati, S. Santra, C. Kaittanis, S. Nath, J. M. Perez*

Oxidase Activity of Polymer-Coated Cerium Oxide Nanoparticles

K. M. Gericke, D. I. Chai, N. Bieler, M. Lautens*

The Norbornene Shuttle: Multicomponent Domino Synthesis of Tetrasubstituted Helical Alkenes through Multiple C–H Functionalization

V. M. Hernández-Rocamora, B. Maestro, B. de Waal, M. Morales, P. García, E. W. Meijer, M. Merks,* J. M. Sanz*

Multivalent Choline Dendrimers as Potent Inhibitors of Pneumococcal Cell Wall Hydrolysis

J.-Q. Wang, S. Stegmaier, T. F. Fässler*

$[\text{Co}@\text{Ge}_{10}]^{3+}$: An Intermetallic Cluster with an Archimedean Pentagonal Prismatic Structure

Author Profile

Johan Hofkens

255

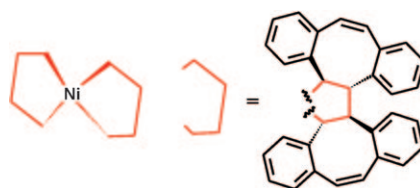
Books

Bile Acids

Gareth J. Jenkins, Laura J. Hardie

reviewed by E. Kolehmainen 258

Four thought: The first nickel(IV) complex that contains only alkyl ligands (see picture) was serendipitously obtained in a reaction between a nickel(0) species and a strained diolefin. The twisted conformation of the ligand provides the necessary steric shielding to stabilize the complex. DFT calculations show this conformation to be the ground state and NMR spectra indicate the diamagnetic nature and high oxidation state of the nickel center.

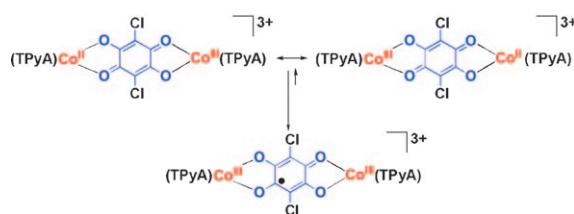


Highlights

Tetraalkyl Nickel

H.-F. Klein,* P. Kraikivskii 260–261

Unexpected Formation of a Molecular Tetraalkyl Nickel Complex from an Olefin/Nickel(0) System



Redox paradox? The initial one-electron oxidation of a metal ion induces a multi-electron rearrangement, leading to oxidation of the second metal ion and reduction of the tetraoxolate dianionic ligand bridging the two metals (see scheme).

These electron-transfer events were observed with numerous spectroscopic, electrochemical, and crystallographic methods (TpyA = tris(2-pyridylmethylamine).

Minireviews

Electron Transfer

J. S. Miller,* K. S. Min 262–272

Oxidation Leading to Reduction: Redox-Induced Electron Transfer (RIET)

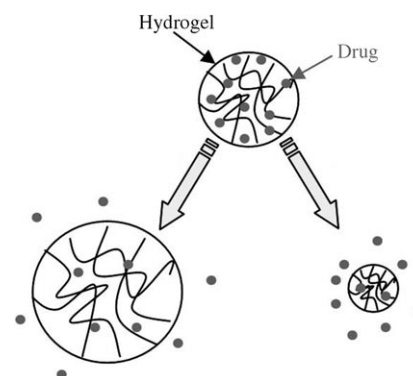
Reviews

Drug Vectors

E. Soussan, S. Cassel, M. Blanzat,*
I. Rico-Lattes* 274–288

Drug Delivery by Soft Matter: Matrix and Vesicular Carriers

How to deliver a drug: The current state of knowledge of drug carriers based on soft matter is presented, and in particular, the advantages and drawbacks of matrix and vesicular systems are discussed. An overview is given of their preparation, transposition to the industrial scale, and possible applications in vectorization.



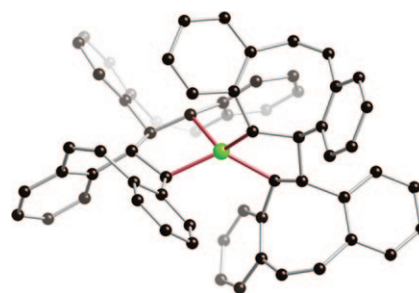
Communications

Nickel Complexes

M. Carnes, D. Buccella, J. Y.-C. Chen,
A. P. Ramirez, N. J. Turro, C. Nuckolls,*
M. Steigerwald* 290–294

A Stable Tetraalkyl Complex of Nickel(IV)

Ni takes a load off: Nickel(0) and a strained alkene react to form a stable tris(alkene) complex, which eliminates the corresponding *trans,trans,trans*-cyclobutane upon heating. A higher proportion of alkene to Ni⁰ precursor yielded the first all-alkyl complex of nickel(IV) (see structure; Ni: green). These reactions, which involve ligand coupling, are driven by relief of ring strain in the alkene.



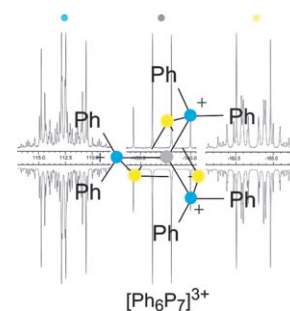
Cationic Phosphorus Clusters

J. J. Weigand,* M. Holthausen,
R. Fröhlich 295–298



Formation of [Ph₂P₅]⁺, [Ph₄P₆]²⁺, and [Ph₆P₇]³⁺ Cationic Clusters by Consecutive Insertions of [Ph₂P]⁺ into P–P Bonds of the P₄ Tetrahedron

Positively phosphorus: A solvent-free melt system (P₄/Ph₂P⁺Cl/GaCl₃) represents a powerful medium for the functionalization of the P₄ tetrahedron to form new cationic phosphorus-rich organophosphorus cage and cluster systems, such as [Ph₂P₅]⁺, [Ph₄P₆]²⁺, and [Ph₆P₇]³⁺ (see picture), by insertion of [Ph₂P]⁺ into P–P bonds.



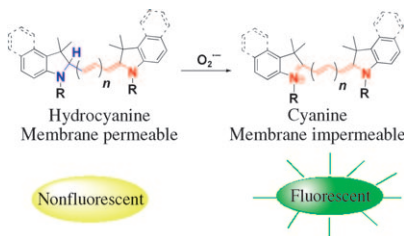
For the USA and Canada:

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electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Accurate and tunable: The title compounds can detect reactive oxygen species (ROS) in cell culture, tissue explants, and for the first time in vivo. The hydrocyanines are synthesized by reduction of the cyanine dyes with NaBH_4 . They can accurately detect nanomolar levels of ROS, have excellent stability against autooxidation, and have tunable emission wavelengths in the range 560–830 nm.

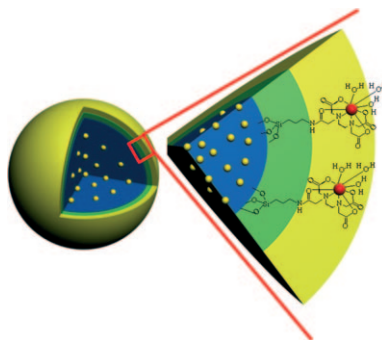


Fluorescence Imaging

K. Kundu, S. F. Knight, N. Willett, S. Lee, W. R. Taylor, N. Murthy* — 299–303

Hydrocyanines: A Class of Fluorescent Sensors That Can Image Reactive Oxygen Species in Cell Culture, Tissue, and In Vivo

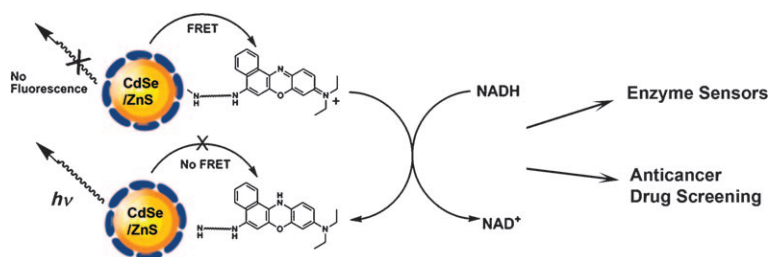
Sensor and sensibility: A sensor that combines the properties of a europium complex and an organic-dye-doped silica nanoparticle allows the rapid and ultra-sensitive detection of an anthrax bio-marker (see picture yellow dots: silica nanoparticles, outer shell: Eu^{III} complex). The sensor response is superior to that obtained with traditional terbium-based sensors.



Nanoparticle Sensors

K. L. Ai, B. H. Zhang, L. H. Lu* — 304–308

Europium-Based Fluorescence Nanoparticle Sensor for Rapid and Ultrasensitive Detection of an Anthrax Biomarker



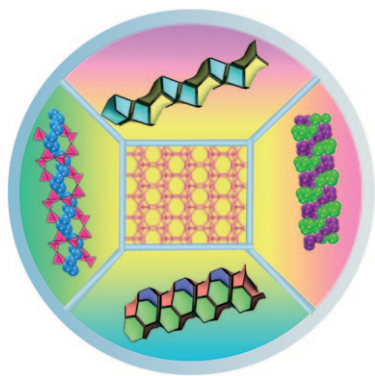
Quantum Dots

R. Freeman, R. Gill, I. Shweky, M. Kotler, U. Banin, I. Willner* — 309–313

Biosensing and Probing of Intracellular Metabolic Pathways by NADH-Sensitive Quantum Dots

On the blue Nile: NAD(P)H-sensitive Nile Blue functionalized CdSe/ZnS quantum dots have been developed for the optical sensing of biocatalytic processes involving NAD⁺-dependent enzymes and the screening of anticancer drugs by monitoring intracellular metabolism (see picture).

ing NAD⁺-dependent enzymes and the screening of anticancer drugs by monitoring intracellular metabolism (see picture).



Intrinsically chiral: The compounds $(\text{C}_4\text{H}_{12}\text{N})_2[\text{M}_2\text{Al}_{10}\text{P}_{12}\text{O}_{48}]$ (denoted MAPO-CJ40; $\text{M} = \text{Co}, \text{Zn}$) were solvothermally synthesized. Their structure contains one-dimensional helical 10-ring channels enclosed by double-helical ribbons of the same handedness made of the edge-sharing of 6-rings along the 2_1 screw axis. The framework is intrinsically chiral and exhibits a new zeotype structure.

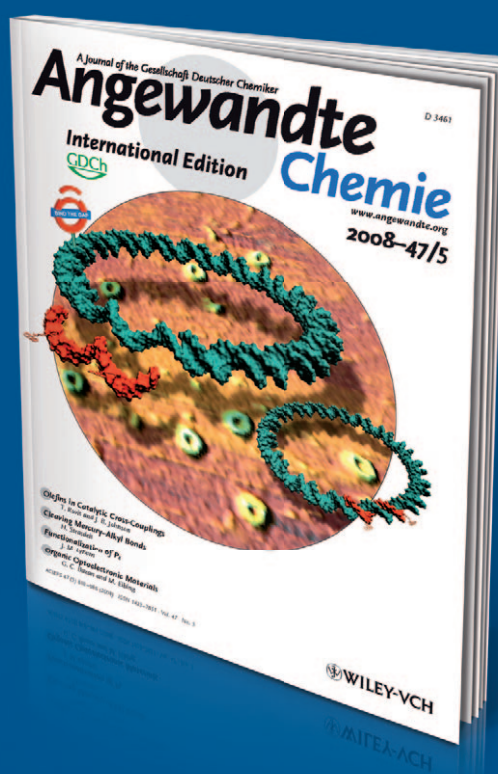
Framework Structures

X. Song, Y. Li, L. Gan, Z. Wang, J. Yu,* R. Xu — 314–317

Heteroatom-Stabilized Chiral Framework of Aluminophosphate Molecular Sieves

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.

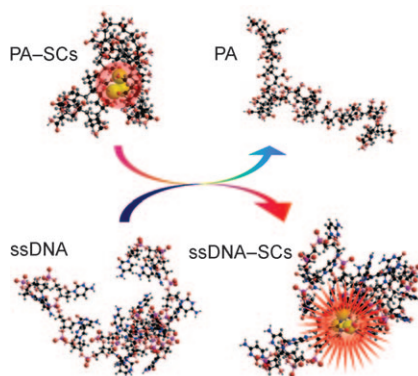


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Clustering together: A shuttle-based fluorogenic cluster transfer, in which silver clusters (SCs) are directly transferred from a low-molecular-weight poly(acrylic acid) (PA) shuttle to a single-stranded DNA (ssDNA) tag on the protein of interest (see picture), proceeds with excellent specificity. Upon transfer, the cluster fluorescence increases more than ten times, which provides bright, photo-stable labeling.



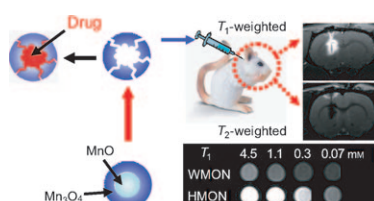
Fluorescent Clusters

J. Yu, S. Choi, R. M. Dickson* 318–320

Shuttle-Based Fluorogenic Silver-Cluster Biolabels



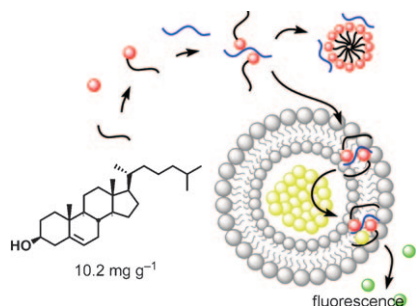
MRI jack-o'-lanterns? Hollow manganese oxide nanoparticles (HMON) show greatly improved relaxivities and drug-loading capacities compared to those with solid interiors (WMON). Their efficient cellular uptake demonstrates their potential as a bifunctional medical system that combines diagnostic imaging and targeted therapy.



Functional Nanoparticles

J. Shin, R. M. Anisur, M. K. Ko, G. H. Im, J. H. Lee,* I. S. Lee* 321–324

Hollow Manganese Oxide Nanoparticles as Multifunctional Agents for Magnetic Resonance Imaging and Drug Delivery

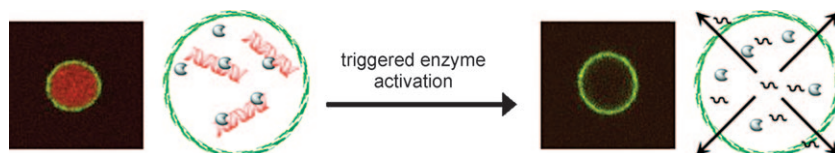


Off-the-shelf, prêt-à-porter multianalyte sensing systems are based on the ability of cell-penetrating peptides (CPPs; see picture, blue) to mediate the export of hydrophilic anions (yellow → green) from lipid bilayer vesicles (gray). Covalent capture of hydrophobic analytes (black) with hydrophilic anions (red) produces amphiphilic anions that can activate CPPs.

Biosensors

S. M. Butterfield, T. Miyatake, S. Matile* 325–328

Amplifier-Mediated Activation of Cell-Penetrating Peptides with Steroids: Multifunctional Anion Transporters for Fluorogenic Cholesterol Sensing in Eggs and Blood



Thinking in compartments is back! The degradation of a fluorescently labeled nucleic acid substrate within a polymer capsule by coencapsulated DNase I was initiated by activation of the enzyme with a chemical trigger. The degraded DNA

diffused from the capsule (see picture). The semipermeable capsule microreactors enable external reaction control, high-throughput tracking of reaction progression, and continuous modification of the DNA cargo.

Encapsulated Enzymes

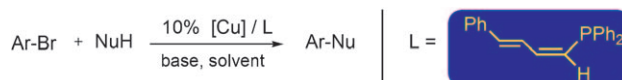
A. D. Price, A. N. Zelikin, Y. Wang, F. Caruso* 329–332

Triggered Enzymatic Degradation of DNA within Selectively Permeable Polymer Capsule Microreactors



Homogeneous Catalysis (1)

H. Kaddouri, V. Vicente, A. Ouali,
F. Ouazzani, M. Taillefer* — 333–336

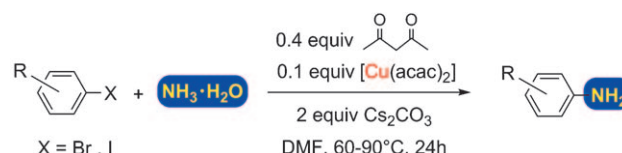


Worth diene for: The butadienylphosphine L (see scheme), obtained on a large scale from a new synthetic method, is an efficient ligand in Ullmann-type copper-catalyzed arylation reactions. The use of

this phosphorus ligand made it possible to follow the reaction by ^{31}P NMR spectroscopy and thus to propose a mechanism for the Ullmann reaction.

Homogeneous Catalysis (2)

N. Xia, M. Taillefer* — 337–339

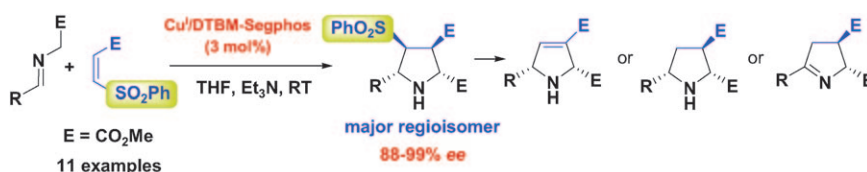


Phasing up to matters: The use of aqueous ammonia in a biphasic system with a copper catalyst and diketone supporting ligands allows the catalytic amination of both activated and unactivated aryl and

heteroaryl iodides and bromides under very mild conditions (see scheme; R = electron-donating or -withdrawing group; acac = acetylacetonate).

Synthetic Methods

A. López-Pérez, J. Adrio,
J. C. Carretero* — 340–343

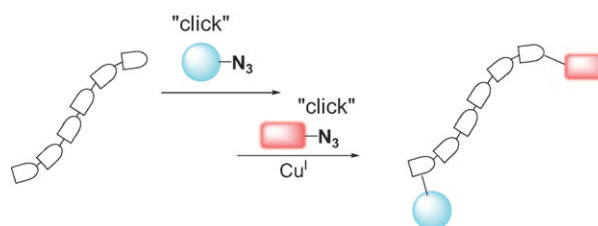


Controlling the regioselectivity: The phenylsulfonyl group controlled the regioselectivity in the title reaction to afford pyrrolidine-2,3-dicarboxylates with good regioselectivity and high *exo* selectivity

and enantioselectivity (see scheme). The products are precursors to substituted pyrrolidines and pyrrolines that are not attainable by direct 1,3-dipolar cycloadditions with typical acrylates.

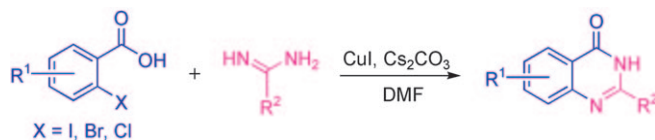
Synthetic Methods

P. Kele,* G. Mezö, D. Achatz,
O. S. Wolfbeis* — 344–347



Click by click: Dual labeling of model compounds was carried out by using copper-free and copper-mediated click chemistry in a sequential manner. This method was used to introduce two labels

onto biological targets or nanoparticles, thus quickly converting them into fluorescence resonance energy transfer systems.



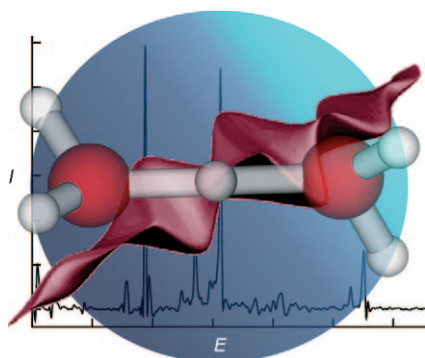
Cop some rings: A simple and highly efficient copper-catalyzed method for the synthesis of quinazolinone derivatives through the reaction of substituted 2-

halobenzoic acids with amidines or guanidines under mild conditions has been developed (see scheme). The method has economical and practical advantages.

Homogeneous Catalysis

X. Liu, H. Fu,* Y. Jiang, Y. Zhao 348–351

A Simple and Efficient Approach to Quinazolinones under Mild Copper-Catalyzed Conditions



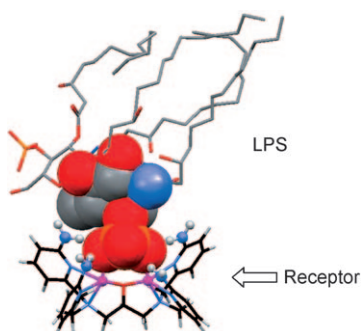
Increasing the mass makes a mess:

Partial or total deuteration of the protonated water dimer drastically alters its vibrations. Coupling between certain vibrational modes is strongly enhanced, whereas other modes are decoupled. Full-dimensional quantum-dynamics simulation and assignment of the IR spectrum of various isotopologues of the cation show the intricate dynamics of the smallest protonated water cluster.

Hydrated Proton

O. Vendrell, F. Gatti, H.-D. Meyer* 352–355

Strong Isotope Effects in the Infrared Spectrum of the Zundel Cation

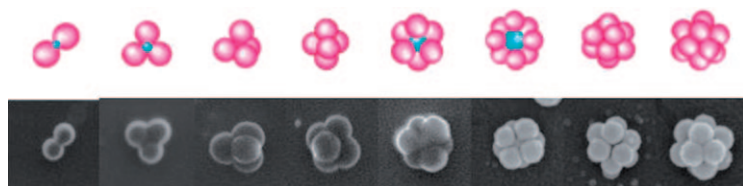


Nature inspired: A synthetic receptor (see picture) that exploits two zinc(II) ions and four convergent amino hydrogen bonding groups binds lipopolysaccharides (LPSs) almost as strongly as the LPS binding protein. This feature is exploited to electrochemically distinguish LPS from other pathogens in water and in complex biological mixtures. Zn pink, N blue, P orange, O red.

Anion Receptors

V. Ganesh, K. Bodewits, S. J. Bartholdson, D. Natale, D. J. Campopiano, J. C. Mareque-Rivas* 356–360

Effective Binding and Sensing of Lipopolysaccharide: Combining Complementary Pattern Recognition Receptors



Sowing the seeds: Binary colloidal particles of controlled morphology, including line segments, triangles, tetrahedra, octahedra, and square antiprisms (see picture) were obtained by an emulsion polymerization of styrene in the presence

of silica seeds. These morphologies result from the minimization of an energy term that is the sum of two forces—an attraction towards the center and two-body particle repulsions that balance the attractive force.

Binary Colloids

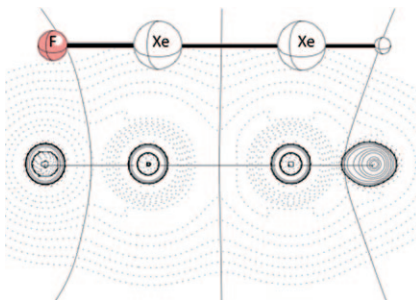
A. Perro, E. Duguet, O. Lambert, J.-C. Taveau, E. Bourgeat-Lami, S. Ravaine* 361–365

A Chemical Synthetic Route towards “Colloidal Molecules”

Noble Gas Compounds

C. Ó. C. Jiménez-Halla, I. Fernández,
G. Frenking* 366–369

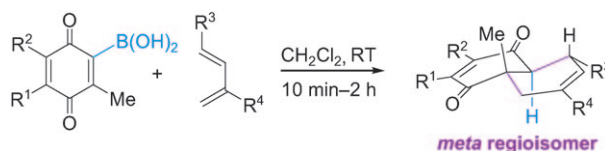
Is it Possible To Synthesize a Neutral Noble Gas Compound Containing a Ng–Ng Bond? A Theoretical Study of H–Ng–Ng–F (Ng = Ar, Kr, Xe)



Marrying nobility: Quantum chemical calculations predict that the dixonon compound HXeXeF has an activation barrier for decomposition of about 11 kcal mol^{−1}, which should be large enough to identify the molecule in a low-temperature matrix.

Domino Reactions

M. C. Redondo, M. Veguillas,
M. Ribagorda, M. C. Carreño* 370–374



Control of the Regio- and Stereoselectivity in Diels–Alder Reactions with Quinone Boronic Acids

It all adds up: The dienophilic reactivity of 2-methyl-substituted quinones has been substantially increased by the introduction of a boronic acid substituent, which makes them equivalent to a highly reactive quinone. The Diels–Alder reactions of

these quinones are followed by spontaneous and stereoselective protodeboronation to give the *trans*-fused adducts. The boron group is a temporal regiocontroller and leads to the uncommon *meta* adduct.

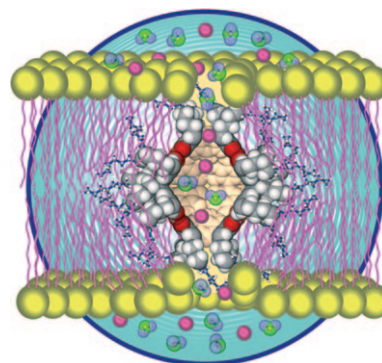
Ion Transport

O. V. Kulikov, R. Li,
G. W. Gokel* 375–377



A Synthetic Ion Channel Derived from a Metallogallarene Capsule That Functions in Phospholipid Bilayers

Changing the channel: Dodecanal and pyrogallol were condensed to give a tetramer, which was crystallized as the bilayer and the hexameric molecular capsule. A copper-seamed metallogallarene capsule functioned as an ion transporter and showed selectivity for potassium over chloride ion transport in a phospholipid bilayer (see picture). The capsule also showed voltage-dependent gating of its open–close behavior when examined in asolectin membranes.

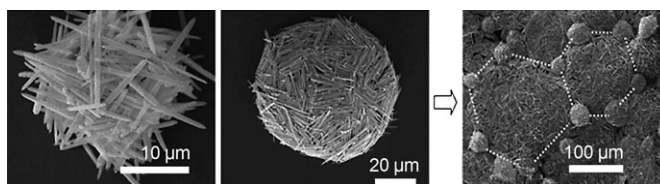


Microstructures

W. Zhou, J. Cao, W. Liu,*
S. Stoyanov* 378–381

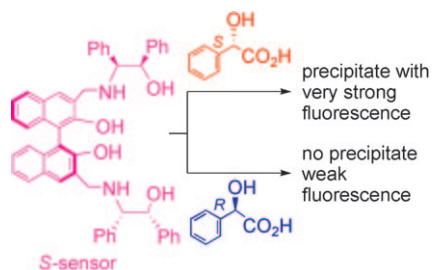


How Rigid Rods Self-Assemble at Curved Surfaces



I'm forever blowing bubbles: Superstable foams comprising air bubbles stabilized by modified, rigid CaCO₃ rods have a bimodal bubble-size distribution. The very high stability and stiffness of the rod-stabilized bubbles means that their

spherical shape is retained when dried on glass substrates and that they could be ordered into 2D binary colloidal crystals, with large bubbles at the bottom and small bubbles filling the spaces in between (see picture).



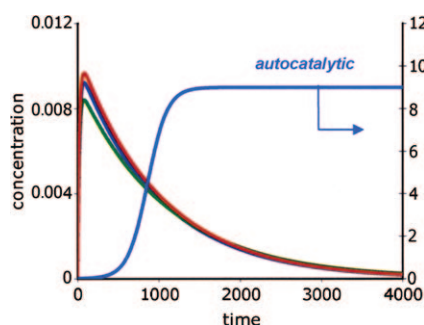
Unusually sensitive: A chiral sensor based on 1,1'-bi-2-naphthol was prepared, which can provide visual enantioselective discrimination of α -hydroxycarboxylic acids. When the sensor and the acid have matched configurations, an enantioselective precipitation occurs, which is accompanied by a dramatic (over 950-fold) solid-state fluorescence enhancement (see picture).

Enantiomer Detection

H.-L. Liu, X.-L. Hou,* L. Pu* — 382–385

Enantioselective Precipitation and Solid-State Fluorescence Enhancement in the Recognition of α -Hydroxycarboxylic Acids

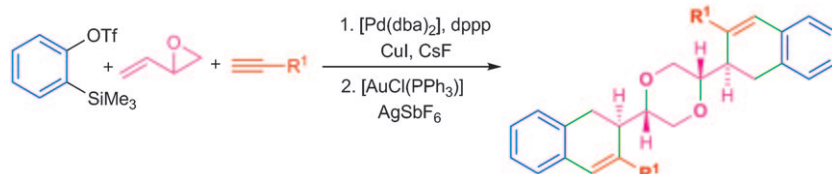
Let's start at the very beginning: Reaction simulations were used to clarify differences between autoinductive and autocatalytic processes in the context of recent models pertaining to the chemical origin of life (see plot). The ability of a catalytic network to persist in the face of disruptive challenges is essential to its potential to play a role in prebiotic chemistry.



Systems Chemistry

D. G. Blackmond* — 386–390

An Examination of the Role of Autocatalytic Cycles in the Chemistry of Proposed Primordial Reactions



A little cooperation: A cooperative copper- and palladium-catalyzed highly regio- and chemoselective three-component coupling of benzynes, allylic epoxides, and terminal alkynes provides an efficient atom-economical route to *ortho*-disubstituted arenes. The resulting product

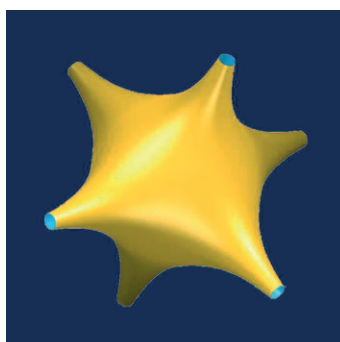
undergoes a gold-catalyzed cyclization reaction (see scheme; dba = dibenzylideneacetone, dppp = 1,3-bis(diphenylphosphanyl)propane).

Multicomponent Reactions

M. Jeganmohan, S. Bhuvaneswari, C.-H. Cheng* — 391–394

A Cooperative Copper- and Palladium-Catalyzed Three-Component Coupling of Benzynes, Allylic Epoxides, and Terminal Alkynes

A Platonic relationship: Calcite single and mesocrystals with two platonic shapes and minimal surfaces are formed by a unified polymer-controlled nanoparticle aggregation. The shapes of the crystals (see picture for example) are tuned by the reactant concentration. The morphogenesis follows a nonclassical mechanism. A rhombohedral primitive minimal surface was observed for the first time in a synthetic crystallization of micrometer-sized particles.



Mesocrystals

R.-Q. Song, A.-W. Xu,* M. Antonietti, H. Cölfen* — 395–399

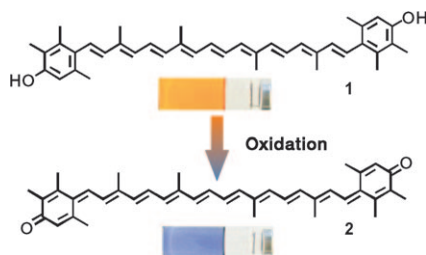
Calcite Crystals with Platonic Shapes and Minimal Surfaces

Carotenoids

H.-D. Martin,* S. Kock, R. Scherrers,
K. Lutter, T. Wagener, C. Hundsdoerfer,
S. Frixel, K. Schaper, H. Ernst, W. Schrader,
H. G€orner, W. Stahl* ————— 400–403



3,3'-Dihydroxyisorenieratene, a Natural
Carotenoid with Superior Antioxidant and
Photoprotective Properties



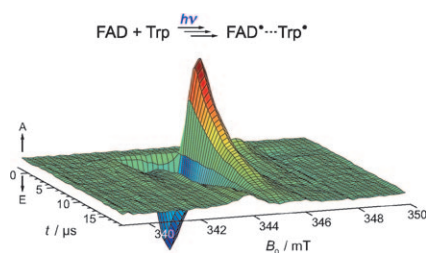
The color of red smear cheeses arises from naturally occurring carotenoids like 3,3'-dihydroxyisorenieratene (**1**). This compound and its oxidation product **2**, which have unusual phenolic and quinoid end groups, respectively, were synthesized. The antioxidant and photoprotective properties of a series of carotenoids were tested with eight different model systems, and **1** proved to be superior to other carotenoids.

Radical Pairs in Proteins

T. Biskup, E. Schleicher, A. Okafuji,
G. Link, K. Hitomi, E. D. Getzoff,
S. Weber* ————— 404–407



Direct Observation of a Photoinduced
Radical Pair in a Cryptochrome Blue-Light
Photoreceptor



Compass component: Blue-light excitation of the photoreceptor cryptochrome generates a transient radical pair by electron transfer from a tryptophan (Trp) at the surface to the flavin cofactor in the center of the protein (see picture; FAD = flavin adenine dinucleotide). Simulated EPR spectra show that the electronic coupling parameters of these radical pairs are suitable for animal magnetoreception.



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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