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:*

*T. J. Kucharski, Z. Huang, Q.-Z. Yang, Y. Tian, N. C. Rubin, C. D. Concepcion, R. Boulatov**
Kinetics of Thiol/Disulfide Exchange Correlates Weakly with the Restoring Force in the Disulfide Moiety

H. Ueda, H. Satoh, K. Matsumoto, K. Sugimoto, TohruFukuyama, H. Tokuyama**
Total Synthesis of (+)-Haplophytine

G. A. Zelada, J. Riu, A. Düzgün, F. X. Rius**
Immediate Detection of Living Bacteria at Ultra-Low Concentrations Using a Carbon-Nanotube-Based Potentiometric Aptasensor

*K. Fuchibe, T. Kaneko, K. Mori, T. Akiyama**
Expedient Synthesis of N-Fused Indoles: A C–F Activation and C–H Insertion Approach

A. Giannis, P. Heretsch, V. Sarli, A. Stößel*
Synthesis of Cyclopamine Using a Biomimetic and Diastereoselective Approach

*W. A. Chalifoux, R. McDonald, M. J. Ferguson, R. R. Tykwinski**
***tert*-Butyl Endcapped Polyynes: Crystallographic Evidence of Reduced Bond-Length Alternation**

*S. T. Scroggins, Y. Chi, J. M. J. Fréchet**
Polarity-Directed One-Pot Asymmetric Cascade Reactions Mediated by Two Catalysts in an Aqueous Buffer

*D. C. K. Rathwell, S.-H. Yang, K. Y. Tsang, M. A. Brimble**
An Efficient Formal Synthesis of the Human Telomerase Inhibitor (±)-γ-Rubromycin

Author Profile

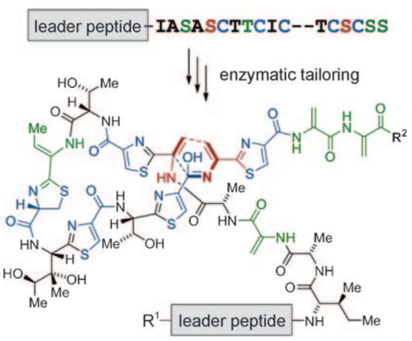
"In a nutshell, my research involves biomaterials and chemical and biomedical engineering. My work is significant because it hopefully helps people to live healthier lives. …"
This and more about Robert S. Langer can be found on page 6762.

Meeting Reviews

Books

Highlights

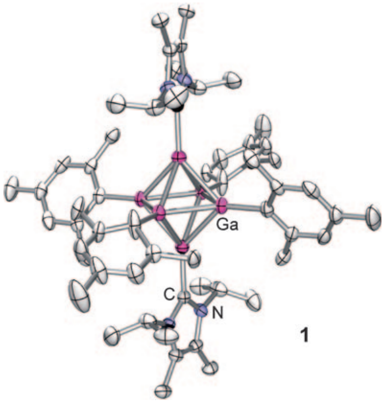
Natural Products



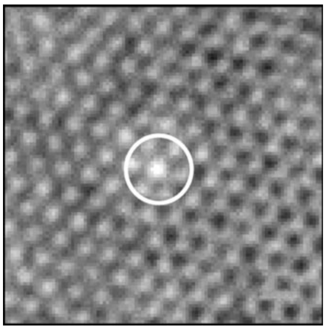
Tailors at work: The structurally intriguing thiopeptide antibiotic natural products have been conclusively and universally shown to be biosynthesized from genetically encoded linear precursor peptides by novel tailoring enzymes. These unique findings challenge previously accepted biosynthesis paradigms and are expected to inspire future discoveries in the chemistry and biology of peptide natural products.

Gallium Clusters

Carbene is key: Utilization of an N-heterocyclic carbene ligand permitted access to the neutral, octahedral *closo* cluster **1**, a prototype of a new class of carbene-stabilized main-group-element clusters. Quantum chemical methods lend insight into the bonding situation in such clusters and reveal systematic relationships.



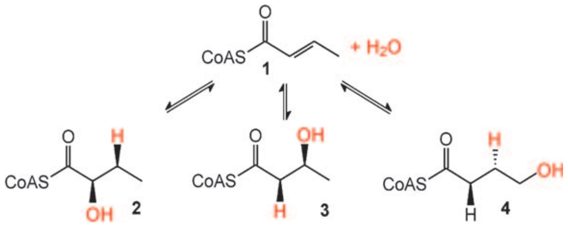
Photonic Crystals



The defect tolerance of soft poly(*N*-isopropylacrylamide) microgels makes them good candidates for the synthesis of large colloidal crystals, which show no lattice defects, even in the presence of large dopant particles (see picture, the single dopant particle is circled). This result, together with progress in core–shell microgels with inorganic cores, should allow the preparation of photonic crystals with tunable bandgaps.

Minireviews

Enzyme Mechanisms



One way or another: Radicals open new reaction pathways (**1**→**2** and **1**→**4**) that two-electron steps cannot achieve (**1**→**3**). Whereas **4** is formed by transient one-electron oxidation and two deprotonations, the addition of water to **1** to form **2** requires a high-energy electron as a cofactor that is recycled after each turnover. Organic chemists have recently applied the same principle that nature invented three billion years earlier.

For the USA and Canada:
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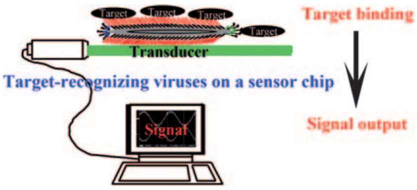
Reviews

Analytical Chemistry

C. B. Mao,* A. Liu, B. Cao **6790 – 6810**

Virus-Based Chemical and Biological Sensing



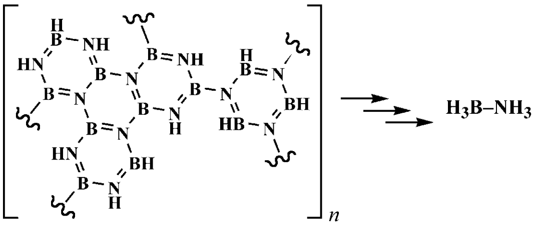
Phages and other viruses can be genetically or chemically modified to bear a motif that can selectively recognize analytes such as explosives, proteins, bacteria, spores, and toxins. Such target-specific viruses can be immobilized on a sensor chip and integrated into an analytical device. The binding of the target analyte by the viruses leads to the generation of a readable signal from a transducer in the analytical device.

Communications

Chemical Hydrogen Storage

B. L. Davis, D. A. Dixon,* E. B. Garner,
J. C. Gordon,* M. H. Matus, B. Scott,
F. H. Stephens **6812 – 6816**

Efficient Regeneration of Partially Spent Ammonia Borane Fuel

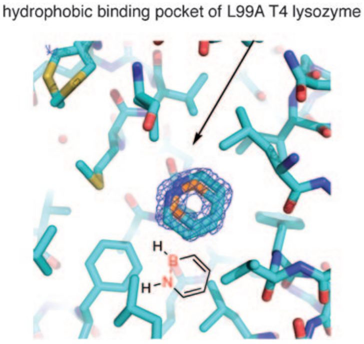


Going full circle: Ammonia borane is a potential H_2-releasing fuel. Polyborazylene, a form of the spent fuel, can be regenerated efficiently in a one-pot process by the stepwise addition of appropriate digesting and reducing agents. A unique feature of this process is the formation of NH_3, which is retained by some of the digested species.

Boron Mimetics

L. Liu, A. J. V. Marwitz, B. W. Matthews,*
S.-Y. Liu* **6817 – 6819**

Boron Mimetics: 1,2-Dihydro-1,2-azaborines Bind inside a Nonpolar Cavity of T4 Lysozyme



Enzymes BN tricked: High-resolution protein crystallography indicates that unnatural 1,2-dihydro-1,2-azaborines bind inside the nonpolar cavity of T4 lysozyme L99A (see picture) in a fashion that is very similar to the binding of their "natural" all-carbon isosteres. These studies show that 1,2-azaborines can serve as boron-containing, hydrophobic arene mimics in biomedical research.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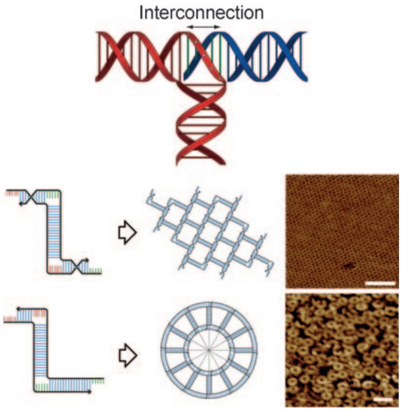
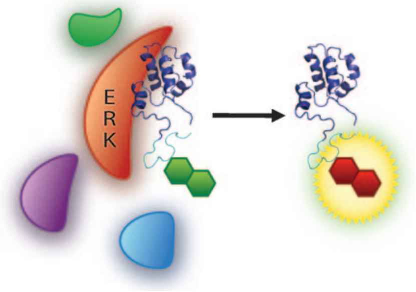


From a T-shaped DNA junction to various DNA nanostructures (see picture, scale bar = 100 nm): This technique overcomes limitations in the available varieties of DNA nanostructures and provides a well-defined geometry for structural design. Moreover, these structures can grow over the whole substrate surface in a substrate-assisted assembly method.

DNA Junctions

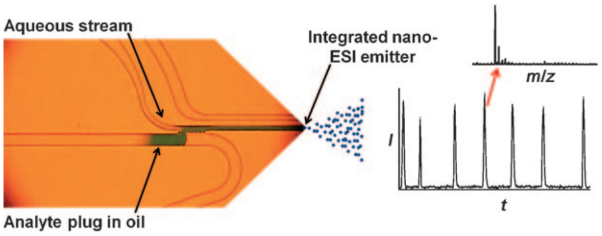
Gold plated: Gold–silver alloy nanoplates (see image) with out-of-substrate orientation are synthesized on large-area supports by growth of silver nanoplates on gallium arsenide wafers followed by an overgrowth and alloying process. The surfaces of the nanoplates are highly exposed to the surrounding environment, thus increasing their catalytic efficiency.

Nanostructures



The best of both worlds: Combining a recombinant docking domain (see picture, blue ribbon) with a chemical sensing module (green hexagons) yields a highly selective ERK sensor. This probe exclusively monitors ERK1/2 activity in unfractionated cell lysates without any off-target kinase inhibitors. Good selectivity and biophysical parameters allow high-throughput analysis of ERK1/2 activity without time-consuming enzyme purification.

Lysate Assays



Packaged, transferred, and delivered: A method has been developed that automatically transfers the contents of oil-encapsulated aqueous plugs to a co-flowing aqueous stream, which enables dilution-free electrospray ionization (ESI) mass spectrometric analysis for droplet-based microfluidics.

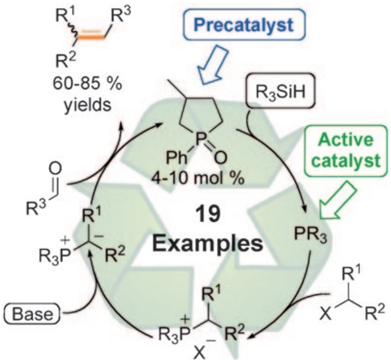
Microfluidics

Olefination

C. J. O'Brien,* J. L. Tellez, Z. S. Nixon,
L. J. Kang, A. L. Carter, S. R. Kunkel,
K. C. Przeworski,
G. A. Chass* ______________ **6836 – 6839**

Recycling the Waste: The Development of a Catalytic Wittig Reaction

It's all in the ring: 3-Methyl-1-phenylphospholane-1-oxide (4–10 mol %) and an organosilane reducing agent are the key components in the first Wittig reaction catalytic in phosphine. The protocol also functions well on larger scale: a reaction on a 30 mmol scale yielded 3.39 g of product, corresponding to a yield of 67 %.

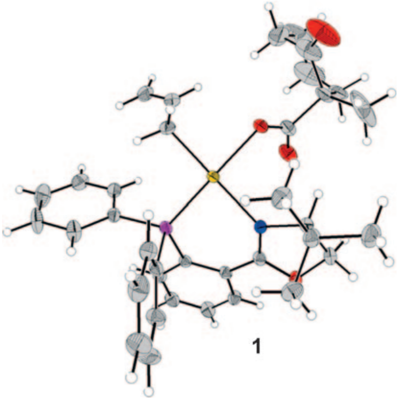


Stereoselective Catalysis

N. H. Sherden, D. C. Behenna, S. C. Virgil,
B. M. Stoltz* ______________ **6840 – 6843**

Unusual Allylpalladium Carboxylate Complexes: Identification of the Resting State of Catalytic Enantioselective Decarboxylative Allylic Alkylation Reactions of Ketones

Palladium pop rocks: Hold on to your CO_2! Enantioselective palladium-catalyzed decarboxylative alkylation of ketone enolates proceeds via η^1-σ-allyl palladium–carboxylate complexes, such as **1** (Pd yellow, O red, N blue, P purple), by slow loss of CO_2. Reminiscent of pop rock candy, impure samples of **1** expel a gas (presumably CO_2) in the solid state and effervesce in solution.

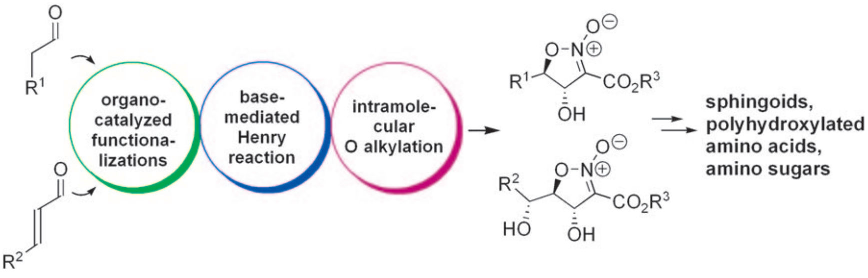


1

Asymmetric Catalysis

H. Jiang, P. Elsner, K. L. Jensen,
A. Falcicchio, V. Marcos,
K. A. Jørgensen* ___________ **6844 – 6848**

Achieving Molecular Complexity by Organocatalytic One-Pot Strategies—A Fast Entry for Synthesis of Sphingoids, Amino Sugars, and Polyhydroxylated α-Amino Acids

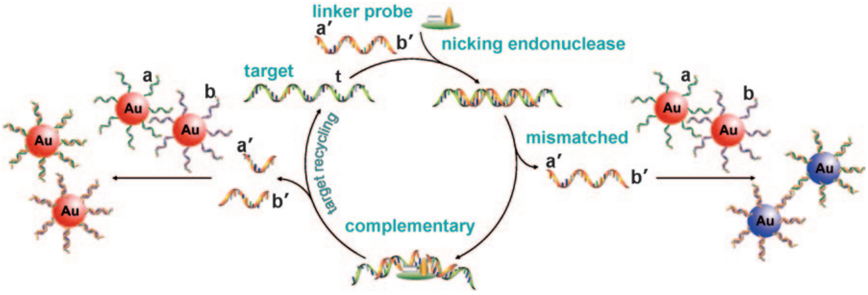


Simple complexity: By developing an organocatalyzed chiral leaving group strategy, molecular complexity was rapidly and efficiently achieved from simple starting materials. The 4,5-disubstituted isoxazoline-*N*-oxide products, obtained in high yield and enantioselectivity from an organocatalyzed one-pot, three-step sequence, served as versatile building blocks for natural products (see scheme).

DNA Detection

W. Xu, X. Xue, T. Li, H. Zeng,
X. Liu* ———— **6849 – 6852**

Ultrasensitive and Selective Colorimetric DNA Detection by Nicking Endonuclease Assisted Nanoparticle Amplification

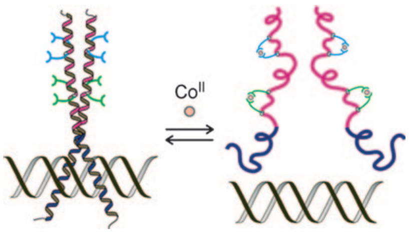


One–two punch: Single stranded DNA sequences can be detected by nicking endonuclease assisted nanoparticle amplification (see picture). The detection system offers a colorimetric detection limit of 0.5 fmol within hours for selected oligonucleotides. Detection of DNA sequences with a single base mismatch or different lengths is also demonstrated.

Metal Switches

Y. Azuma, M. Imanishi, T. Yoshimura,
T. Kawabata, S. Futaki* ———— **6853 – 6856**

Cobalt(II)-Responsive DNA Binding of a GCN4-bZIP Protein Containing Cysteine Residues Functionalized with Iminodiacetic Acid



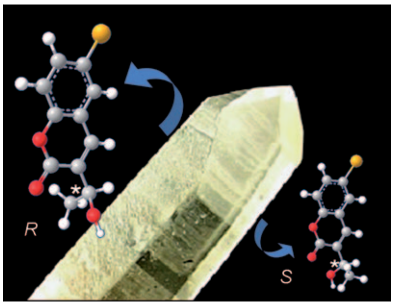
Two pairs to win: Two pairs of iminodiacetic acid (Ida) moieties were incorporated in the leucine zipper segment of the GCN4-bZIP protein in such a way that the Ida moieties of each pair were in *i* and *i*+2 positions. Complex formation of the Ida groups with Co^{II} led to destabilization of the helical structure and thus enabled reversible switching of the binding of the protein to the target AP-1 site (see picture).

Asymmetric Synthesis

A. Kuhn,* P. Fischer ———— **6857 – 6860**

Absolute Asymmetric Reduction Based on the Relative Orientation of Achiral Reactants

Interested in chirality? Absolutely! The breaking of molecular symmetry in the absence of a chiral species is known as absolute asymmetric synthesis. In a purely geometric absolute method for the enantioselective reduction of prochiral ketones, the appropriate surface of an achiral single crystal of the ketone was exposed to $NaBH_4$, and the relative spatial orientation of the achiral reactants determined the handedness of the product (see picture).

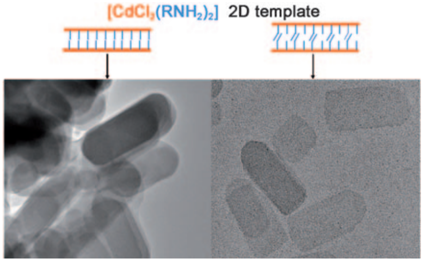


Nanosheets

J. S. Son, X.-D. Wen, J. Joo, J. Chae,
S.-i. Baek, K. Park, J. H. Kim, K. An,
J. H. Yu, S. G. Kwon, S.-H. Choi, Z. Wang,
Y.-W. Kim, Y. Kuk, R. Hoffmann,
T. Hyeon* ———— **6861 – 6864**

Large-Scale Soft Colloidal Template Synthesis of 1.4 nm Thick CdSe Nanosheets

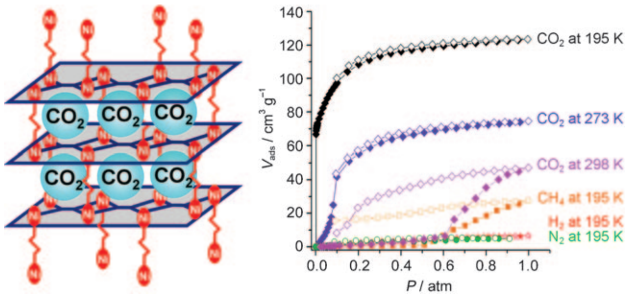
Soft as silk: Single-layered (right) and lamellar-structured two-dimensional (2D) CdSe nanocrystals (left) as thin as 1.4 nm can be prepared by a soft colloidal template method. Assembly of the 2D nanocrystals can be controlled by variation of the interaction between organic layers in soft templates. The current synthetic process is relatively easy to scale up, and multigram quantities can be obtained in a single batch.



Carbon Dioxide Capture

H.-S. Choi, M. P. Suh* ____ **6865 – 6869**

Highly Selective CO_2 Capture in Flexible 3D Coordination Polymer Networks

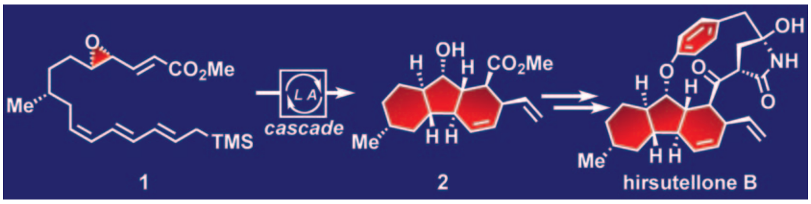


Keeping limber: Three-dimensional coordination polymers incorporating flexible pillars (see picture, left) exhibit highly selective adsorption of CO_2 over N_2, H_2, and CH_4 (see picture, right), thermal stability up to 300 °C, as well as air and water stability, and allow efficient CO_2 capture, storage, and sensing.

Natural Product Synthesis

K. C. Nicolaou,* D. Sarlah, T. R. Wu, W. Zhan ____ **6870 – 6874**

Total Synthesis of Hirsutellone B



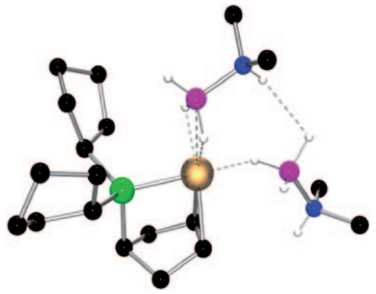
Cascading reactions, including the conversion of a TMS-epoxy tetraene **1** into the hirsutellone tricyclic core **2**, feature heavily in the first total synthesis of the antituberculosis fungal metabolite hirsutellone B. TMS = trimethylsilyl, LA = Lewis acid.

Amine–Boranes

R. Dallanegra, A. B. Chaplin, A. S. Weller* ____ **6875 – 6878**

Bis(σ-amine–borane) Complexes: An Unusual Binding Mode at a Transition-Metal Center

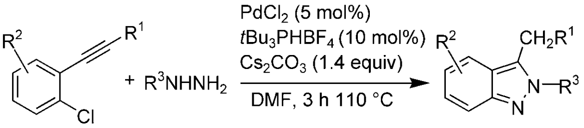
Getting a fix: Bis(σ-amine–borane) rhodium complexes featuring a new binding mode (two amine–borane ligands) have been prepared (see picture; Rh yellow, P green, B pink, N blue). These complexes undergo dehydrocoupling to afford di- or trimeric cyclic aminoboryl products.



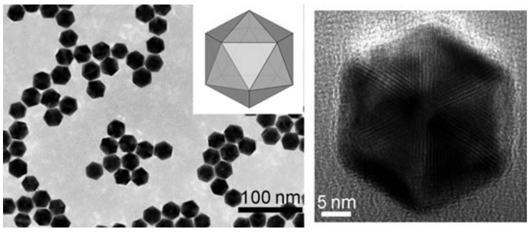
Heterocycles

N. Halland,* M. Nazaré, O. R'kyek, J. Alonso, M. Urmann, A. Lindenschmidt* ____ **6879 – 6882**

A General and Mild Palladium-Catalyzed Domino Reaction for the Synthesis of 2*H*-Indazoles



Practical and highly versatile, the reaction of readily available (2-chlorophenyl)acetylene and hydrazine substrates affords substituted 2*H*-indazoles in just a few hours under very mild reaction conditions (see scheme; DMF = *N*,*N*-dimethylformamide). The catalyzed domino sequence consists of a regioselective coupling followed by an intramolecular hydroamination and subsequent isomerization of the resulting exocyclic bond.

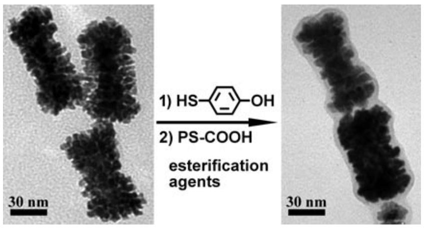


Tailored nanoparticles: Uniform Pd icosahedra (see TEM images) were controllably synthesized in high yield by a facile polyol process. Their size can be readily tailored from 15 to 42 nm by tuning the reaction parameters. The high density of twin boundaries and sharp edges on the surfaces of the Pd icosahedra could make them promising for many applications, for example, catalysis.

Icosahedral Nanoparticles

C. Li, R. Sato, M. Kanehara, H. Zeng,
Y. Bando, T. Teranishi* ____ **6883 – 6887**

Controllable Polyol Synthesis of Uniform Palladium Icosahedra: Effect of Twinned Structure on Deformation of Crystalline Lattices

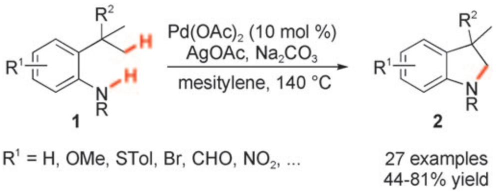


Plastic-wrapped: A polycrystalline shell of platinum can be deposited on single-crystalline gold rods. The surfaces of these structures can be covalently functionalized with organic molecules to form Au/Pt/PS nanorods (see picture, PS = polystyrene) which are soluble in organic solvents. The grafted polymer chains are visualized by electron microscopy and detected by ^{1}H NMR spectroscopy.

Nanostructures

B. P. Khanal, E. R. Zubarev* **6888 – 6891**

Polymer-Functionalized Platinum-On-Gold Bimetallic Nanorods

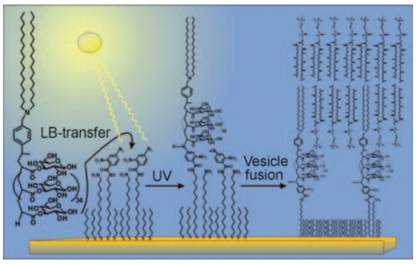


Unreactive C—H to attractive C—N: A palladium-catalyzed intramolecular direct amidation of unactivated C(sp^3)—H bonds combines C—H activation and C—N bond formation into one efficient process. Under the optimized conditions, an extraordinary tolerance of functional groups was observed, and numerous indoline derivatives were formed (see scheme).

C—H Activation

J. J. Neumann, S. Rakshit, T. Dröge,
F. Glorius* ____ **6892 – 6895**

Palladium-Catalyzed Amidation of Unactivated C(sp^3)—H Bonds: From Anilines to Indolines



Polymers on parade: Using multifunctional building blocks and a sophisticated combination of nanotechnological surface preparation techniques, lipoglycopolymers have been utilized to construct a new type of biomimetic cell membrane (see scheme; LB = Langmuir–Blodgett). For the first time, the selective photochemical immobilization of multifunctional polymeric amphiphiles on metal substrates with defined orientation of the supramolecular architecture has been demonstrated.

Biomimetic membranes

S. M. Schiller,* A. Reisinger-Friebis,
H. Götz, C. J. Hawker, C. W. Frank,
R. Naumann, W. Knoll ____ **6896 – 6899**

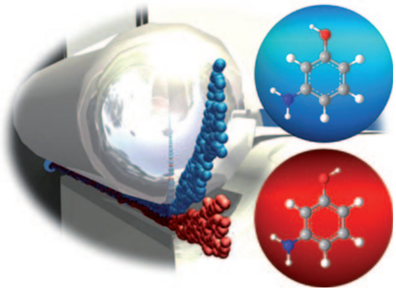
Biomimetic Lipoglycopolymer Membranes: Photochemical Surface Attachment of Supramolecular Architectures with Defined Orientation

Contents

Separation of Isomers

F. Filsinger, J. Küpper,* G. Meijer,
J. L. Hansen, J. Maurer, J. H. Nielsen,
L. Holmegaard,
H. Stapelfeldt* ____ **6900 – 6902**

Pure Samples of Individual Conformers: The Separation of Stereoisomers of Complex Molecules Using Electric Fields



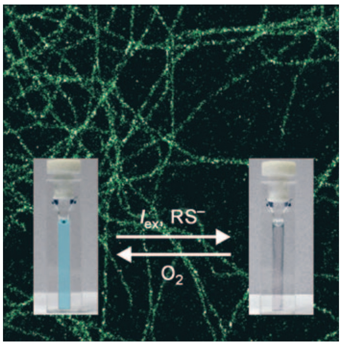
Keep 'em separated: Stereoisomers of complex molecules generally have very different electric dipole moments for the same mass. The different dipole-moment-to-mass ratios can be exploited in the separation of these species using electric fields. The pure samples thus created offer opportunities in isomer-specific and stereoselective investigations.

Microscopy

M. Heilemann,* S. van de Linde,
A. Mukherjee, M. Sauer* ____ **6903 – 6908**

Super-Resolution Imaging with Small Organic Fluorophores

What's your color? A universal and facile method for reversible photoswitching of commercially available Alexa Fluor and ATTO dyes spanning the entire visible range yields an optical resolution of approximately 20 nm. The intriguing simplicity of the method facilitates applications and opens avenues for multicolor super-resolution imaging in fixed and living cells.

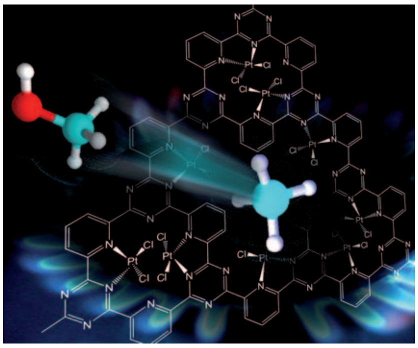


Methane Oxidation

R. Palkovits, M. Antonietti, P. Kuhn,
A. Thomas, F. Schüth* ____ **6909 – 6912**

Solid Catalysts for the Selective Low-Temperature Oxidation of Methane to Methanol

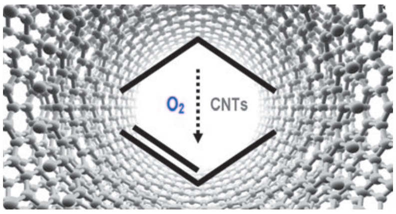
Again and again and again: The title reaction was achieved on a solid catalyst in a covalent triazine-based framework formed by trimerization of 2,6-dicyanopyridine in a $ZnCl_2$ melt. The material possesses bipyridine units as coordination sites for platinum. It shows high activity and can be separated easily from the reaction mixture and recycled several times without significant loss of activity.



Metal-Free Catalysis

B. Frank, J. Zhang, R. Blume, R. Schlögl,
D. S. Su* ____ **6913 – 6917**

Heteroatoms Increase the Selectivity in Oxidative Dehydrogenation Reactions on Nanocarbons



Boron makes it selective: Carbon nanotubes (CNTs) modified by boron oxide catalyze the oxidative dehydrogenation of propane to propene with remarkable selectivity. Nanocarbon can be an attractive alternative to conventional metal oxides, as it enables a feasible investigation of the reaction mechanism and provides a sustainable technology for alkane conversion.

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

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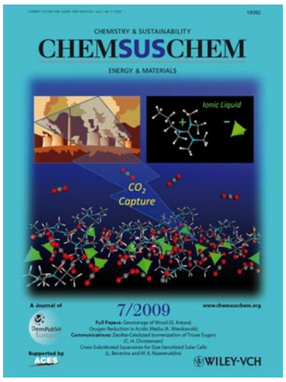

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