



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:

H. Chinen, K. Mawatari, Y. Pihosh, K. Morikawa, Y. Kazoe, T. Tsukahara, T. Kitamori*

Enhancement of Proton Mobility in Extended-Nanospace Channels

S. Handa, L. M. Slaughter*

Enantioselective Alkynylbenzaldehyde Cyclizations Catalyzed By Chiral Gold(I) Acyclic Diaminocarbene Complexes Containing Weak Au–Arene Interactions

C. Kolbeck, I. Niedermaier, N. Taccardi, P. S. Schulz, F. Maier, P. Wasserscheid, H.-P. Steinrück*

Monitoring Liquid-Phase Organic Reactions by Photoelectron Spectroscopy

Y. Li, W. Xiao, K. Xiao, L. Berti, J. Luo, H. P. Tseng, K. S. Lam*
Well-Defined, Reversible Boronate Crosslinked Nanocarriers for Targeted Drug Delivery in Response to pH Value and *cis*-Diols

A. Marrero, S. Duquerroy, S. Trapani, T. Goulas, T. Guevara, G. R. Andersen, J. Navaza, L. Sottrup-Jensen, F. X. Gomis-Rüth*

The Crystal Structure of Human α_2 -Macroglobulin Reveals a Unique Molecular Cage

C. Hoch,* A. Simon

Na₁₁Hg₅₂⁺ Complexity in a Polar Metal

U. Basu, I. Khan, A. Hussain, P. Kondaiah,* A. R. Chakravarty*
Photodynamic Effect in Near-IR Light by a Photocytotoxic Iron(III) Cellular Imaging Agent

A. Patzer, M. Schütz, T. Möller, O. Dopfer*

Infrared Spectrum and Structure of the Adamantane Cation: Direct Evidence for Jahn–Teller Distortion



“My motto is “We are condemned to hope!”
(Manès Sperber).

When I was eighteen I wanted to be a chemist,
mathematician, or aircraft designer. ...”

This and more about Uwe Rosenthal can be found on
page 2280.

Author Profile

Uwe Rosenthal _____ 2280

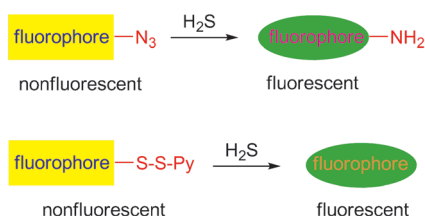
Molecular Switches

Ben L. Feringa, Wesley R. Browne

Books

reviewed by H. A. Wegner _____ 2281

Detective work: Three highly sensitive and selective fluorescent probes for the detection of H₂S have been developed. Two of the probes detect H₂S by the reduction of an azide moiety to an amine group, which changes the probes into their fluorescent forms and generates a fluorescent signal. In the third method, the fluorescent signal is created by using H₂S as a nucleophile in a reaction that unmasks fluorescein.



Highlights

Fluorescent Probes

W.-M. Xuan, C.-Q. Sheng,* Y.-T. Cao,
W.-H. He, W. Wang* _____ 2282–2284

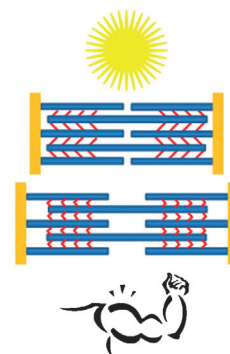
Fluorescent Probes for the Detection of Hydrogen Sulfide in Biological Systems

Light-Driven Muscle

G. M. Spinks* ————— 2285 – 2287

Deforming Materials With Light:
Photoresponsive Materials Muscle In On
the Action

Pump it: Materials that show intriguing shape changes induced by simple light exposure are emerging as candidates for artificial muscles. Recent examples are highlighted to illustrate the various molecular conformational changes induced by irradiation. Assemblies of these photoresponsive molecules are now being prepared that show functions that resemble real muscle.

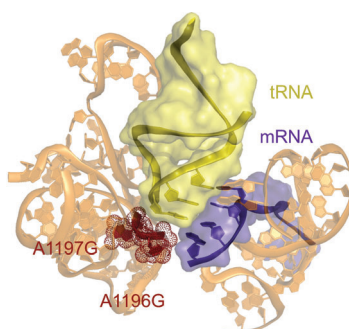


Minireviews

Protein Design

K. Wang, W. H. Schmied,
J. W. Chin* ————— 2288 – 2297

Reprogramming the Genetic Code: From
Triplet to Quadruplet Codes



On all fours: Recent work has used quadruplet codons to encode unnatural amino acids. Multiple unnatural amino acids have been incorporated into proteins through orthogonal protein translation using a quadruplet decoding ribosome (see figure; mutations to ribosome are shown in red).

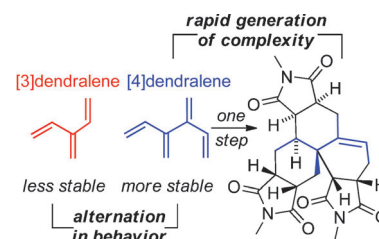
Reviews

Synthetic Methods

H. Hopf,* M. S. Sherburn* - 2298 – 2338

Dendralenes Branch Out: Cross-
Conjugated Oligoenes Allow the Rapid
Generation of Molecular Complexity

From significant primary properties through to unparalleled complexity-generating synthetic transformations, the fundamental oligoalkene family known as the dendralenes is coming of age. Synthetic approaches to acyclic and cyclic dendralenes are analyzed and classified in this Review. The most powerful synthetic transformations of the dendralenes, diene-transmissive Diels–Alder reactions, are surveyed in detail.



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Communications

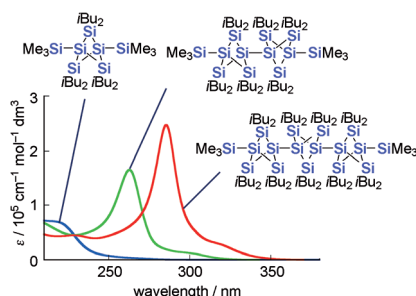
Polysilanes

T. Iwamoto,* D. Tsushima, E. Kwon,
S. Ishida, H. Isobe — 2340–2344

Persilastaffanes: Design, Synthesis,
Structure, and Conjugation between
Silicon Cages

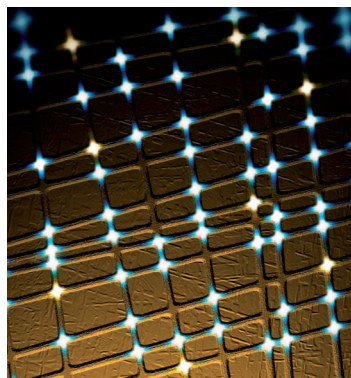


Frontispiece



By stepwise catenation of bicyclo-[1.1.1]pentasilane units persila[n]staffanes ($n = 1, 2$, and 3) were synthesized as air-stable colorless crystals. A remarkable red-shift of the UV/Vis absorption bands with increasing number of bicyclo-[1.1.1]pentasilane units suggests remarkable interactions between bridgehead Si–Si σ orbitals and between cage Si–Si σ orbitals (see picture).

Ultrasmall fluorescent sensors and their application for fabrication of wavelength-addressable virtual sensor arrays capable of sensing metal cations are described. The fluorescent probes generated in situ within the fiber mats can be used as wearable sensors for identifying heavy metal ions in a qualitative and quantitative fashion.



Sensor Arrays

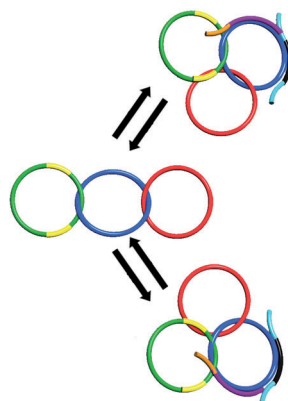
P. Anzenbacher, Jr.,* F. Li,
M. A. Palacios — 2345–2348

Toward Wearable Sensors: Fluorescent
Attoreactor Mats as Optically Encoded
Cross-Reactive Sensor Arrays



Front Cover

Linking in: Two-ring and three-ring catenane nanostructures that are made from sequences of DNA have been shown to undergo programmed and reversible reconfiguration across defined topologies by using strand displacement. The switchable nature of the configurations may enable a more flexible approach to the transport and delivery of molecular cargoes, or for the use of such structures as labels in an intracellular environment.



Nanodevices

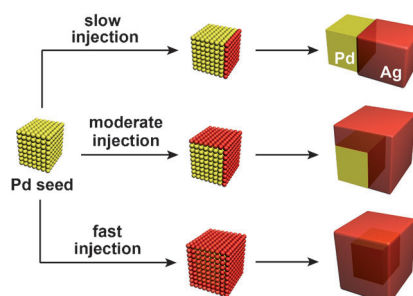
J. Elbaz, Z.-G. Wang, F. Wang,
I. Willner* — 2349–2353

Programmed Dynamic Topologies in DNA
Catenanes



Inside Cover

Tell the atoms where to go: By manipulating the rate at which Ag atoms were generated from a precursor, the nucleation and growth of Ag on Pd nanocubes with six equivalent {100} facets were controlled to generate three different types of bimetallic nanocrystals: Pd–Ag hybrid dimers, Pd–Ag eccentric nanobars, and Pd@Ag core–shell nanocrystals (see scheme).



Nanocrystals

J. Zeng, C. Zhu, J. Tao, M. Jin, H. Zhang,
Z.-Y. Li, Y. Zhu, Y. Xia* — 2354–2358

Controlling the Nucleation and Growth of
Silver on Palladium Nanocubes by
Manipulating the Reaction Kinetics



Back Cover

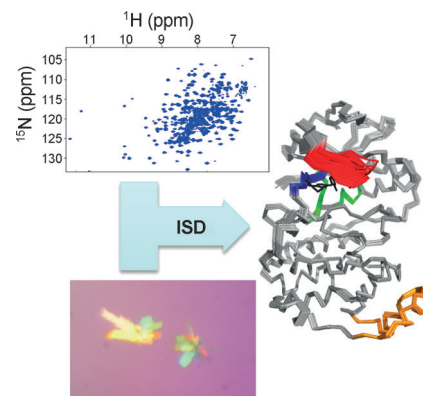
Enzyme Structures

V. S. Honndorf, N. Coudeville, S. Laufer,
S. Becker, C. Griesinger,*
M. Habeck* ————— 2359 – 2362



Inferential NMR/X-ray-Based Structure
Determination of a Dibenzo[*a,d*]-
cycloheptenone Inhibitor–p38 α MAP
Kinase Complex in Solution

Complex problem: The crystal structure of p38 α mitogen-activated protein kinase in complex with a dibenzo[*a,d*]cycloheptenone inhibitor was found to be incompatible with NMR data of the same complex in solution. By using inferential structure determination (ISD) with restraints from X-ray crystallography and NMR spectra, a structure that is compatible with both data sets and very close to the X-ray crystal structure was generated (see picture).

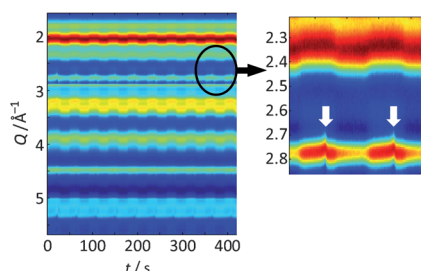


Heterogeneous Catalysis

M. A. Newton,* M. Di Michiel,
A. Kubacka, A. Iglesias-Juez,
M. Fernández-García* — 2363 – 2367



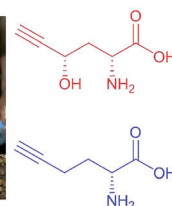
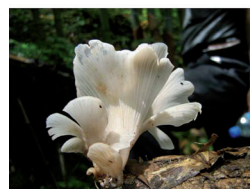
Observing Oxygen Storage and Release at
Work during Cycling Redox Conditions:
Synergies between Noble Metal and Oxide
Promoter



Intimacy promotes good chemistry: Time-resolved hard X-ray diffraction (see picture) and dispersive X-ray absorption spectroscopy coupled to time-resolved IR spectroscopy allows direct observation and quantification of the ability of materials to store and release gases under specific conditions. The nanoscale Pd/CeZrO₄ interface plays a reactively deterministic role in inducing a superior performance in these catalysts.

Natural Products

Z.-Y. Zhou, G.-Q. Shi, R. Fontaine, K. Wei,
T. Feng, F. Wang, G.-Q. Wang, Y. Qu,
Z.-H. Li, Z.-J. Dong, H.-J. Zhu, Z.-L. Yang,
G. Zeng,* J.-K. Liu* — 2368 – 2370



Life saver: Two unusual and toxic amino acids, 2*R*-amino-4*S*-hydroxy-5-hexynoic acid (red, see scheme) and 2*R*-amino-5-hexynoic acid (blue) have been isolated from the fruiting bodies of the mushroom *Trogia venenata*. Toxicology studies suggest that these compounds may be the cause of Sudden Unexplained Death (SUD) in Yunnan Province, China.



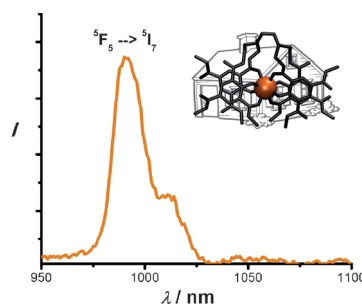
Evidence for the Natural Toxins from the
Mushroom *Trogia venenata* as a Cause of
Sudden Unexpected Death in Yunnan
Province, China

Lanthanide Complexes

G.-L. Law, T. A. Pham, J. Xu,
K. N. Raymond* — 2371 – 2374



A Single Sensitizer for the Excitation of
Visible and NIR Lanthanide Emitters in
Water with High Quantum Yields



Eight makes a happy Ho(l)me: The versatile octadentate TIAM ligand forms lanthanide complexes (Ln = Sm, Eu, Tb, Dy, Ho) with high quantum yields in water. This ligand is an efficient sensitizer, and also shields the metal center from solvent quenching, as shown by an X-ray diffraction study of the Ho complex.



Call for Nominations 2012

Novartis Early Career Award in Organic Chemistry

The Novartis Early Career Award in Organic Chemistry was created to mark Novartis' commitment to science and innovation in chemistry. The award is presented annually to outstanding scientists who are active in the areas of organic or bioorganic chemistry in the broadest sense, and is intended to provide support for investigators early in their career. We are now seeking nominations of candidates who began their independent academic career in or after 2002, from all academic institutions. The nominations will be assessed by Novartis senior scientists together with leading external experts in the field. Two winners will be identified, each of whom will receive an unrestricted research grant. Deadline for the submission of nominations, including a letter of recommendation and a curriculum vitae, is April 30, 2012.*

Past Awardees: David Chen, Seoul National University (2011); David Spiegel, Yale University (2011); Karl Gademann, University of Basel (2010); Jin-Quan Yu, The Scripps Research Institute (2010); Magnus Rueping, RWTH Aachen University (2009); Christopher J. Chang, University of California, Berkeley (2009); Matthew J. Gaunt, University of Cambridge (2008); Jeffrey S. Johnson, University of North Carolina at Chapel Hill (2008); Lukas J. Goossen, Technische Universität Kaiserslautern (2007); Anna K. Mapp, University of Michigan Ann Arbor (2007); Armido Studer, University of Münster (2006); F. Dean Toste, University of California Berkeley (2006); Benjamin List, Max-Planck-Institute Mülheim an der Ruhr (2005); Dirk Trauner, University of California Berkeley (2005); J. Stephen Clark, University of Nottingham (2004); Jonathan P. Clayden, University of Manchester (2004); Thorsten Bach, Technical University of Munich (2003); Bernhard Breit, University of Freiburg (2002); Thomas Carell, University of Munich (2002); Tim Donohoe, University of Oxford (2001); Andrew Miller, Imperial College London (2000); Alan Armstrong, Imperial College London (1999); Mark Bradley, University of Southampton (1998).

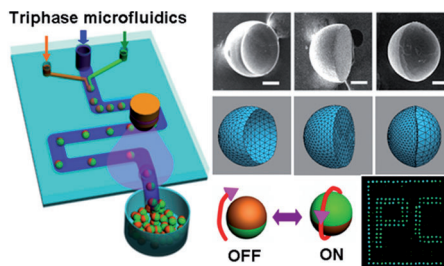
*Nominations should be sent to Dr. Tom Hunt, Novartis Institutes for Biomedical Research, Horsham Research Centre, Horsham, West Sussex, UK; e-mail: tom.hunt@novartis.com
Details are also available online: http://www.nibr.com/newsroom/stories/2011/2011Dec15_EarlyCareerAward.shtml

Triphase Microfluidics

Z. Y. Yu, C. F. Wang, L. T. Ling, L. Chen,
S. Chen* 2375–2378



Triphase Microfluidic-Directed Self-Assembly: Anisotropic Colloidal Photonic Crystal Supraparticles and Multicolor Patterns Made Easy



Three not of a kind: A triphasic microfluidic route provides a flexible and promising way to fabricate colloidal photonic crystal supraparticles that are an-

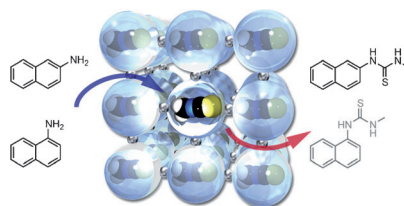
isotropic in both geometry and function. These supraparticles are promising for applications including novel color displays (see scheme).

Molecular Capsules

Y. Inokuma, G.-H. Ning,
M. Fujita* 2379–2381



Reagent-Installed Capsule Network: Selective Thiocarbamoylation of Aromatic Amines in Crystals with Preinstalled CH_3NCS



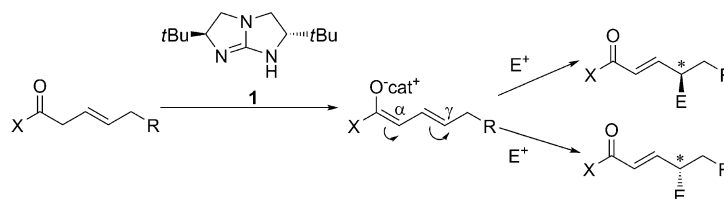
Crystalline reagent capsules were prepared by installing CH_3NCS into networked molecular capsules. While the tight encapsulation completely prevented leaching of reagent molecules into the supernatant, introduction of amines into the interstitial pores triggered reagent delivery. As a result, enhanced substrate selectivity was observed in crystalline-state thiocarbamoylation (see picture; 86:14 in favor of 2- vs. 1-naphthylamine).

Organocatalysis

J. Wang, J. Chen, C. W. Kee,
C.-H. Tan* 2382–2386



Enantiodivergent and γ -Selective Asymmetric Allylic Amination



Double agent: The title reaction using the guanidine catalyst **1** can deliver both enantiomers of the product with excellent enantioselectivity by judicious choice of the double bond geometry of the β,γ -unsaturated carbonyl compound. Com-

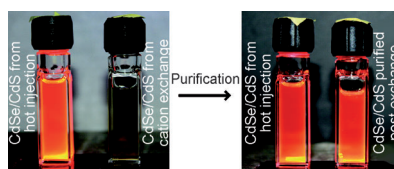
putational studies reveal the possible origin of the inversed enantioselectivity, and the potential for enantiodivergent synthesis chiral amine-containing substrates is attractive.

Nanoparticles

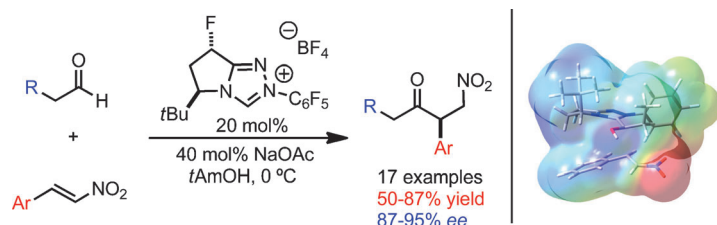
P. K. Jain, B. J. Beberwyck, L. K. Fong,
M. J. Polking,
A. P. Alivisatos* 2387–2390



Highly Luminescent Nanocrystals From Removal of Impurity Atoms Residual From Ion-Exchange Synthesis



Pure crystals: Ion exchange of semiconductor nanocrystals yielded materials with poor optoelectronic properties such as low photoluminescence quantum yields. The reason for the low quantum yields of these nanocrystals are impurities at the level of a few atoms per nanocrystal. Cation-exchanged nanostructures, however, could be purified post exchange from such impurities resulting in high-quality nanocrystals (see picture).



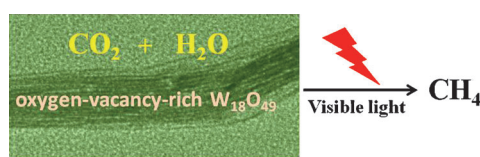
Fluorine helps: A fluorinated triazolium salt precatalyst has been developed that efficiently promotes the asymmetric intermolecular Stetter reaction of enolizable aldehydes and nitrostyrenes (see scheme). *Trans* fluorination of the catalyst

architecture results in unparalleled reactivity and enantioselectivity in the desired transformation. A DFT study provides evidence of an electrostatic interaction as the source of the increased enantio-induction.

Asymmetric Catalysis

D. A. DiRocco, E. L. Noey, K. N. Houk,*
T. Rovis* 2391–2394

Catalytic Asymmetric Intermolecular Stetter Reactions of Enolizable Aldehydes with Nitrostyrenes: Computational Study Provides Insight into the Success of the Catalyst



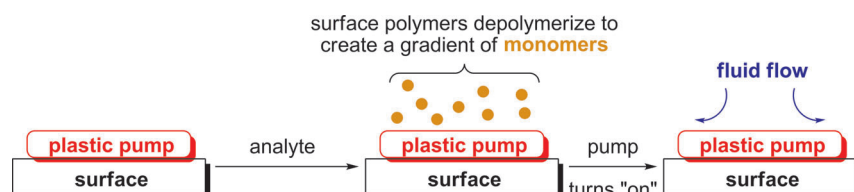
Open vacancies: A facile one-pot synthesis of oxygen-vacancy-rich ultrathin $W_{18}O_{49}$ nanowires up to several micrometers long is described. In addition to unique optical properties, such as NIR absorption and blue-light emission, the

nanowires show an unexpected ability to photochemically reduce carbon dioxide to methane (see picture) as a result of its defect structure caused by large quantities of oxygen vacancies.

Nanostructures

G. C. Xi, S. X. Ouyang, P. Li, J. H. Ye,*
Q. Ma, N. Su, H. Bai,
C. Wang 2395–2399

Ultrathin $W_{18}O_{49}$ Nanowires with Diameters below 1 nm: Synthesis, Near-Infrared Absorption, Photoluminescence, and Photochemical Reduction of Carbon Dioxide



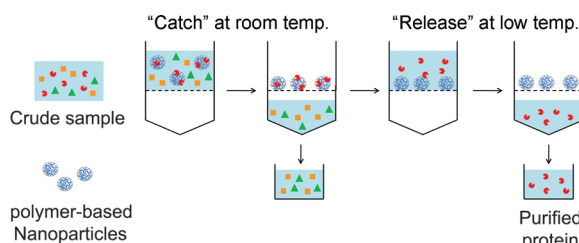
Pump it up: Insoluble polymer films that depolymerize to release soluble monomeric products when exposed to a specific analyte act as a microscale pump. Products formed as a result of depolymerization amplify the signal and create a con-

centration gradient that pumps fluids and insoluble particles away from the bulk polymer by a diffusio-phoretic mechanism. These pumps can respond to a variety of analytes, from small molecules to enzymes.

Microfluidic Pumps

H. Zhang, K. Yeung, J. S. Robbins,
R. A. Pavlick, M. Wu, R. Liu, A. Sen,*
S. T. Phillips* 2400–2404

Self-Powered Microscale Pumps Based on Analyte-Initiated Depolymerization Reactions



Catch me if you can: Multifunctional, polymer-based nanoparticles that are capable of temperature-responsive "catch-and-release" of a target protein have been synthesized. The process is

reversible and does not denature the proteins. An optimized combination of functional monomers imparts binding selectivity toward a target protein over other proteins.

Protein Purification

K. Yoshimatsu, B. K. Lesel, Y. Yonamine,
J. M. Beierle, Y. Hoshino,
K. J. Shea* 2405–2408

Temperature-Responsive "Catch and Release" of Proteins by using Multifunctional Polymer-Based Nanoparticles

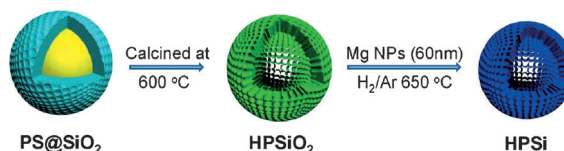


Lithium Storage

D. Chen, X. Mei, G. Ji, M. Lu, J. Xie,* J. Lu,*
J. Y. Lee* ————— 2409–2413



Reversible Lithium-Ion Storage in Silver-Treated Nanoscale Hollow Porous Silicon Particles



Easy to hollow: A hollow porous Si nanocomposite with Ag nanoparticles (NPs) is prepared (see scheme; PS = polystyrene, HP = hollow porous). The free volume in the HPSi structure effectively cushioned

the volume change in Li–Si alloying and de-alloying reactions, giving an impressive performance as a high-capacity anode for lithium-ion batteries.

Magnetic Surfactants

P. Brown, A. Bushmelev, C. P. Butts,
J. Cheng, J. Eastoe,* I. Grillo,
R. K. Heenan,
A. M. Schmidt ————— 2414–2416



Magnetic Control over Liquid Surface Properties with Responsive Surfactants



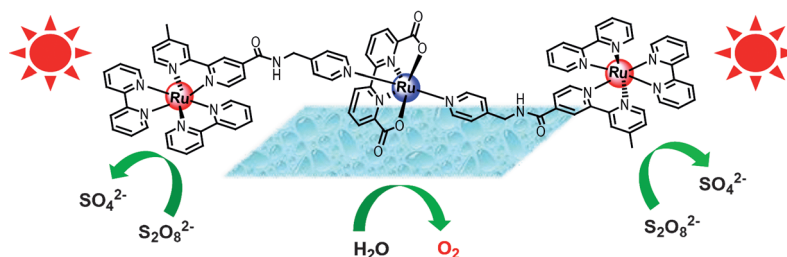
Droplet attraction: Surfactants responsive to magnetic fields are reported for the first time. This new class of magnetic ionic liquid surfactants (MILSs; see picture) shows remarkable effects on surface and interfacial tension and allows access to magneto-responsive emulsions and new methods of separation, recovery, catalysis, and potential magnetophoretic applications.

Water Splitting

F. Li,* Y. Jiang, B. Zhang, F. Huang,
Y. Gao, L. Sun* ————— 2417–2420



Towards A Solar Fuel Device: Light-Driven Water Oxidation Catalyzed by a Supramolecular Assembly



Time to split: Supramolecular assemblies containing both photosensitizers and a ruthenium water-oxidation catalyst were prepared and characterized. The pictured

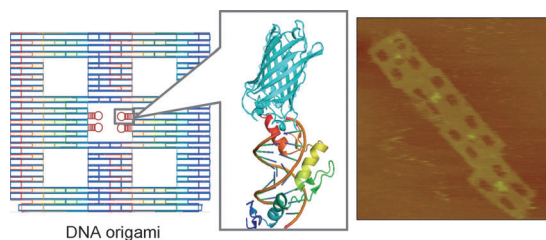
assembly exhibits, for the first time, enhanced visible-light-driven water oxidation activity.

DNA Nanotechnology

E. Nakata, F. F. Liew, C. Uwatoko,
S. Kiyonaka, Y. Mori, Y. Katsuda, M. Endo,
H. Sugiyama, T. Morii* — 2421–2424

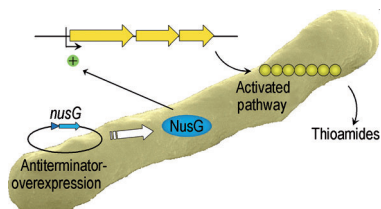


Zinc-Finger Proteins for Site-Specific Protein Positioning on DNA-Origami Structures



Point the finger: Zinc-finger proteins are convenient and site-selective adaptors for targeting specific locations within DNA-origami structures. Orthogonal targeting of the specific locations in the structures

was demonstrated by using two adaptors, and the application of *Escherichia coli* lysate that contained the adaptor-fused proteins successfully afforded the expected protein–DNA assembly.

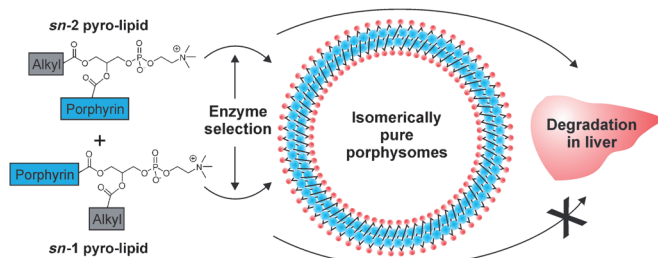


Anti-Terminator: Rise of the Molecules: Overexpression of an antiterminator gene (*nusG*) in *Clostridium cellulolyticum* induced the biosynthesis of the novel antibiotic closthoamide and related thioamides. This is the first successful genetic engineering of an anaerobe to trigger a cryptic pathway. Furthermore, synthetic probes provide valuable insights into the biogenetic relationship of the rare thioamide metabolites.

Natural Products

S. Behnken, T. Lincke, F. Kloss, K. Ishida, C. Hertweck* 2425–2428

Antiterminator-Mediated Unveiling of Cryptic Polythioamides in an Anaerobic Bacterium



A select few: An enzyme screen is used to identify two enzymes that selectively cleave porphyrin–lipid regioisomers (see picture). Either of the isomerically pure conjugates assembles into physically

similar porphysome nanovesicles. Although porphysomes formed from both regioisomers are stable in serum in vivo, only one regioisomer rapidly degrades upon uptake in the liver.

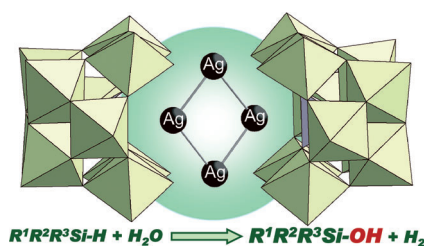
Nanoparticle Biodegradation

J. F. Lovell, C. S. Jin, E. Huynh, T. D. MacDonald, W. Cao, G. Zheng* 2429–2433

Enzymatic Regioselection for the Synthesis and Biodegradation of Porphysome Nanovesicles



An Ag₄ diamond is encapsulated by silicotungstate ligands in $\text{TBA}_4[\text{Ag}_4(\text{DMSO})_2(\gamma\text{-H}_2\text{SiW}_{10}\text{O}_{36})_2] \cdot 2 \text{DMSO} \cdot 2 \text{H}_2\text{O}$ (**Ag₄**; DMSO = dimethyl sulfoxide, TBA = tetra-*n*-butylammonium), which was obtained by reaction of $\text{TBA}_4\text{H}_4[\gamma\text{-SiW}_{10}\text{O}_{36}]$ with AgOAc in an organic medium. Polyoxometalate **Ag₄** (see picture) selectively catalyzes hydrolytic oxidation of various silanes to the corresponding silanols in high yields (72–96%).



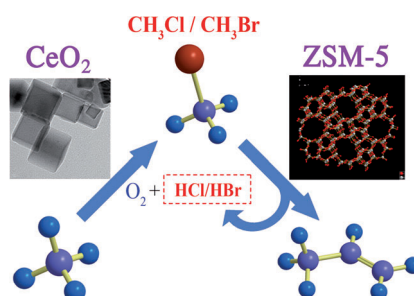
Polyoxometalates

Y. Kikukawa, Y. Kuroda, K. Yamaguchi, N. Mizuno* 2434–2437

Diamond-Shaped $[\text{Ag}_4]^{4+}$ Cluster Encapsulated by Silicotungstate Ligands: Synthesis and Catalysis of Hydrolytic Oxidation of Silanes



Propylene from methane: The transformation of methane to propylene has been realized in a two-step route via CH_3Cl or CH_3Br . CeO_2 serves as an efficient and stable catalyst for the oxidative chlorination and bromination of methane to CH_3Cl and CH_3Br . In the second step, a modified zeolite is highly a selective and stable catalyst for the conversion of CH_3Cl or CH_3Br into propylene.



Propylene Synthesis

J. He, T. Xu, Z. Wang, Q. Zhang,* W. Deng, Y. Wang* 2438–2442

Transformation of Methane to Propylene: A Two-Step Reaction Route Catalyzed by Modified CeO_2 Nanocrystals and Zeolites

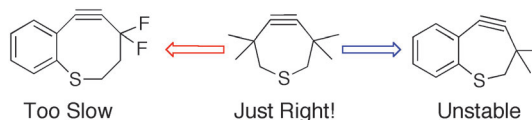


Bioorthogonal Reagents

G. de Almeida, E. M. Sletten,
H. Nakamura, K. K. Palaniappan,
C. R. Bertozzi* ————— 2443 – 2447



Thiacycloalkynes for Copper-Free Click Chemistry



The heteroatom helps! The introduction of an endocyclic sulfur atom enables fine-tuning of the reactivity and stability of thiacycloalkynes for copper-free click chemistry. The stabilizing effect of the

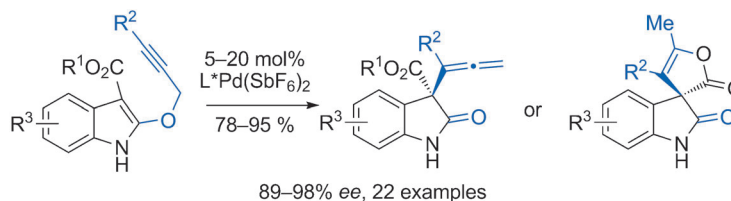
endocyclic sulfur atom allows the use of highly activated seven-membered rings as reagents for bioorthogonal copper-free click chemistry.

Asymmetric Catalysis

T. Cao, J. Deitch, E. C. Linton,
M. C. Kozlowski* ————— 2448 – 2451



Asymmetric Synthesis of Allenyl Oxindoles and Spirooxindoles by a Catalytic Enantioselective Saucy–Marbet Claisen Rearrangement



Saucy selection: The first catalytic, enantioselective Saucy–Marbet Claisen rearrangement has been achieved. Palladium(II) (*R*)-binap or *t*Buphox catalysts

$L^*Pd(SbF_6)_2$ were employed to generate allenyl oxindoles or spirooxindoles bearing a quaternary center with up to 98% *ee*.

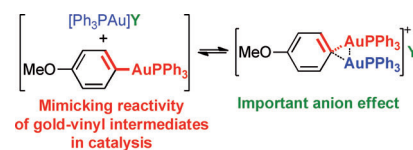
Gold Catalysis

D. Weber, T. D. Jones, L. L. Adduci,
M. R. Gagné* ————— 2452 – 2456



Strong Electronic and Counterion Effects on Geminal Digold Formation and Reactivity as Revealed by Gold(I)–Aryl Model Complexes

Geminal diauration of $[Ph_3PAu(aryl)]$ complexes has been investigated to model the intermediacy of geminally diaurated gold(I)–vinyl complexes in catalysis (see scheme). The results advance our understanding of the factors influencing the stability, reactivity, and dynamics of these organometallic intermediates.

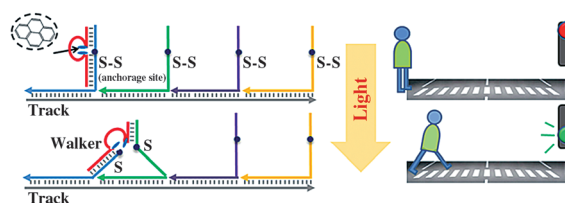


Molecular Devices

M. You, Y. Chen, X. Zhang,* H. Liu,
R. Wang, K. Wang, K. R. Williams,
W. Tan* ————— 2457 – 2460



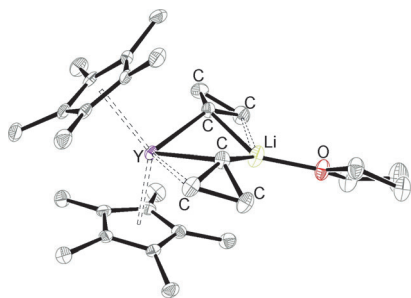
An Autonomous and Controllable Light-Driven DNA Walking Device



Regulatable nanorobots: A DNA-based walking device was designed that is capable of autonomous locomotion, with light control of initiation, termination, and

velocity (see picture). This device is reminiscent of cellular protein motors in nature, especially those of green plants.

Inside Back Cover



Two better than one! The structural distortions in a bis(cyclopropyl) heterobimetallic lithium yttrium complex can be interpreted as two types of C–C agostic interactions (see structure), one with a more covalent character with Y, the other with a more electrostatic character with Li. The C–C agostic interaction with Y is reinforced by a C–H agostic interaction.

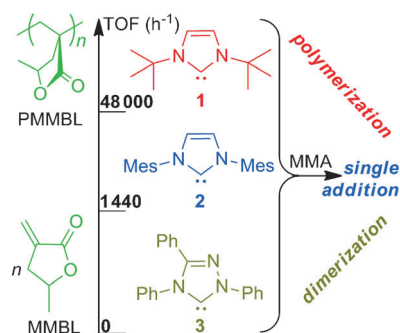
CC Agostic Interactions

Y. Escudié, C. Dinoi, O. Allen, L. Vendier, M. Etienne* — 2461 – 2464

An Unsymmetrical bis C–C Agostic Heterobimetallic Lithium Yttrium Complex



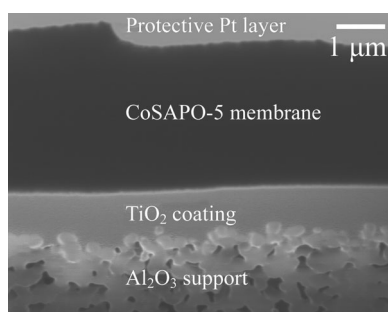
It's rapid and selective: In contrast to the dimerization of α,β -unsaturated esters (acrylics) by carbene **3**, the more nucleophilic carbene **2** selectively forms the single-addition product, and **1**, the most nucleophilic carbene of the series, polymerizes acrylics. The biomass-derived methylene butyrolactones are quantitatively polymerized to produce medium- to high-molecular-weight bioplastics in less than one minute at ambient temperature. Mes = 2,4,6-trimethylphenyl, TOF = turn-over frequency.



Organopolymerization

Y. Zhang, E. Y.-X. Chen* — 2465 – 2469

Conjugate-Addition
Organopolymerization: Rapid Production of Acrylic Bioplastics by N-Heterocyclic Carbenes

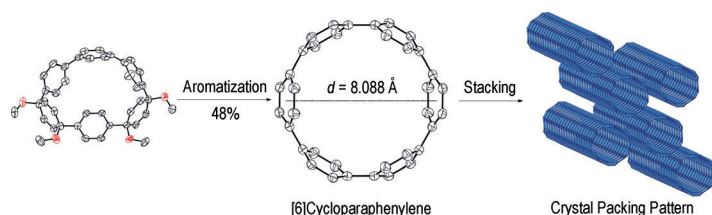


Microwaving plates: A facile method was developed for the fabrication of preferentially c -oriented cobalt-substituted silico-aluminophosphate-5 (CoSAPO-5) membranes on porous alumina supports. In situ microwave growth using a slip-coated TiO_2 layer on the support surface resulted in an oriented CoSAPO-5 crystal layer, which was evolved into a defect-free membrane by improving crystalline intergrowth through secondary hydrothermal microwave growth.

Aluminophosphate Membranes

J. A. Stoeger, M. Palomino, K. V. Agrawal, X. Zhang, G. N. Karanikolos, S. Valencia, A. Corma, M. Tsapatsis* — 2470 – 2473

Oriented CoSAPO-5 Membranes by Microwave-Enhanced Growth on TiO_2 -Coated Porous Alumina



Strained: [6]Cycloparaphenylene, a molecule with 97 kcal mol^{-1} of strain energy, was synthesized. The synthetic strategy relied on two sequential oxidative dearomatization/addition sequences and a final reductive aromatization reaction (see

scheme). The optoelectronic properties of [6]cycloparaphenylene were measured, and the analysis of the X-ray crystal structure revealed a linear packing geometry reminiscent of a carbon nanotube.

Carbon Nanostructures

J. Xia, R. Jasti* — 2474 – 2476

Synthesis, Characterization, and Crystal Structure of [6]Cycloparaphenylene

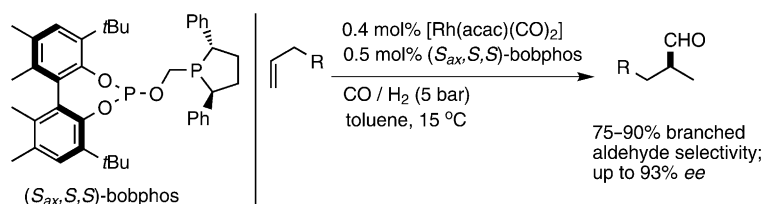


Hydroformylation

G. M. Noonan, J. A. Fuentes, C. J. Cobley,*
M. L. Clarke* 2477–2480



An Asymmetric Hydroformylation Catalyst that Delivers Branched Aldehydes from Alkyl Alkenes



Surprising selectivity: The first enantioselective hydroformylations of simple alkenes of type RCH₂CH=CH₂ to preferentially deliver the branched aldehyde product have been discovered using a new

chiral ligand, named bobbphos (see scheme). Established ligands are unselective in this reaction or show a slight preference towards the linear aldehyde.

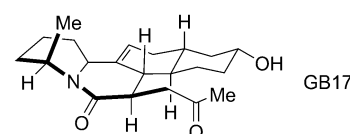
Natural Product Synthesis

R. T. Larson, M. D. Clift,
R. J. Thomson* 2481–2484



Total Synthesis of the *Galbulimima* Alkaloid (–)-GB17

A tale of two Michaels: The first enantioselective total synthesis of (–)-GB17 is reported. Construction of this unique naphthoquinolizinone skeleton was achieved by two stereoselective intramolecular Michael additions, one under catalyst control and the other under substrate control.

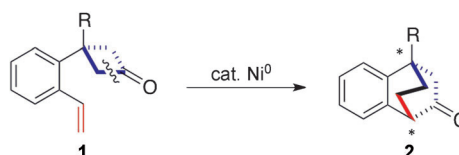


Homogeneous Catalysis

L. Liu, N. Ishida,
M. Murakami* 2485–2488



Atom- and Step-Economical Pathway to Chiral Benzobicyclo[2.2.2]octenones through Carbon–Carbon Bond Cleavage



In the nick of time: A nickel-catalyzed asymmetric intramolecular alkene insertion reaction into cyclobutanones (**1**) has been developed. The reaction significantly

reduces the number of steps required for the synthesis of chiral benzobicyclo[2.2.2]octenones (**2**).

Metal-Free Activation

F. Lavigne, E. Maerten,* G. Alcaraz,
V. Branchadell, N. Saffon-Merceron,
A. Baceiredo* 2489–2491

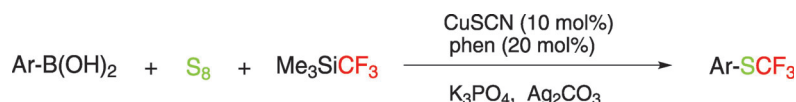


Activation of CO₂ and SO₂ by Boryl(phosphino)carbenes



Dismembering molecules: The stable boryl(phosphino)carbene **1** can cleave small organic dioxide molecules. With CO₂ and SO₂, **1** gives, respectively, the phosphacumulene ylide [Mes(iPr₂N)B-O-

P(CCO)(NiPr₂)Mes] (see scheme and structure) and boryl(phosphoryl)sulfine [Mes(iPr₂N)B-C(SO)-P(O)(NiPr₂)Mes] which have been structurally and spectroscopically characterized.



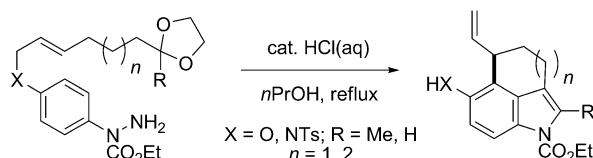
Fluorinated functionality: The copper-catalyzed oxidative trifluoromethylthiolation of aryl boronic acids with TMSCF₃ and elemental sulfur at room temperature is described for the first time. This reaction

provides a concise and efficient method for the synthesis of aryl trifluoromethyl thioethers (ArSCF₃) under mild conditions. Phen=Phenanthroline.

Thioether Synthesis

C. Chen, Y. Xie, L. Chu, R.-W. Wang, X. Zhang, F.-L. Qing* — 2492–2495

Copper-Catalyzed Oxidative Trifluoromethylthiolation of Aryl Boronic Acids with TMSCF₃ and Elemental Sulfur



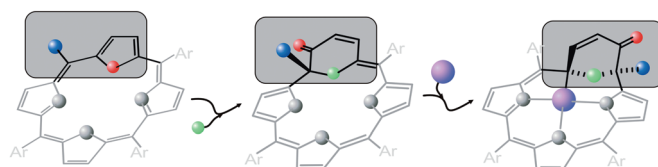
At the end of the tether: Aryl hydrazides that have carbonyl groups tethered at the *para* position of the aromatic ring undergo an intramolecular Fischer indolization reaction to give the corresponding indo-

lophanes. Strategic insertion of a double bond in the tether enables a tandem aromatic [3,3] sigmatropic rearrangement reaction to occur to give tricyclic benzo[cd]indoles.

Synthetic Methods

I.-K. Park, J. Park, C.-G. Cho* — 2496–2499

Intramolecular Fischer Indole Synthesis and its Combination with an Aromatic [3,3]-Sigmatropic Rearrangement for the Preparation of Tricyclic Benzo[cd]indoles



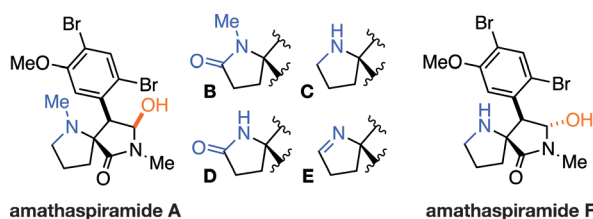
Be independent: Under basic conditions a furan ring entrapped in an aromatic macrocycle readily recovered the properties characteristic for a free molecule and assimilated a water molecule forming the Achmatowicz rearrangement product with

a 3-pyranone subunit built in. Coordination of palladium(II) created a complex stabilizing the second tautomer with two sp³ carbon atoms (oxygen red, water green, palladium purple, and the aryl group blue).

Rearrangements

M. Pawlicki, D. Bykowski, L. Szterenberg, L. Latos-Grażyński* — 2500–2504

From 21,23-Dioxaporphyrin to a 3-Pyranone Dioxacorrrole Skeleton: The Achmatowicz Rearrangement in the Porphyrin Frame



Six in one blow: Total syntheses of all the amathaspiramide alkaloids have been accomplished. Rapid construction of the diazaspiro[3.3]nonane core combined with regio- and diastereoselective reduction of the cyclic imide moiety with DIBAL

established the route to the common structural motif. The late-stage reduction of the lactam to an imine functionality mediated by Schwartz's reagent was the key to the streamlined syntheses.

Natural Product Synthesis

K. Chiyoda, J. Shimokawa, T. Fukuyama* — 2505–2508

Total Syntheses of All the Amathaspiramides



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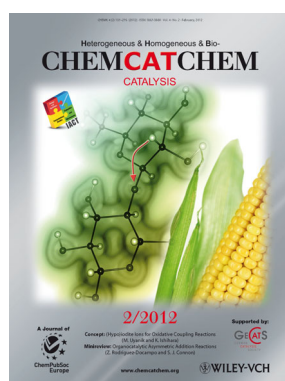
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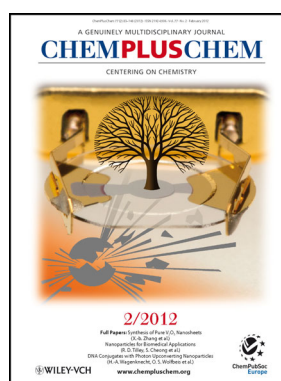
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