

Spotlight on Angewandte's Sister Journals

Service

10438 – 10440



"My mottos are 'be naïve' and 'be creative'.
My favorite way to spend a holiday is fishing in a mountain stream. ..."
This and more about Noritaka Mizuno can be found on page 10442.

Author Profile

Noritaka Mizuno _____ 10442 – 10443

News



C. P. R. Hackenberger



A. J. von Wangelin



P. S. Baran



N. Garg



A. Doyle

ORCHEM Prize for Young Investigators:
C. P. R. Hackenberger and
A. Jacobi von Wangelin _____ 10444

Teva Pharmaceuticals Scholar Grant:
P. S. Baran _____ 10444

Roche Excellence in Chemistry Award:
N. Garg and A. Doyle _____ 10444

Obituaries



Ivano Bertini, one of the pioneers of bioinorganic chemistry, recently passed away at the age of 71. His work on determining the solution structures of the metalloproteins with paramagnetic centers was one of his many achievements.

Ivano Bertini (1940–2012)

C. Luchinat* _____ 10445

Books

Circular Dichroism and Magnetic Circular
Dichroism Spectroscopy for Organic
Chemists

Nagao Kobayashi, Atsuya Muranaka, John
Mack

reviewed by B. Borhan _____ 10446

Highlights

Palladium Catalysis

R. S. Paton,*
J. M. Brown* ——— 10448 – 10450

Dinuclear Palladium Complexes—
Precursors or Catalysts?

Calculations help: Recent work from Schoenebeck's group has demonstrated beyond reasonable doubt that the dimeric $\text{LPd}^{\text{I}}\text{Br}$ catalysts that are widely used in coupling chemistry operate through prior formal reduction to an LPd^0 species. Conversely, L_2Pd^0 catalysts can be activated by oxidation. In other cases a binuclear species can persist through the catalytic cycle.

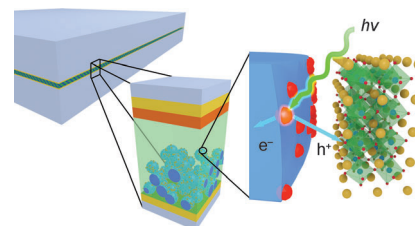


Solar Energy

U. Bach,* T. Daeneke — 10451 – 10452

A Solid Advancement for Dye-Sensitized
Solar Cells

Switching to solids: Solid-state dye-sensitized solar cells are achieving efficiencies similar to those of their counterparts with liquid electrolytes. The new p-type semiconductor CsSnI_3 was found to be an excellent replacement for the traditional I^-/I_3^- redox system. The picture shows a cross section of a dye-sensitized solar cell based on CsSnI_3 .



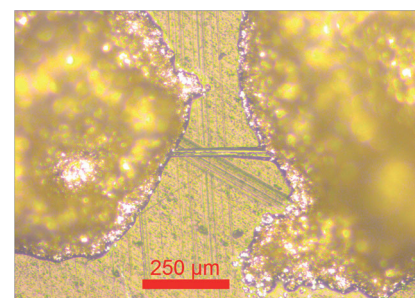
Correspondence

Proton Conductivity (1)

K.-D. Kreuer,*
A. Wohlfarth ——— 10454 – 10456

Limits of Proton Conductivity

Parasitic current seems to be the cause for the “highest proton conductivity” of a material reported to date. Kreuer and Wohlfarth verify this hypothesis by measuring the conductivity of the same materials after preparing them in a different way. They further explain the limits of proton conductivity and comment on the problems of determining the conductivity of small objects (e.g., whiskers, see picture).

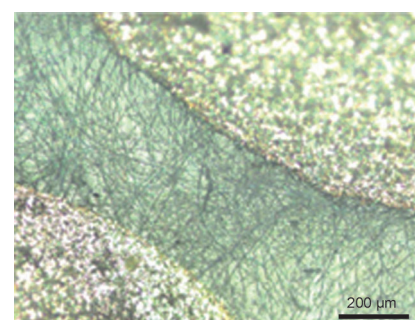


Proton Conductivity (2)

N. Johnson, H. Ji* ——— 10457 – 10458

Reply: High Proton Conductivity of Water
Channels in a Highly Ordered Nanowire

Nanowires of trimesic acid and melamine are shown to be proton conductive, however the magnitude of conductivity is highly dependent on the quality of the nanowire, sample preparation, and measurement conditions. These problems need to be addressed in order to obtain reproducible results for practical use of this new family of proton-conductive materials.



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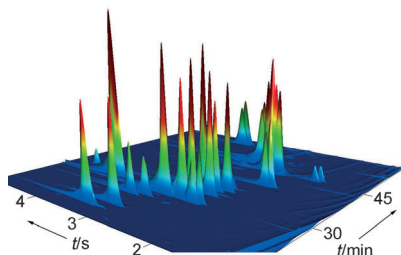
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Minireviews

Gas Chromatography

C. Meinert,
U. J. Meierhenrich* — 10460–10470

A New Dimension in Separation Science:
Comprehensive Two-Dimensional Gas
Chromatography



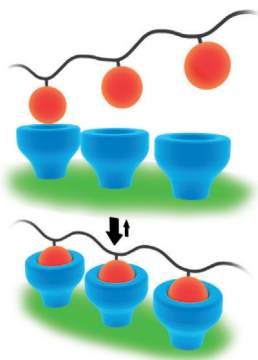
Dimension jump: The ability to obtain multidimensional chromatograms by passing analytes over two different stationary phases connected by a modulator led to the invention of comprehensive gas chromatography. The increased resolution offered by GC×GC techniques (see picture) compared to that of traditional GC is useful for multiple applications, including the resolution of enantiomers.

Reviews

Multivalency

C. Fasting, C. A. Schalley, M. Weber,
O. Seitz, S. Hecht, B. Koks, J. Dornedde,
C. Graf, E.-W. Knapp,
R. Haag* — 10472–10498

Multivalency as a Chemical Organization
and Action Principle



Unified strength: Multivalent structures function in a number of biological systems to generate a strong but reversible interaction between two objects. The chemical realization of this natural principle with organized multiple interactions enables, for example, the development of multivalent drugs for an effective inhibition of viral cell attachment.

Front Cover

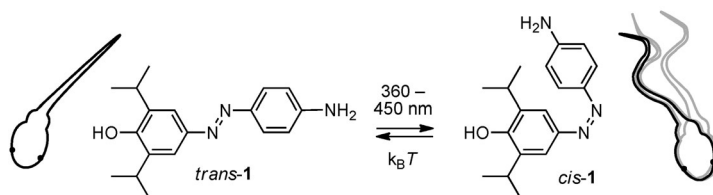


Communications

Photopharmacology

M. Stein, S. J. Middendorp, V. Carta,
E. Pejo, D. E. Raines, S. A. Forman,
E. Sigel,* D. Trauner* — 10500–10504

Azo-Propofols: Photochromic
Potentiators of GABA_A Receptors



Shine and rise! GABA_A receptors are ligand-gated chloride ion channels that respond to γ -aminobutyric acid (GABA), which is the major inhibitory neurotransmitter of the mammalian central nervous system. Azobenzene derivatives of propofol, such as compound **1** (see scheme),

increase GABA-induced currents in the dark form and lose this property upon light exposure and thus function as photochromic potentiators. Compound **1** can be employed as a light-dependent general anesthetic in translucent tadpoles.

Frontispiece



The German Chemical Society (GDCh) invites you to:



Angewandte Anniversary Symposium

GDCh
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Tuesday, March 12, 2013

Henry Ford Building / FU Berlin

Speakers



Carolyn R.
Bertozzi



François
Diederich



Alois
Fürstner



Roald Hoffmann
(Nobel Prize 1981)



Susumu
Kitagawa



Jean-Marie Lehn
(Nobel Prize 1987)



E.W. "Bert"
Meijer



Frank
Schirrmacher
(Publisher, FAZ)



Robert
Schlögl



George M.
Whitesides



Ahmed Zewail
(Nobel Prize 1999)

More information:

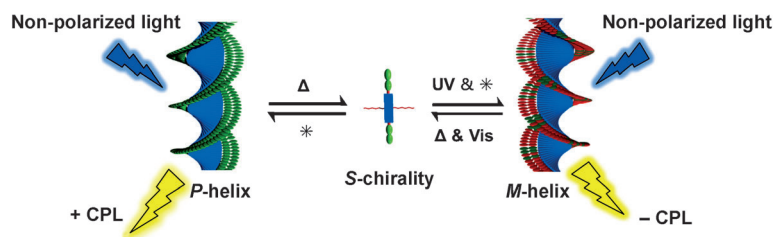


angewandte.org/symposium



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Spiraling into control: A photoresponsive supramolecular assembly demonstrates that light, along with heating (Δ) and cooling (*), can cause chiral communication between molecules. This effect

leads to bias in the helicity of the complex, causing a reversible switching of macroscopic handedness, as shown by a reversal of sign of the circularly polarized luminescence (CPL) that is emitted.

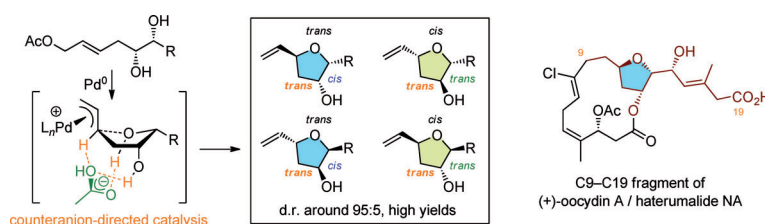
Photoswitchable Helicity

A. Gopal, M. Hifsudheen, S. Furumi, M. Takeuchi, A. Ajayaghosh* — 10505 – 10509

Thermally Assisted Photonic Inversion of Supramolecular Handedness



Inside Cover



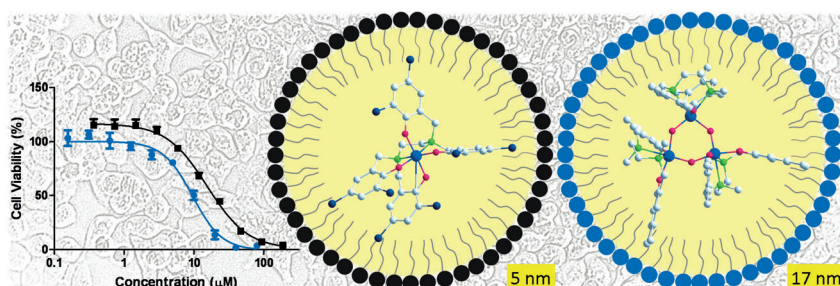
Hydrogen bonds can play a prominent role in organometallic catalysis, as shown for the title reaction, in which a counteranion directs the cyclization through the formation of hydrogen bonds that likely involve a proton of the π -allyl/palladium

species itself. The reaction allows access to four out of the eight stereoisomers of 2,5-disubstituted 3-hydroxy-tetrahydrofurans and thus fragments of complex natural products.

Stereoselective Catalysis

M. Arthuis, R. Beaud, V. Gandon,* E. Roulland* — 10510 – 10514

Counteranion-Directed Catalysis in the Tsuji–Trost Reaction: Stereocontrolled Access to 2,5-Disubstituted 3-Hydroxy-Tetrahydrofurans



A nanoformulated trinuclear hydrolysis product of a bis(alkoxo) salan–Ti^{IV} complex shows high antitumor activity (see picture), which identifies it as an active species in cells. Additional highly stable

mononuclear derivatives also show high activity, when formulated into nanoparticles, thus evincing that biologically friendly Ti^{IV} can provide high cytotoxicity with controlled biological function.

Drug Discovery

S. Meker, K. Margulis-Goshen, E. Weiss, S. Magdassi,* E. Y. Tshuva* — 10515 – 10517

High Antitumor Activity of Highly Resistant Salan–Titanium(IV) Complexes in Nanoparticles: An Identified Active Species



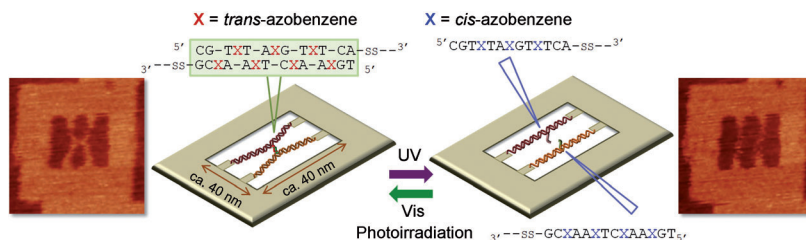
Back Cover

Single-Molecule Imaging

M. Endo,* Y. Yang, Y. Suzuki, K. Hidaka,
H. Sugiyama* — 10518–10522



Single-Molecule Visualization of the Hybridization and Dissociation of Photoresponsive Oligonucleotides and Their Reversible Switching Behavior in a DNA Nanostructure

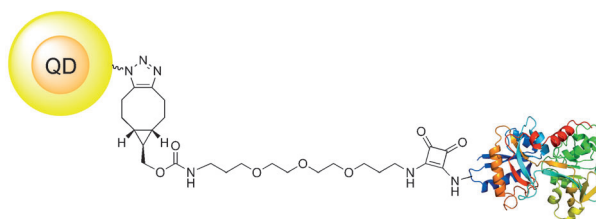


A framed photo of DNA: A pair of photoresponsive oligonucleotides containing azobenzene moieties was introduced into double-stranded DNA within the cavity of a DNA nanostructure (see scheme). The

two dsDNAs, in contact at the center, were dissociated using UV irradiation and hybridized with visible light; this was directly observed using high-speed atomic force microscopy.

Quantum Dot Biolabeling

C. Schieber,* A. Bestetti, J. P. Lim,
A. D. Ryan, T.-L. Nguyen, R. Eldridge,
A. R. White, P. A. Gleeson,
P. S. Donnelly,* S. J. Williams,*
P. Mulvaney* — 10523–10527



Conjugation of Transferrin to Azide-Modified CdSe/ZnS Core-Shell Quantum Dots using Cyclooctyne Click Chemistry

Twinkle twinkle quantum dot: Conjugation of biomolecules to azide-modified quantum dots (QDs) through a bifunctional linker, using strain-promoted azide-alkyne cycloaddition with the QD

and a squaramide linkage to the biomolecule (see scheme). Transferrin-conjugated QDs were internalized by transferrin-receptor expressing HeLa cells.

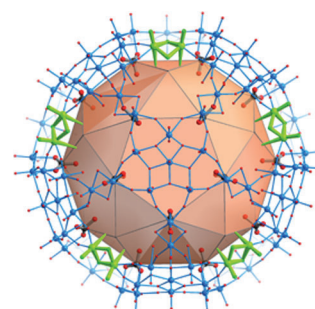
CO₂ Fixation

S. Garai, E. T. K. Haupt,* H. Bögge,
A. Merca, A. Müller* — 10528–10531



Picking up 30 CO₂ Molecules by a Porous Metal Oxide Capsule Based on the Same Number of Receptors

30 receptors in waiting position: In the porous (pentagon)₁₂(linker)₃₀-type molybdenum oxide capsule (see picture), the 30 positively charged linkers (five unsaturated shown for illustration in green, the others contain CO₃²⁻ ligands) can act as receptors for neutral and negatively charged ligands. Bubbling CO₂ into the solution containing the acetate-type capsules leads to the upload of CO₂ based on 30 coordinated CO₃²⁻ ligands.

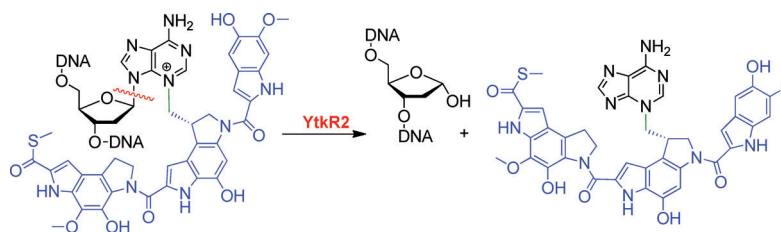


Antibiotic Resistance

H. Xu, W. Huang, Q.-L. He, Z.-X. Zhao,
F. Zhang, R. Wang, J. Kang,
G.-L. Tang* — 10532–10536

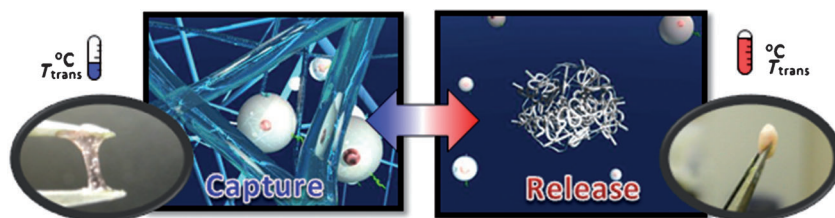


Self-Resistance to an Antitumor Antibiotic: A DNA Glycosylase Triggers the Base-Excision Repair System in Yatakemycin Biosynthesis



Resistance is (not) futile: The yatakemycin biosynthetic gene cluster involves the *ytkR2* gene, which encodes a protein with homology to a recently discovered bacterial DNA glycosylase. Genetic validation

in vivo, biochemical assays, and in vitro mutagenesis studies revealed that YtkR2 confers resistance for the bacteria by specifically recognizing and cleaving the YTM-modified base (see scheme).



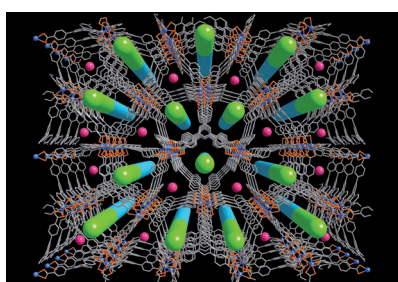
Caught in a web: Photo-cross-linkable temperature-responsive polymer-based nanofiber webs have been synthesized that have the ability to capture, encapsulate, and release cells by dynamically

transforming the fibrous structure into hydrogel-like structures by wrapping, swelling, and deswelling processes in response to external temperature changes (see picture).

Smart Materials

Y.-J. Kim, M. Ebara,
T. Aoyagi* 10537 – 10541

A Smart Nanofiber Web That Captures and Releases Cells

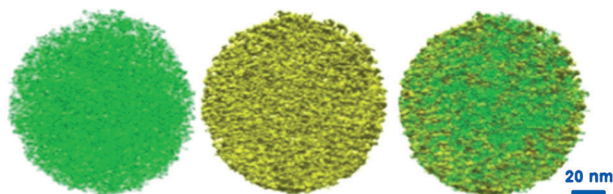


Frequency doubling: A strategy for incorporating dipolar organic chromophores into the one-dimensional channels of an anionic metal–organic framework (MOF) has been developed to generate highly active nonlinear optical materials (see picture). The resulting MOF material shows a second-harmonic generation intensity of 18.3 versus α quartz.

Metal–Organic Frameworks

J. C. Yu, Y. J. Cui,* C. D. Wu, Y. Yang,
Z. Y. Wang, M. O’Keeffe, B. Chen,*
G. D. Qian* 10542 – 10545

Second-Order Nonlinear Optical Activity Induced by Ordered Dipolar Chromophores Confined in the Pores of an Anionic Metal–Organic Framework



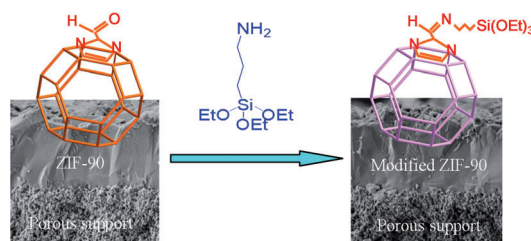
From droplets to “spheres”: A platform technology enables the rapid and continuous synthesis of mesoporous metal and metal alloy particles (see picture). The

confined growth of nanocrystals in aerosol droplets leads to the formation of these particles with defined composition.

Nanocrystal Networks

X. F. Xiao, H. Sohn, Z. Chen, D. Toso,
M. Mechlenburg, Z. H. Zhou, E. Poirier,
A. Dailly, H. Wang, Z. Wu,* M. Cai,*
Y. Lu* 10546 – 10550

Mesoporous Metal and Metal Alloy Particles Synthesized by Aerosol-Assisted Confined Growth of Nanocrystals



A clear separation: A post-synthetic functionalization method is reported to obtain a highly permselective zeolitic imidazolate framework (ZIF-90) membrane. The

intercrystalline defects of the ZIF-90 membrane are minimized to enhance the separation selectivity while a high permeance is maintained.

Metal–Organic Frameworks

A. Huang,* N. Wang, C. Kong,
J. Caro* 10551 – 10555

Organosilica-Functionalized Zeolitic Imidazolate Framework ZIF-90 Membrane with High Gas-Separation Performance



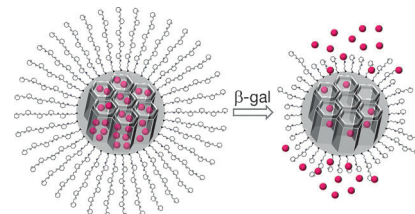
Drug-Carrying Nanoparticles

A. Agostini, L. Mondragón, A. Bernardos, R. Martínez-Mañez,* M. D. Marcos, F. Sancenón, J. Soto, A. Costero, C. Manguan-García, R. Perona,* M. Moreno-Torres, R. Aparicio-Sanchis, J. R. Murguía* — 10556 – 10560



Targeted Cargo Delivery in Senescent Cells Using Capped Mesoporous Silica Nanoparticles

Learning to let go with age: Intracellular controlled release of molecules within senescent cells was achieved using mesoporous silica nanoparticles (MSNs) capped with a galacto-oligosaccharide (GOS) to contain the cargo molecules (magenta spheres; see scheme). The GOS is a substrate of the senescent biomarker, senescence-associated β -galactosidase (SA- β -gal), and releases the cargo upon entry into SA- β -gal expressing cells.

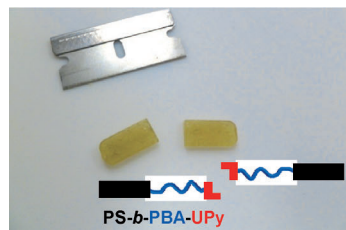


Materials Science

J. Hentschel, A. M. Kushner, J. Ziller, Z. Guan* — 10561 – 10565



Self-Healing Supramolecular Block Copolymers



self-heal
damage



Polymer, heal thyself! Supramolecular ABA triblock copolymers formed by dimerization of 2-ureido-4-pyrimidinone (UPy) end-functionalized polystyrene-*b*-poly(*n*-butyl acrylate) (PS-*b*-PBA) AB diblock copolymers have been synthe-

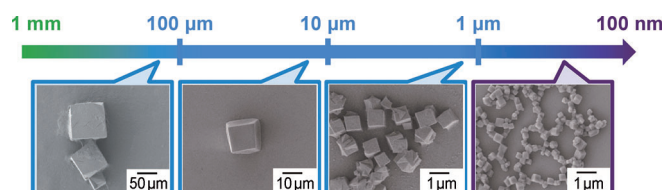
sized, resulting in a self-healing material that combines the advantageous mechanical properties of thermoplastic elastomers and the dynamic self-healing features of supramolecular materials.

Gel Nanocubes

Y. Furukawa, T. Ishiwata, K. Sugikawa, K. Kokado, K. Sada* — 10566 – 10569



Nano- and Microsized Cubic Gel Particles from Cyclodextrin Metal–Organic Frameworks



Sweet cube o' mine: Bottom-up control of gel particles has been regarded as a great challenge. By employing internal cross-linking of cyclodextrin metal–organic frameworks, cubic sugar gels were formed

with sharp edges that reflect the shape of the crystals. This enabled the fabrication of shape- and size-controlled polymer gels from porous crystals (see picture).

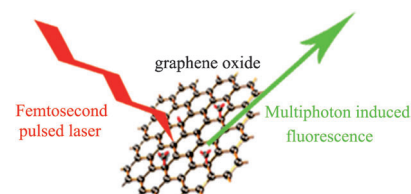
Bionanotechnology

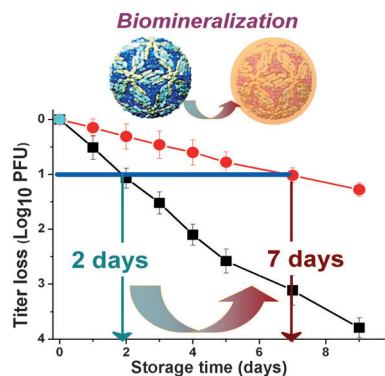
J. Qian, D. Wang, F. H. Cai, W. Xi, L. Peng, Z. F. Zhu, H. He, M. L. Hu, S. He* — 10570 – 10575



Observation of Multiphoton-Induced Fluorescence from Graphene Oxide Nanoparticles and Applications in In Vivo Functional Bioimaging

Lightening organelles: A femtosecond laser can excite multiphoton-induced luminescence of graphene oxide nanoparticles. The flow, distributions, and clearance of intravenously injected GO-PEG nanoparticles in the blood vessel of mice could be observed clearly by two-photon imaging. The 3D distribution of microinjected GO-PEG nanoparticles in a mice brain could also be reconstructed with two-photon microscopy.



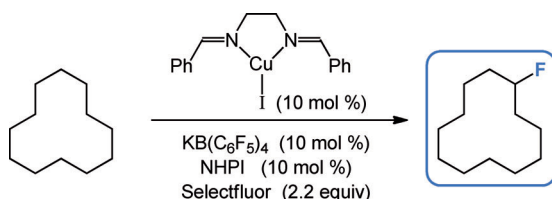


We're not gonna bake it: In situ biomineralization creates an egg-like shell on vaccine particles to improve their thermostability. Different from the bare vaccine (squares), the biomineralized vaccine (red circles) can be stored at ambient temperature without refrigeration for up to a week and retain biological activity both in vitro (see graph), as well as in a mouse model.

Vaccine Stabilization

G. Wang, X. Li, L. Mo, Z. Song, W. Chen, Y. Deng, H. Zhao, E. Qin, C. Qin,* R. Tang* ————— **10576–10579**

Eggshell-Inspired Biomineralization Generates Vaccines that Do Not Require Refrigeration



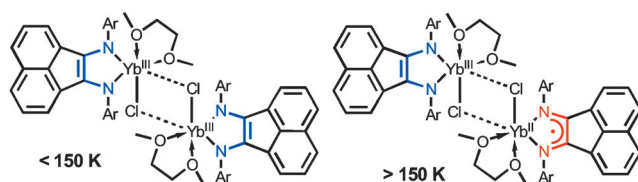
A group effort: Reported is the title reaction using a polycomponent catalytic system involving commercially available Selectfluor, a putative radical precursor *N*-hydroxyphthalimide, an anionic phase-transfer catalyst ($\text{KB}(\text{C}_6\text{F}_5)_4$), and a cop-

per(I) bis(imine). The catalyst system formed leads to monofluorinated compounds selectively (see example) without the necessity for an excess of the alkane substrate.

Synthetic Methods

S. Bloom, C. R. Pitts, D. C. Miller, N. Haselton, M. G. Holl, E. Urheim, T. Lectka* ————— **10580–10583**

A Polycomponent Metal-Catalyzed Aliphatic, Allylic, and Benzylic Fluorination



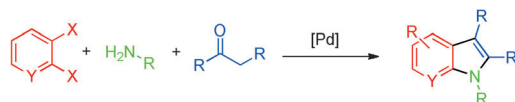
Redox isomerism is observed for a lanthanide complex for the first time. Upon lowering the temperature, an electron of $[(\text{dpp-bian})\text{Yb}(\mu\text{-Cl})(\text{dme})_2]_2$ (**1**) is transferred from the metal to the ligand (see picture), giving rise to marked shortening

of Yb–N bonds and a hysteric jump in the magnetic moment. The crystal packing is of a crucial importance, as two other crystal modifications of **1** do not undergo this effect.

Rare Earths

I. L. Fedushkin,* O. V. Maslova, A. G. Morozov, S. Dechert, S. Demeshko, F. Meyer* ————— **10584–10587**

Genuine Redox Isomerism in a Rare-Earth-Metal Complex



Highly substituted indoles were synthesized by a palladium-catalyzed reaction involving three independent components in a one-pot reaction. Two distinct palladium-catalyzed coupling reactions occur

with a single catalytic system: a Buchwald-Hartwig reaction and an arene-alkene coupling. Quantum chemical computations provide insight into the mechanism of the latter coupling step.

Indole Synthesis

J. M. Knapp, J. S. Zhu, D. J. Tantillo, M. J. Kurth* ————— **10588–10591**

Multicomponent Assembly of Highly Substituted Indoles by Dual Palladium-Catalyzed Coupling Reactions

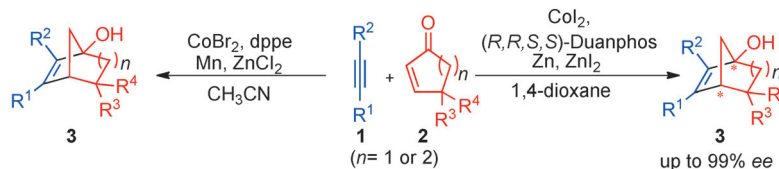


Asymmetric Synthesis

C.-H. Wei, S. Mannathan,
C.-H. Cheng* 10592–10595



Regio- and Enantioselective Cobalt-Catalyzed Reductive [3+2] Cycloaddition Reaction of Alkynes with Cyclic Enones: A Route to Bicyclic Tertiary Alcohols



Round and round: An unusual cobalt-catalyzed regio- and enantioselective reductive [3+2] cycloaddition of cyclic enones with alkynes affording bicyclic

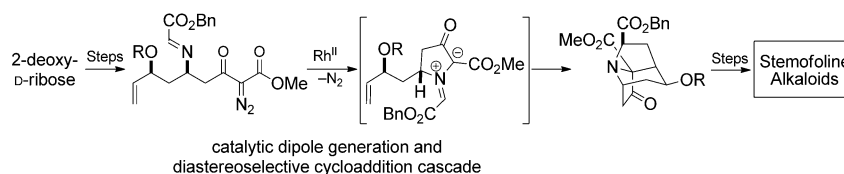
tertiary alcohols is described. A possible mechanism involving the formation of a cobaltacyclopentene intermediate is proposed.

Natural Product Synthesis

C. Fang, C. S. Shanahan, D. H. Paull,
S. F. Martin* 10596–10599



Enantioselective Formal Total Syntheses of Didehydrostemofoline and Isodidehydrostemofoline through a Catalytic Dipolar Cycloaddition Cascade



Sweet to the core: Enantioselective formal total syntheses of the title compounds were accomplished in 24 steps from 2-deoxy-D-ribose. The synthesis features a novel cascade of reactions culminating

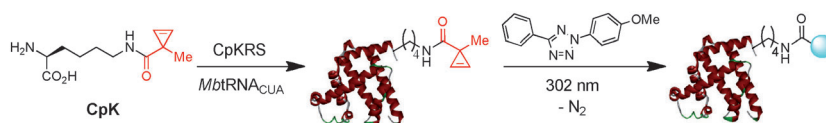
in an intramolecular dipolar cycloaddition to form the tricyclic core of the stemofoline alkaloids from an acyclic diazo imine intermediate.

Bioorthogonal Chemistry

Z. Yu, Y. Pan, Z. Wang, J. Wang,*
Q. Lin* 10600–10604



Genetically Encoded Cyclopropene Directs Rapid, Photoclick-Chemistry-Mediated Protein Labeling in Mammalian Cells



We just click: Genetic incorporation of a cyclopropene amino acid CpK (see scheme) site-specifically into proteins in *E. coli* and mammalian cells was achieved using an orthogonal aminoacyl-tRNA

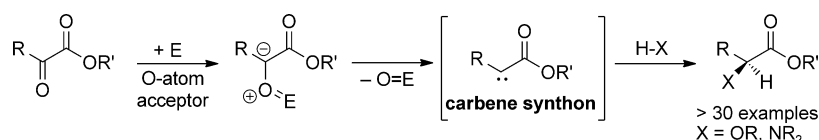
synthetase/tRNA_{CUA} pair (CpKRS/MbtRNA_{CUA}). Cyclopropene exhibited fast reaction kinetics in the photoclick reaction and allowed rapid (ca. 2 min) labeling of proteins.

Carbenoids

E. J. Miller, W. Zhao, J. D. Herr,
A. T. Radosevich* 10605–10609

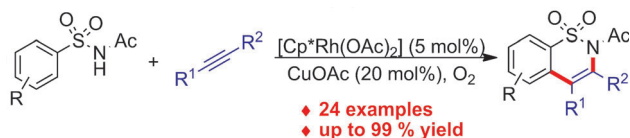


A Nonmetal Approach to α -Heterofunctionalized Carbonyl Derivatives by Formal Reductive X–H Insertion



Keeping it organic: A direct synthesis of α -alkoxy and α -amino ester derivatives by direct reductive coupling of widely available, stable α -keto esters and protic pronucleophiles is described (see

scheme; X = OR, NR₂). The method serves as a convenient nonmetal alternative to X–H insertion by diazo decomposition.



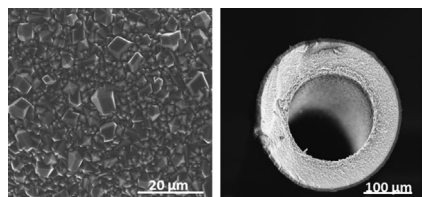
Director's cut: The pharmaceutically relevant sulfonamide group is shown to be a competent directing group for $[\text{Cp}^*\text{Rh}(\text{OAc})_2]$ -catalyzed C–H functionalizations. Reactions of the cyclometalated intermediate with internal alkynes provide

access to a wide range of sultam derivatives. The reaction is high yielding and works best under aerobic conditions with catalytic amounts of CuOAc as an oxidation mediator. $\text{Cp}^* = \text{C}_5\text{Me}_5$.

Homogenous Catalysis

M. V. Pham, B. Ye,
N. Cramer* 10610–10614

Access to Sultams by Rhodium(III)-Catalyzed Directed C–H Activation

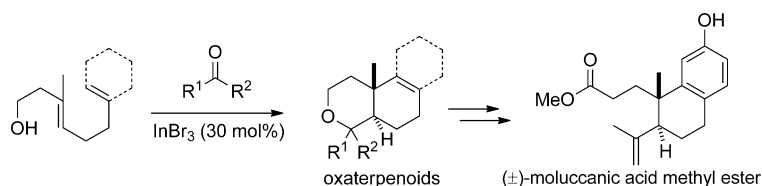


Headed for a membrane: Continuous, polycrystalline ZIF-90 membranes (picture, left) can be grown at 65 °C from methanolic precursor solutions on nano-crystal-seeded surfaces of poly(amide-imide) macroporous hollow fibers (right). The ZIF-90 membranes exhibit good separation properties for linear over cyclic hydrocarbons, as well as gas permeation selectivities higher than Knudsen values.

Membrane Fabrication

A. J. Brown, J. R. Johnson, M. E. Lydon,
W. J. Koros, C. W. Jones,
S. Nair* 10615–10618

Continuous Polycrystalline Zeolitic Imidazolate Framework-90 Membranes on Polymeric Hollow Fibers



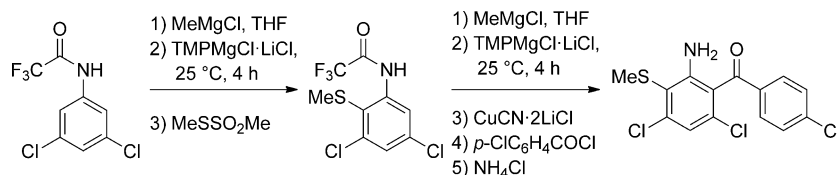
Cascades: An InBr_3 -catalyzed intermolecular polyene cyclization initiated by a Prins reaction provides a concise approach to 3-oxaterpenoid derivatives. The reaction is compatible with various aldehydes, ketones, and polyolefin–alcohol sub-

strates. In addition, the total synthesis of (±)-moluccanic acid methyl ester was achieved in seven steps by using such a Prins–polyene cyclization as the key step.

Synthetic Methods

B. Li, Y. C. Lai, Y. Zhao, Y. H. Wong,
Z. L. Shen, T. P. Loh* 10619–10623

Synthesis of 3-Oxaterpenoids and Its Application in the Total Synthesis of (±)-Moluccanic Acid Methyl Ester



A practical *ortho*, *meta*, (or even *ortho*, *ortho'*) magnesiation of trifluoroacetamides of anilines, aminopyridines, and aminopyrazines at room temperature was performed with $\text{TMPMgCl} \cdot \text{LiCl}$ or

$\text{TMP}_2\text{Mg} \cdot 2\text{LiCl}$. These magnesiations are compatible with several carbonyl functionalities and allow access to polysubstituted anilides in satisfactory yields.

Synthetic Methods

G. Monzón, I. Tirota,
P. Knochel* 10624–10627

The *ortho* and *meta* Magnesiation of Functionalized Anilines and Amino-Substituted Pyridines and Pyrazines at Room Temperature

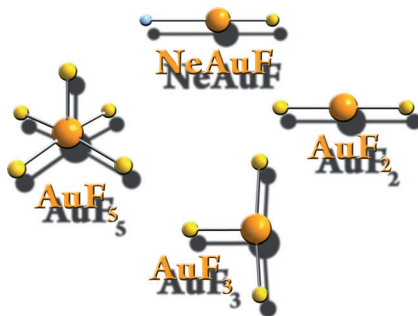


Gold Fluorides

X. Wang, L. Andrews, K. Willmann,
F. Brosi, S. Riedel* — 10628–10632



Investigation of Gold Fluorides and Noble
Gas Complexes by Matrix-Isolation
Spectroscopy and Quantum-Chemical
Calculations



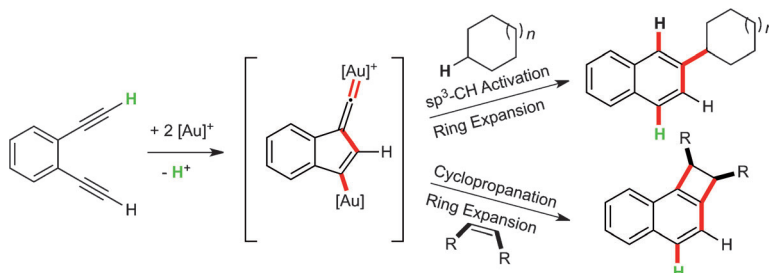
Noble with a difference: Matrix-isolation experiments and quantum-chemical calculations have led to the characterization of two new compounds, namely first open-shell binary gold fluoride, AuF_2 , and a NeAuF complex. Moreover, ArAuF , AuF_3 , Au_2F_6 , and monomeric AuF_5 have been produced and identified under cryogenic conditions in neon and argon matrices.

Dual Activation

A. S. K. Hashmi,* M. Wieteck, I. Braun,
M. Rudolph, F. Rominger — 10633–10637



Gold Vinylidene Complexes:
Intermolecular $\text{C}(\text{sp}^3)\text{--H}$ Insertions and
Cyclopropanations Pathways



Highly reactive gold vinylidene species are used for intermolecular $\text{C}(\text{sp}^3)\text{--H}$ insertions into unactivated alkanes (see scheme). In addition, they can be regarded as synthons for alkylidene car-

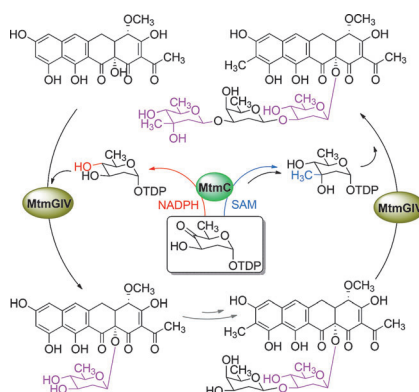
benes. Initiated by cyclopropanation of the vinylidene species/alkylidene carbenoid, cyclobutene derivatives are formed in a diastereoselective fashion by a ring-enlargement cascade in only one step.

Biosynthesis

G. Wang, P. Pahari, M. K. Kharel, J. Chen,
H. Zhu, S. G. Van Lanen,
J. Rohr* — 10638–10642



Cooperation of Two Bifunctional Enzymes
in the Biosynthesis and Attachment of
Deoxysugars of the Antitumor Antibiotic
Mithramycin



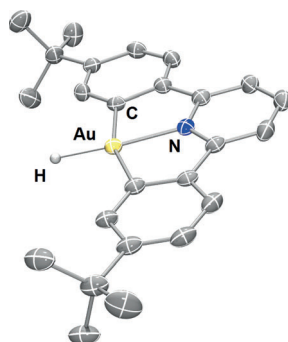
Two bifunctional enzymes cooperate in the assembly and the positioning of two sugars, D-olivose and D-mycarose, of the anticancer antibiotic mithramycin. MtmC finishes the biosynthesis of both sugar building blocks depending on which MtmGIV activity is supported. MtmGIV transfers these two sugars onto two structurally distinct acceptor substrates. The dual function of these enzymes explains two essential but previously unidentified activities.

Gold(III) Hydrides

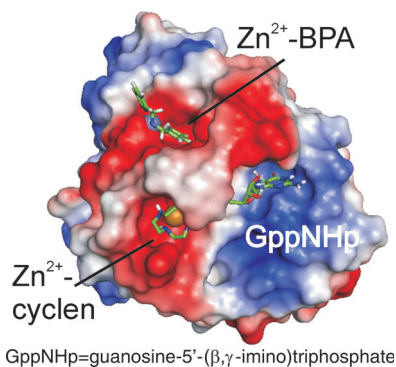
D.-A. Roşca, D. A. Smith, D. L. Hughes,
M. Bochmann* — 10643–10646



A Thermally Stable Gold(III) Hydride:
Synthesis, Reactivity, and Reductive
Condensation as a Route to Gold(II)
Complexes



Going for gold: The first thermally stable gold(III) hydride $[(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})\text{AuH}]$ is presented. It undergoes regioselective insertions with allenes to give gold(III) vinyl complexes, and reductive condensation with $[(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})\text{AuOH}]$ to the air-stable Au^{II} product, $[(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})_2\text{Au}_2]$, with a short nonbridged gold–gold bond.

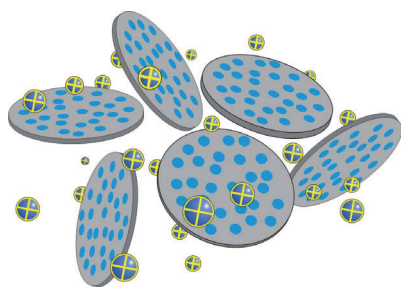


Allosteric interactions: Metal(II) cyclens inhibit Ras–effector interactions by stabilizing a weak effector-binding state of Ras, state 1(T), and binding directly in the active site. The novel state (1T) inhibitor Zn^{2+} –BPA (BPA = bis(2-picoly)amine) binds outside the nucleotide binding pocket but nevertheless allosterically stabilizes state 1(T) and thus inhibits the Ras–Raf interaction.

Inhibitors

I. C. Rosnizeck, M. Spoerner, T. Harsch, S. Kreitner, D. Filchinski, C. Herrmann, D. Engel, B. König, H. R. Kalbitzer* — 10647 – 10651

Metal–Bis(2-picoly)amine Complexes as State 1(T) Inhibitors of Activated Ras Protein



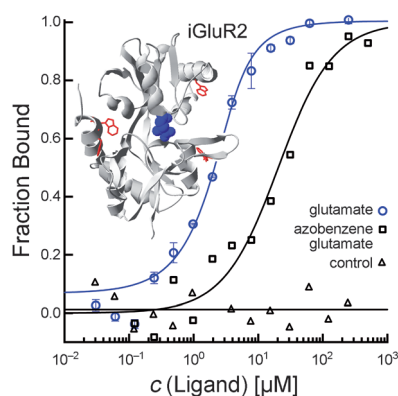
The neutral organic dye indigo forms an inorganic–organic hybrid material with nanoclays (see picture; blue circles on disks symbolizing indigo, spheres indicating liberated cations) and can thus be transferred into aqueous solution. Solids recovered from these solutions resemble the ancient Maya Blue pigment. The method can also be applied to other hydrophobic species and may open the gate for novel solution chemistry, including photonic and catalytic applications.

Water Solubilized Indigo

M. M. Lezhnina, T. Grewe, H. Stoeher, U. Kynast* — 10652 – 10655

Laponite Blue: Dissolving the Insoluble

Inside Back Cover



Look, no label! Microscale thermophoresis makes use of the intrinsic fluorescence of proteins to quantify the binding affinities of ligands and discriminate between binding sites. This method is suitable for studying binding interactions of very small amounts of protein in solution. The binding of ligands to iGluR membrane receptors, small-molecule inhibitors to kinase p38, aptamers to thrombin, and Ca^{2+} ions to synaptotagmin was quantified.

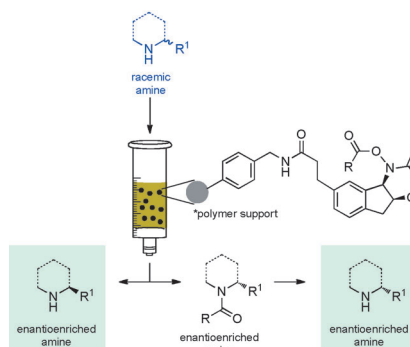
Protein–Ligand Interactions

S. A. I. Seidel, C. J. Wienken, S. Geissler, M. Jerabek-Willemsen, S. Duhr, A. Reiter, D. Trauner, D. Braun, P. Baaske* — 10656 – 10659

Label-Free Microscale Thermophoresis Discriminates Sites and Affinity of Protein–Ligand Binding



Shake it up baby! Simply shaking a polymer-supported reagent and the racemic amine at room temperature kinetically resolves a broad range of N-heterocycles with good selectivity. The polymer-supported reagents are robust, easy to regenerate, and can be reused dozens of times. Cleavable acyl groups can be used to give access to both amine enantiomers in a single resolution.



Enantioenriched Amines

I. Kreituss, Y. Murakami, M. Binanzer, J. W. Bode* — 10660 – 10663

Kinetic Resolution of Nitrogen Heterocycles with a Reusable Polymer-Supported Reagent

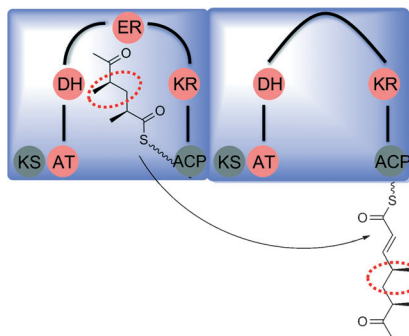


Combinatorial Biosynthesis

S. Kushnir, U. Sundermann, S. Yahiaoui,
A. Brockmeyer, P. Janning,
F. Schulz* ————— **10664–10669**



Minimally Invasive Mutagenesis Gives
Rise to a Biosynthetic Polyketide Library



Not in the public domain: Site-directed mutagenesis of megasynthases was the key to the generation of a library of polyketides in bacteria. Redox derivatizations are used to change the bioactivity profile of the compounds.



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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Angewandte Corrigendum

Formal Asymmetric Synthesis of
Echinopine A and B

P. A. Peixoto, R. Severin, C.-C. Tseng,
D. Y.-K. Chen* ————— **3013–3016**

Angew. Chem. Int. Ed. **2011**, 50

DOI: 10.1002/anie.201008000

The authors of this communication wish to cite additional publications as reference [4b–f]. The complete reference [4] is shown below.

- [4] a) V. Michelet, P. Y. Toullec, J.-P. Genet, *Angew. Chem.* **2008**, 120, 4338–4386; *Angew. Chem. Int. Ed.* **2008**, 47, 4268–4315. For pioneering studies in palladium-mediated enyne cycloisomerizations and subsequent cycloadditions, see: b) B. M. Trost, M. Lautens, *J. Am. Chem. Soc.* **1985**, 107, 1781–1783; c) B. M. Trost, J. Y. L. Chung, *J. Am. Chem. Soc.* **1985**, 107, 4586–4588; d) B. M. Trost, D. T. MacPherson, *J. Am. Chem. Soc.* **1987**, 109, 3483–3484; e) B. M. Trost, G. J. Tanoury, M. Lautens, C. Chan, D. T. MacPherson, *J. Am. Chem. Soc.* **1989**, 116, 4255–4267; f) B. M. Trost, P. A. Hipskind, J. Y. L. Chung, C. Chan, *Angew. Chem.* **1989**, 101, 1559–1561; *Angew. Chem. Int. Ed. Engl.* **1989**, 28, 1502–1504.

Polarization Rotation in the Monoclinic
Perovskite $\text{BiCo}_{1-x}\text{Fe}_x\text{O}_3$

K. Oka,* T. Koyama, T. Ozaaki, S. Mori,
Y. Shimakawa, M. Azuma — **7977–7980**

Angew. Chem. Int. Ed. **2012**, 51

DOI: 10.1002/anie.201202644

The wrong tilting angles of polarization vector were shown in this Communication. The polarization tilts in the same direction to the monoclinic distortion, and the correct tilting angles are -2° for $x = 0.63$, 12° for $x = 0.70$, and 15° for $x = 0.72$ from $[001]_m$ direction, corresponding to -1° for $x = 0.63$, 13° for $x = 0.70$, and 17° for $x = 0.72$ from $[001]_c$ direction. Figure 5 is accordingly corrected. The authors apologize for this mistake and any inconvenience it may have caused.

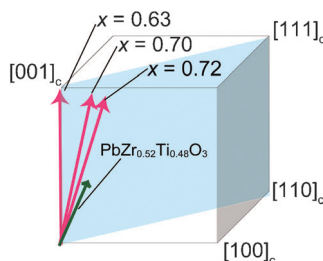


Figure 5. The polarization vectors of the monoclinic C_m phase of $\text{BiCo}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0.63, 0.70$, and 0.72) at 300 K and $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ at 20 K.^[2b] The indices $[001]_c$, $[100]_c$, $[110]_c$, and $[111]_c$ are based on the pseudo cubic unit cell.

Angewandte Addition

The authors of this communication wish to add the following sentence to their acknowledgement:

“V.G. acknowledges the support of DOE grant DE-SC0002040.”

C–H Activation in S-Alkenyl
Sulfoximines: An Endo 1,5-Hydrogen
Migration

X. Gao, V. Gaddam, E. Altenhofer,
R. R. Tata, Z. Cai, N. Yongpruksa,
A. K. Garimallaprabhakaran,
M. Harmata* _____ **7016–7019**

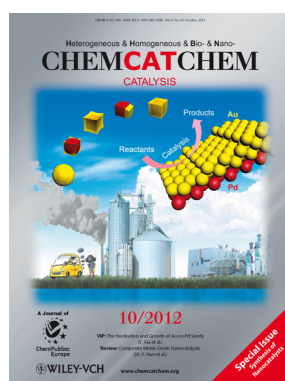
Angew. Chem. Int. Ed. **2012**, *51*

DOI: 10.1002/anie.201203258

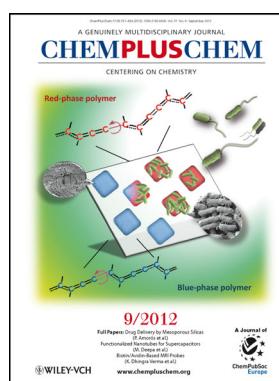
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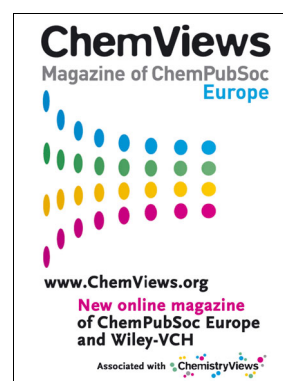
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