



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:

B. L. Merner, L. N. Dawe, G. J. Bodwell*

1,1,8,8-Tetramethyl[8](2,11)teropyrenophane: Half of an Aromatic Belt and a Segment of an (8,8) Single-Walled Carbon Nanotube

B. Liu, H. Wang, H. Xie, B. Zeng, J. Chen, J. Tao, T. B. Wen, Z. Cao, H. Xia*

Osmapyridine and Osmapyridinium from a Formal [4+2] Cycloaddition Reaction

J. Tolosa, C. Kub, U. H. F. Bunz*

Hyperbranched: A Universal Conjugated Polymer Platform?

D. Xu, Z. Liu, H. Yang, Q. Liu, J. Zhang, J. Fang,* S. Zou,* K. Sun
Solution-Based Evolution of Monodisperse Pt–Cu Nanocubes and Their Enhanced Methanol Oxidation Activity

J. L. Alonso-Gómez, P. Rivera-Fuentes, N. Harada, N. Berova, F. Diederich*

An Enantiomerically Pure Allen-acylenic Macrocyclic: Synthesis and Rationalization of Its Outstanding Chiroptical Response

P. García-García, M. A. Fernández-Rodríguez, E. Aguilar*
Gold-Catalyzed Cycloaromatization of 2,4-Dien-6-yne Carboxylic Acids: Synthesis of 2,3-Disubstituted Phenols and Unsymmetrical Bi- and Terphenyls

H. Jiang, P. Elsner, K. L. Jensen, A. Falcicchio, V. Marcos, K. A. Jørgensen*

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

P. A. Rugar, R. Bandyopadhyay, B. F. T. Cooper, M. R. Stinchcombe, P. J. Ragogna, C. L. B. Macdonald,* K. M. Baines*

Cationic Crown Ether Complexes of Germanium(II)

X. Zeng, H. Beckers, H. Willner*

Difluoro- λ^5 -Phosphinonitrile $F_2P=N$: Matrix Isolation and Photoisomerization into $FP=NF$

H. Huang, B. Chung, J. Jung, H.-W. Park, T. Chang*

Toroidal Micelles of Uniform Size from Diblock Copolymer

R. Koller, K. Stanek, D. Stolz, R. Aardoom, K. Niedermann, A. Togni*

Zn-Mediated Formation of Trifluoromethyl Ethers From Alcohols Using Hypervalent Iodine Trifluoromethylation Reagents

A. D. Payne, G. Bojase, M. N. Paddon-Row,* M. S. Sherburn*
Practical Synthesis of the Dendralene Family Reveals Alternation in Behavior

A. S. Iyer, L. A. Lyon*

Self-Healing Colloidal Crystals

Author Profile



„When I wake up I row. When I was eighteen I wanted to be Morrissey. ...“

This and more about Benjamin G. Davis can be found on page 3900.

Benjamin G. Davis _____ 3900

News



A. Kobayashi



E. Kumacheva



T. Nyokong

Materials Science:
L'Oréal–UNESCO Prizes to
A. Kobayashi, E. Kumacheva,
and T. Nyokong _____ 3901

Books

Highlights in Colloid Science

D. Platikanov, D. Exerowa

reviewed by J.-H. Fuhrhop _____ 3902

Metal Oxide Catalysis

S. David Jackson, Justin S. J. Hargreaves

reviewed by G. Thornton _____ 3902

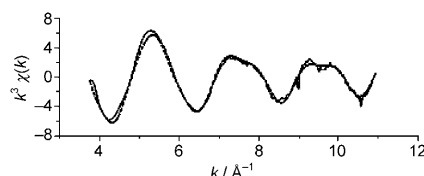
Highlights

Heterogeneous Catalysis

J. M. Thomas,*

J.-C. Hernandez-Garrido _____ 3904–3907

Probing Solid Catalysts under Operating Conditions: Electrons or X-rays?

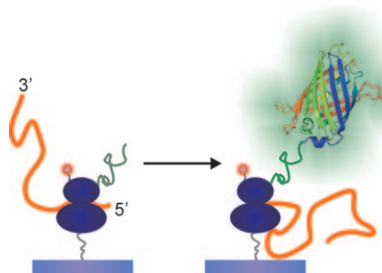


Seeing is believing: In light of recent advances, the pros and cons of using electrons and X-rays for in situ studies of catalysts are analyzed: by using X-rays the structure of bound reactants at steady state are obtained from extended X-ray adsorption fine structure spectroscopy (EXAFS) data (see graph), thereby affording mechanistic insights.

Single-Molecule Studies

M. Heilemann* _____ 3908–3910

Light at the End of the Tunnel

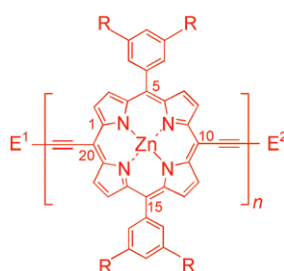


Turn the light on: The synthesis, folding and maturation kinetics of individual green fluorescent protein (GFP) molecules have been studied using a cell-free transcription–translation system and single-molecule fluorescence. Ribosomes, which were labeled with a red fluorophore and tethered to a glass surface, were used to synthesize GFP Emerald molecules that become fluorescent after maturation.

Conducting Oligomers

H. Meier* _____ 3911–3913

High Electrical Conductance of Single Molecules: A Challenge in the Series of Conjugated Oligomers



En route to molecular electronics: As extended, conjugated oligomers are desirable for molecular electronics, their electrical conductance should display a low attenuation factor. Zinc-complexed oligo(ethynylene)porphyrindiylethynylene)s have been prepared that are distinguished by ultralow attenuation factors in single-molecule conductance.

For the USA and Canada:

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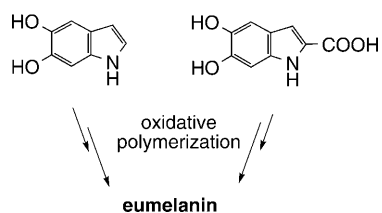
electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Minireviews

Biopolymers

M. d'Ischia,* A. Napolitano, A. Pezzella, P. Meredith,* T. Sarna* — 3914–3921

Chemical and Structural Diversity in Eumelanins: Unexplored Bio-Optoelectronic Materials



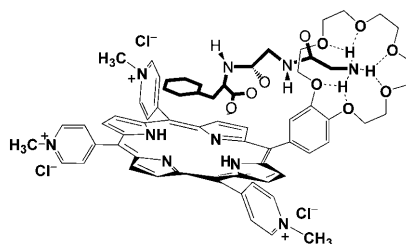
A black whole: The black insoluble biopolymer eumelanin is prepared through the oxidative polymerization of 5,6-dihydroxyindoles (see scheme). It has a largely unknown heterogeneous structure and unique optoelectronic properties. Current structural models are presented and possible applications are discussed.

Reviews

Supramolecular Chemistry

H.-J. Schneider* — 3924–3977

Binding Mechanisms in Supramolecular Complexes



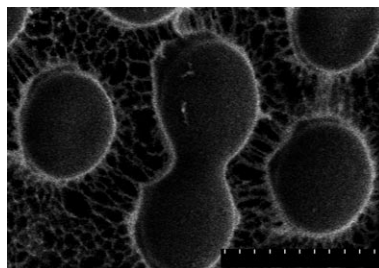
Forces to reckon with: Supramolecular complexes, such as the one shown, are normally based on a combination of different interactions such as ion pairing, hydrogen bonds, and stacking interactions. The not always simple characterization of the nature and strength of intermolecular forces provides assistance to the understanding of biomimetic systems, as well as for the design of synthetic receptors, drugs, and intelligent materials.

Communications

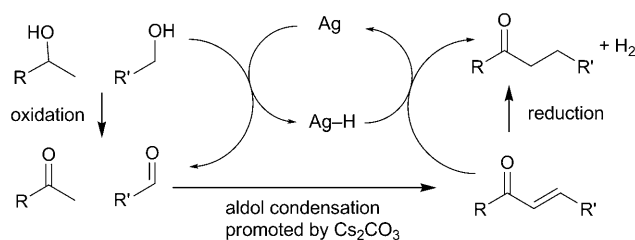
Emulsions

B. Brugger, S. Rütten, K.-H. Phan, M. Möller, W. Richtering* — 3978–3981

The Colloidal Suprastructure of Smart Microgels at Oil–Water Interfaces



Oil on troubled waters: Stimuli-sensitive emulsions have been used to prepare temperature- and pH-responsive microgels. The emulsion stability at oil–water interfaces is not governed by the particle packing density, and structural changes induced by the interface lead to connections between the individual microgels (see picture; scale bar 1 μm), which behave very differently compared to solid-particle-stabilized emulsions.



Let's drink to that! Two alcohols (one primary and one secondary) can be coupled in an atom-efficient process by a hydrogen-autotransfer catalytic system in the form of silver subnanoclusters sup-

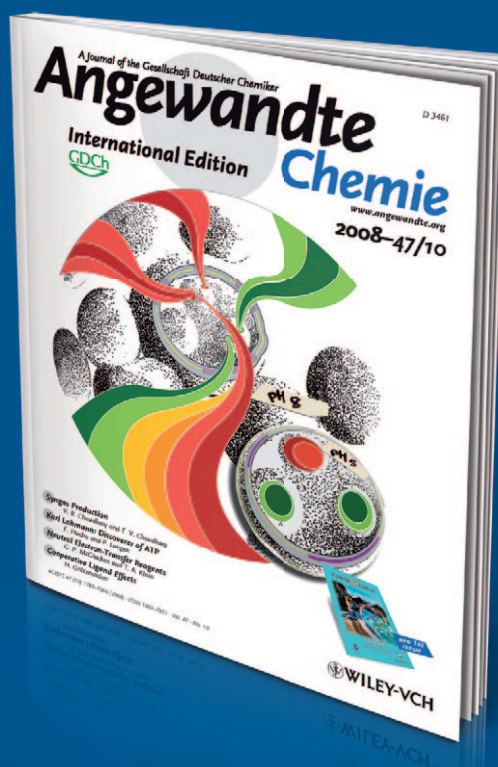
ported on $\gamma\text{-Al}_2\text{O}_3$. The recyclable heterogeneous catalyst promoted the one-pot C–C cross-coupling in the presence of a catalytic amount of the weak base Cs_2CO_3 (see reaction mechanism).

Heterogeneous Catalysis

K.-i. Shimizu,* R. Sato, A. Satsuma — 3982–3986

Direct C–C Cross-Coupling of Secondary and Primary Alcohols Catalyzed by a γ -Alumina-Supported Silver Subnanocluster

Incredibly inexpensive.



Do chemistry journals really cost so much? Perhaps some do, but certainly not *Angewandte Chemie*! In 2008, an entire institution could subscribe through Wiley InterScience* for 5000 € and get access to 52 issues with over 1600 articles and all associated online search options, and for just 5 % more, the printed issues could be included as well. For full members of the German Chemical Society (GDCh), a personal subscription cost not much more than 300 €, and student GDCh members paid less than 150 €, which is just under 3 € per issue - a price that even compares with high-circulation newsstand publications!

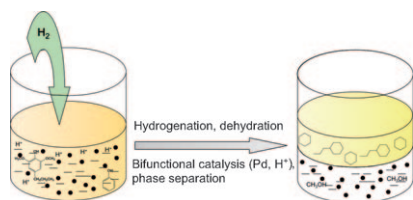
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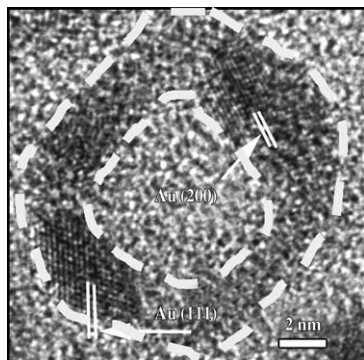


Oil and water: A new energy-efficient and atom-economical catalytic route for the production of alkanes and methanol by upgrading the phenolic fraction of bio-oil has been developed. The one-pot aqueous-phase hydrodeoxygenation process is based on two catalysts facilitating consecutive hydrogenation, hydrolysis, and dehydration reactions.

Biofuels

C. Zhao, Y. Kou,* A. A. Lemonidou, X. Li, J. A. Lercher* **3987–3990**

Highly Selective Catalytic Conversion of Phenolic Bio-Oil to Alkanes

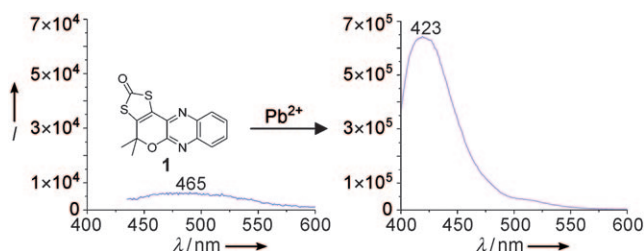


Turing lead into gold: Hollow hybrid PbS_x -Au nanostructures of about 10 nm in diameter were synthesized using a one-step reaction under mild experimental conditions. The redox reaction of gold precursors with PbS nanocrystals in the presence of dodecylamine leads to the hollow feature of hybrid nanostructures (see picture).

Nanostructures

J. Yang,* J. Peng, Q. B. Zhang, F. Peng, H. Wang, H. Yu **3991–3995**

One-Step Synthesis and Characterization of Gold-Hollow PbS_x Hybrid Nanoparticles



A real turn-on: The emission intensity of heterocycle **1** increases upon binding to Pb^{2+} . Thus, **1** acts as a small-molecule

“turn-on” fluorescent sensor for lead. The sensor is highly selective and is functional over a wide range of pH values.

Lead Sensors

L. Marbella, B. Serli-Mitasev, P. Basu* **3996–3998**

Development of a Fluorescent Pb^{2+} Sensor



Ring leader: PtCl_2 catalyzes intramolecular cyclization of *o*-isopropyl or *o*-benzyl aryl alkynes to give substituted indene derivatives with good yields and high

selectivity. This reaction appears to proceed through an sp^3 C–H activation and 1,4-hydrogen migration pathway (see scheme).

C–H Activation

S. Yang, Z. Li, X. Jian, C. He* **3999–4001**

Platinum(II)-Catalyzed Intramolecular Cyclization of *o*-Substituted Aryl Alkynes through sp^3 C–H Activation

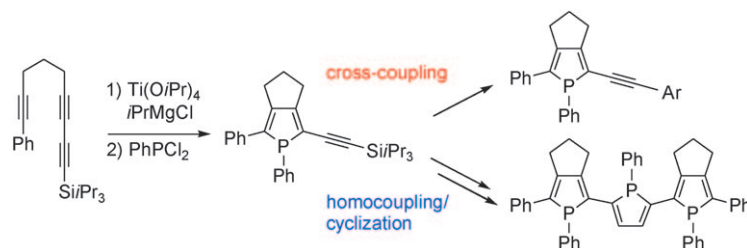


Phospholes

Y. Matano,* M. Nakashima,
H. Imahori ————— 4002–4005



A Convenient Method for the Synthesis of α -Ethyneylphospholes and Modulation of Their π -Conjugated Systems



Mind the (narrow) gap: α -Ethyneylphospholes generated in situ from the corresponding silyl-capped precursors were converted into a series of α -(arylethyne) phospholes bearing functional substitu-

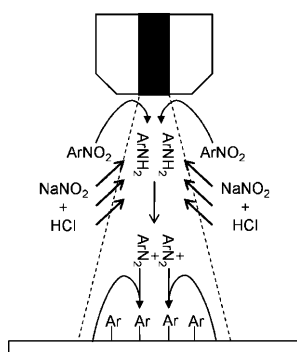
ents as well as an α,α' -linked terphosphole (see scheme). The terphosphole has a narrow HOMO–LUMO gap owing to efficient π conjugation over the three phosphole rings.

Diazonium Chemistry

C. Cougnon,* F. Gohier, D. Bélanger,
J. Mauzeroll ————— 4006–4008



In Situ Formation of Diazonium Salts from Nitro Precursors for Scanning Electrochemical Microscopy Patterning of Surfaces



Give me a tip: In situ production of diazonium salts from nitro compounds allows the use of diazonium chemistry for microelectrochemical patterning of surfaces by scanning electrochemical microscopy. The nitro precursor is reduced at the tip to the amine, which is diazotized in the interelectrode space as it diffuses (see picture). The tip acts as a source of diazonium salts, allowing sample derivatization just beneath the tip.

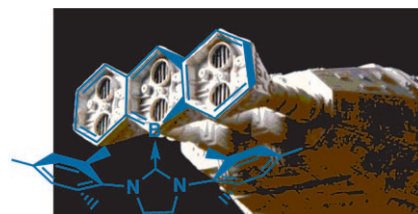
Boron Heterocycles

T. K. Wood, W. E. Piers,* B. A. Keay,
M. Parvez ————— 4009–4012



9-Boraanthracene Derivatives Stabilized by N-Heterocyclic Carbenes

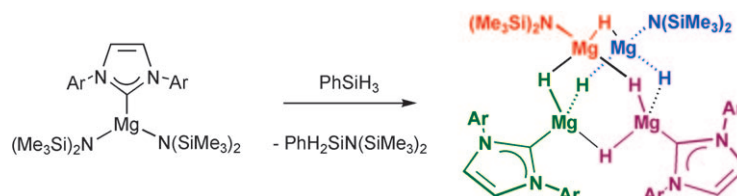
2009: A boraanthracene odyssey: General routes to boraanthracene derivatives—long proposed, but never observed—are disclosed, along with the structural and photophysical properties of these compounds and their remarkable reactivity towards oxygen.



Cluster Chemistry

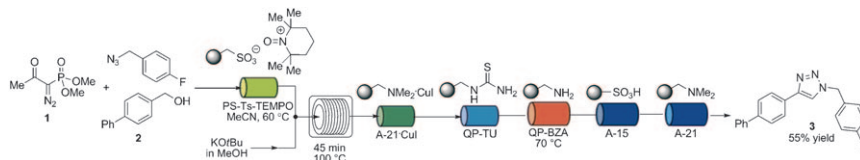
M. Arrowsmith, M. S. Hill,*
D. J. MacDougall,
M. F. Mahon ————— 4013–4016

A Hydride-Rich Magnesium Cluster



High-de-hydride! A straightforward reaction between a magnesium silylamido/N-heterocyclic carbene adduct and phenylsilane provides a $\{Mg_4H_6\}$ cluster mole-

cule that may be regarded as a combination of two magnesium dihydride and two magnesium monohydride moieties.



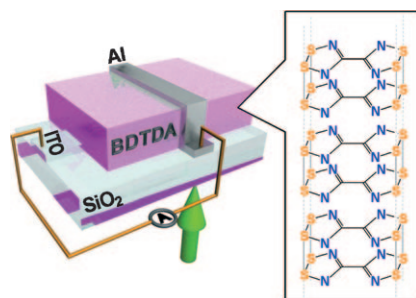
Multistep in flow: The Seyferth–Gilbert reagent **1** has been applied in a flow system to rapidly synthesize terminal alkynes. The system has been further applied to synthesize triazole **3** from

alcohol **2** in a three-step oxidation/homologation/copper(I)-catalyzed azide–alkyne cycloaddition sequence without isolation of intermediates (see scheme).

Continuous-Flow Synthesis

I. R. Baxendale, S. V. Ley,* A. C. Mansfield, C. D. Smith 4017–4021

Multistep Synthesis Using Modular Flow Reactors: Bestmann–Ohira Reagent for the Formation of Alkynes and Triazoles

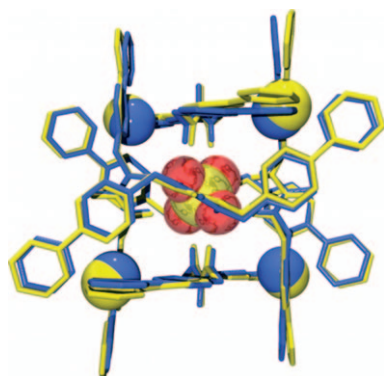


Fully interactive: Overlap between extended unoccupied molecular orbitals leads to the high photoconductivity of interactive radical dimers. Sandwich-type cells (see picture; ITO = indium tin oxide) comprising highly oriented thin films of a disjoint diradical, 4,4'-bis(1,2,3,5-dithiadiazolyl) (BDTDA) exhibit a photocurrent with a high on/off ratio at reverse bias voltages and photovoltaic behavior at zero bias voltage.

Organic Electronics

A. Iwasaki, L. Hu, R. Suizu, K. Nomura, H. Yoshikawa, K. Awaga,* Y. Noda, K. Kanai, Y. Ouchi, K. Seki, H. Ito 4022–4024

Interactive Radical Dimers in Photoconductive Organic Thin Films

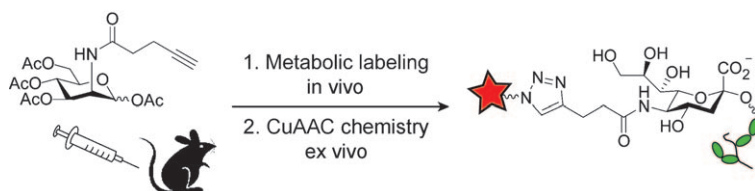


Custom built: A promising new approach towards more efficient self-assembled cage receptors through computer-aided design is demonstrated. The resulting M_4L_6 tetrahedral cage, internally functionalized with accurately positioned urea hydrogen-bonding groups (see structure; yellow: predicted, blue: experimental, space-filling: SO_4^{2-}), proved to be a remarkably strong sulfate receptor in water.

Self-Assembled Cages

R. Custelcean,* J. Bosano, P. V. Bonnesen, V. Kertesz, B. P. Hay* 4025–4029

Computer-Aided Design of a Sulfate-Encapsulating Receptor



Sialome sweet sialome: As sialic acids are involved in many host–pathogen recognition events and are markers of embryonic and malignant tissues, there is great interest in methods for the enrichment and identification of sialylated glycopro-

teins from complex tissues. Now *N*-(4-pentynoyl)mannosamine can be used to metabolically label sialylated glycoproteins in living animals, enabling future identification of new biomarkers.

Glycobiology

P. V. Chang, X. Chen, C. Smyrniotis, A. Xenakis, T. Hu, C. R. Bertozzi,* P. Wu* 4030–4033

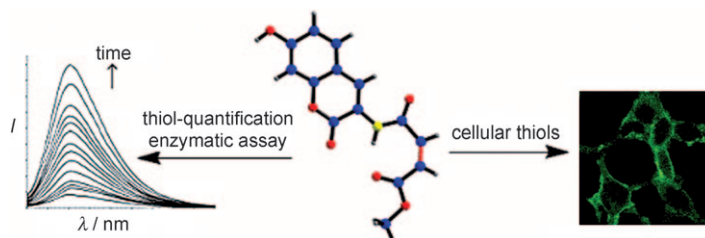
Metabolic Labeling of Sialic Acids in Living Animals with Alkynyl Sugars

Fluorescent Probes

L. Yi, H. Li, L. Sun, L. Liu, C. Zhang,
Z. Xi* 4034–4037



A Highly Sensitive Fluorescence Probe for Fast Thiol-Quantification Assay of Glutathione Reductase



Fast detection of cellular thiols in aqueous medium was achieved using a newly developed fluorescence probe (see pic-

ture). Based on this probe, a high-throughput fluorescence assay for glutathione reductase was developed.

OLEDs

P. Zacharias, M. C. Gather, A. Köhnen,
N. Rehm, K. Meerholz* 4038–4041



Photoprogrammable Organic Light-Emitting Diodes

Enlightening the memory: The integration of a crosslinkable photochromic dithienylperfluorocyclopentene (DTE) into organic light-emitting diodes (OLED) allows for the individualization of the emissive area of the OLED device, for example, for signage applications. The operation principle is based on switching the injection barrier for holes (positive charge carriers). Very large ON/OFF ratios of up to 3000 for current as well as electroluminescence have been achieved.

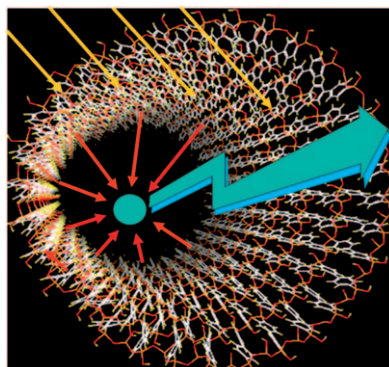


Organic–Inorganic Materials

S. Inagaki,* O. Ohtani, Y. Goto,
K. Okamoto, M. Ikai K. Yamanaka, T. Tani,
T. Okada 4042–4046



Light Harvesting by a Periodic Mesoporous Organosilica Chromophore



Light aqueduct: Periodic mesoporous organosilica exhibits strong light absorption due to densely packed organic chromophores within the pore walls. Light energy absorbed by 125 biphenyl groups in the pore walls is funneled into a single coumarin 1 molecule in the mesochannels with almost 100% quantum efficiency, and results in significant enhancement of emission from the coumarin 1 dye.

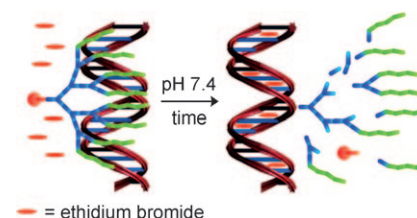
DNA Binding

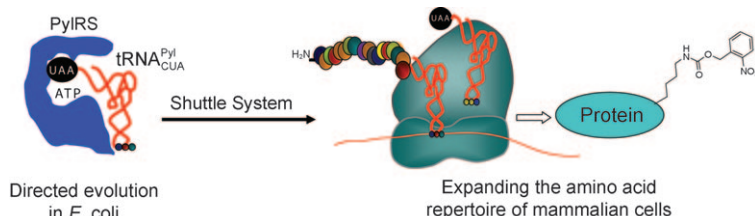
D. J. Welsh, S. P. Jones,
D. K. Smith* 4047–4051



“On-Off” Multivalent Recognition: Degradable Dendrons for Temporary High-Affinity DNA Binding

Now you bind it—now you don’t! Chemical degradation of a dendritic scaffold allows multivalent interactions with DNA to be “switched off” as the multivalent array of ligands breaks down into smaller fragments, offering an approach by which a molecule can be temporarily endowed with high affinity for a biological target—an important concept in the development of new synthetic systems to intervene in biological pathways.





A **shuttle system** has been developed to genetically encode unnatural amino acids in mammalian cells using aminoacyl-tRNA synthetases (aaRSs) evolved in *E. coli*. A pyrrolysyl-tRNA synthetase (PylRS) mutant was evolved in *E. coli* that selectively aminoacylates a cognate non-

sense suppressor tRNA with a photo-caged lysine derivative. Transfer of this orthogonal tRNA–aaRS pair into mammalian cells made possible the selective incorporation of this unnatural amino acid into proteins.

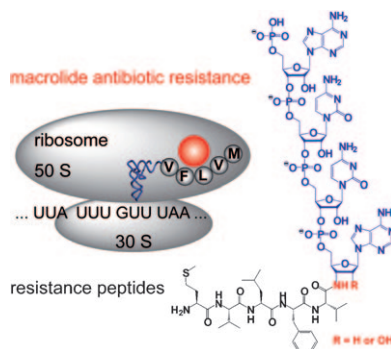
Expanded Genetic Code

P. R. Chen, D. Groff, J. Guo, W. Ou, S. Cellitti, B. H. Geierstanger,*
P. G. Schultz* _____ **4052 – 4055**

A Facile System for Encoding Unnatural Amino Acids in Mammalian Cells



Translation of specific small peptides on the ribosome can confer resistance to macrolide antibiotics. To reveal the molecular details of this and related phenomena, stable RNA–peptide conjugates that mimic peptidyl-tRNA would be desirable, especially for ribosome structural biology. A flexible solid-phase synthesis strategy now allows efficient access to these highly requested derivatives without restriction on the RNA and peptide sequences.



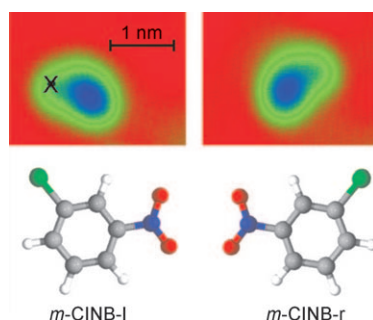
RNA–Peptide Conjugates

H. Moroder, J. Steger, D. Graber, K. Fauster, K. Trappl, V. Marquez, N. Polacek, D. N. Wilson, R. Micura* _____ **4056 – 4060**

Non-Hydrolyzable RNA–Peptide Conjugates: A Powerful Advance in the Synthesis of Mimics for 3'-Peptidyl tRNA Termini



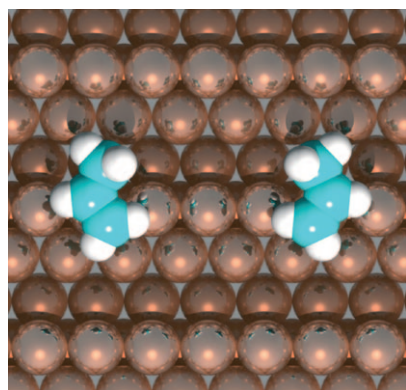
Chirality chameleon: Inelastic electron tunneling manipulation can be used to change a single chloronitrobenzene (CINB) molecule, randomly adsorbed on Au(111), into its desired enantiomeric form (*r* or *l*, see STM images and ball-and-stick representation) and to vary its rotational orientation. The different threshold voltages for chirality change (260 mV) and rotation (380 mV) allow these processes to be induced separately.



Single-Molecule Manipulation

V. Simic-Milosevic, J. Meyer, K. Morgenstern* _____ **4061 – 4064**

Chirality Change of Chloronitrobenzene on Au(111) Induced by Inelastic Electron Tunneling



Pumped up: Propene molecules form chiral complexes when adsorbed on a copper surface. Inelastically scattered tunneling electrons from the tip of a scanning tunneling microscope induce rotation or diffusion of the adsorbate on the surface. Higher tunneling currents can lead to conversion of the adsorbate into the opposite enantiomer.

Chirality

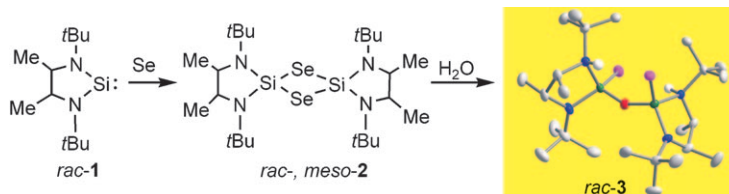
M. Parschau, D. Passerone, K.-H. Rieder, H. J. Hug, K.-H. Ernst* _____ **4065 – 4068**

Switching the Chirality of Single Adsorbate Complexes



Silaselenones

A. Mitra, J. P. Wojcik, D. Lecoanet,
T. Müller,* R. West* — 4069–4072



A Bis(silaselenone) with Two Donor-Stabilized Si=Se Bonds from an Unexpected Stereoconvergent Hydrolysis of a Diselenadisiletane

SiSe matters: Diselenadisiletane **2**, formed from direct reaction of a racemic silylene **1** with elemental selenium, gives the first bis(silaselenone) upon hydrolysis with water (**3**; see picture, C gray, H white,

N blue, O red, Se purple, Si green; $d(\text{Si}=\text{Se})=215\text{ pm}$). The reaction is stereoconvergent: only racemic forms of **3** are obtained from a mixture of racemic and *meso* forms of **2**.



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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Keywords — 4074

Authors — 4075

Preview — 4077

Corrigendum

Pseudo-Bridging Silanols as Versatile Brønsted Acid Sites of Amorphous Aluminosilicate Surfaces

C. Chizallet,* P. Raybaud — 2891–2893

Angew. Chem. Int. Ed. **2009**, 48

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In the methods section of this communication on page 2893 Equation (1) was reported incorrectly. The correct equation is:

$$\Gamma_{(T)} = \Gamma_{(0K)} + \frac{\theta_{OH}}{2} \left[T S_{(T)}^{\circ} - H_{(T)}^{\circ} + H_{(0K)}^{\circ} - k T \ln \left(\frac{P}{P^{\circ}} \right) \right] \quad (1)$$