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. Lewis, M. Faubel, B. Winter, J. C. Hemminger**
CO_2 Capture in an Aqueous Solution of an Amine: Role of the Solution Interface

*Y. H. Kim, S. Banta**
Complete Oxidation of Methanol in an Enzymatic Biofuel Cell by a Self-Assembling Hydrogel Created from Three Modified Dehydrogenases

R. M. Culik, A. L. Serrano, M. R. Bunagan, F. Gai**
Achieving Secondary Structural Resolution in Kinetic Measurements of Protein Folding: A Case Study of the Folding Mechanism of Trp-cage

L. P. Hansen, Q. M. Ramasse, C. Kisielowski, M. Brorson, E. Johnson, H. Topsøe, S. Helveg
Atomic-Scale Edge Structures on Industrial MoS_2 Nanocatalysts

*C. Pirez, M. Capron, H. Jobic, F. Dumeignil, L. Jalowiecki-Duhamel**
Highly Efficient and Stable $CeNiH_ZO_Y$ Nano-oxyhydride Catalyst for H_2 Production from Ethanol at Room Temperature

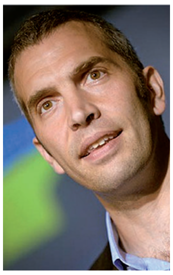
*X. Xin, M. He, W. Han, J. Jung, Z. Lin**
Low-Cost Counter Electrodes for High-Efficiency Dye-Sensitized Solar Cells

Author Profile

"What I look for first in a publication is a new idea. If I were not a scientist, I would be a drummer in a struggling jazz band...."
This and more about Eric T. Kool can be found on page 9532.

News

E. F. Aziz



B. G. Davis

Z.-J. Shi

R. S. Langer

A.-V. Mudring

Obituaries

Jürgen Sauer (1931–2011)

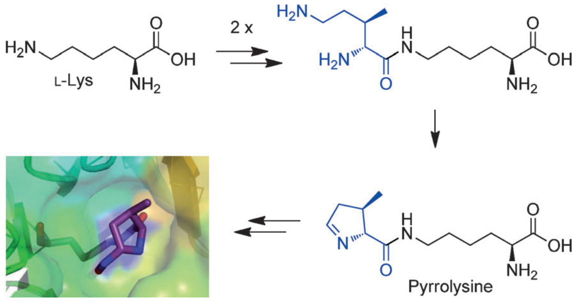
Books

Highlights

Rare Amino Acids

C. Hertweck* ______________ **9540 – 9541**

Biosynthesis and Charging of Pyrrolysine, the 22nd Genetically Encoded Amino Acid

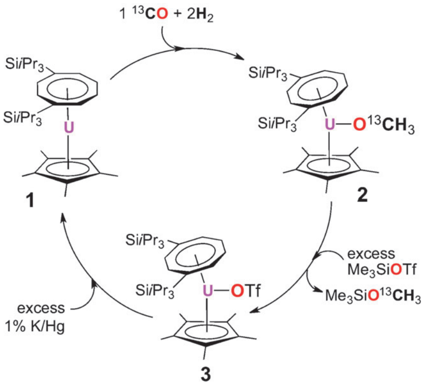


Two become one: Pyrrolysine, a critical component of several methyltransferases in archaebacteria, is the latest addition to the inventory of genetically encoded amino acids. Studies at the genetic, biochemical, and chemical levels have now revealed that this rare amino acid is assembled from two lysine units via an unusual ε-dipeptide, and is then charged by a designated translational machinery.

CO Hydrogenation

O. P. Lam, K. Meyer* ________ **9542 – 9544**

Hydrogenation of CO at a Uranium(III) Center



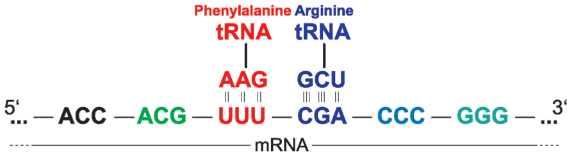
Mining the reactivity of uranium: Current highlights in the uranium-mediated reactions of CO include reductive coupling, CO homologation, and, most recently, the remarkable hydrogenation of CO to methanolate by the U^{III} mixed-sandwich complex **1**. The theoretical catalytic cycle proceeds through the hydrogenation of ^{13}CO to give the methanolate complex **2**, which upon treatment with Me_3SiOTf, releases $Me_3SiO^{13}CH_3$ and the uranium triflate **3**, which in turn can be reduced with K/Hg to regenerate **1** (see scheme).

Essays

History of Science

V. A. Erdmann,*
J. Barciszewski ______________ **9546 – 9552**

2011: 50th Anniversary of the Discovery of the Genetic Code



On May 27, 1961 Nirenberg and Matthaei performed an in vitro translation experiment in which bacterial ribosomes were supplemented with a fraction of low-molecular-weight RNAs; they demonstrated that polyuridilic acid codes for polyphenylalanine—the first information on the genetic code. This Essay recalls the major achievements prior to the discovery of the genetic code, the experiments leading to its identification, and the developments in the field of molecular biology thereafter.

For the USA and Canada:
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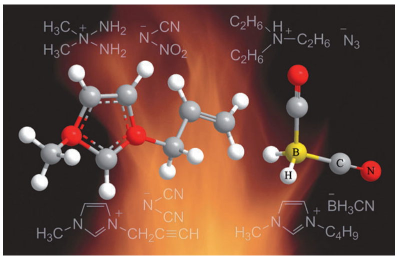
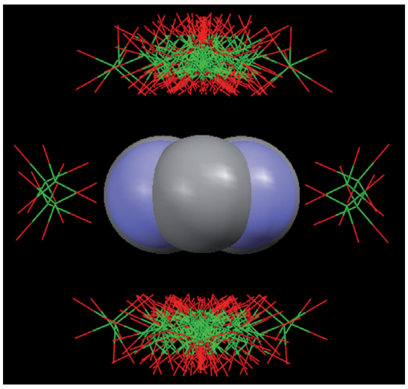
Minireviews



Ignite my fire: Design and synthesis of ionic-liquid-based energetic materials provides a powerful methodology in the development of a new type of hypergolic fuel (one that undergoes instantaneous ignition on contact with oxidizers). A new family of dicyanoborate ionic liquids is presented (see picture), which are synthesizable in water, and has met nearly all of the desired important criteria for well performing fuels.

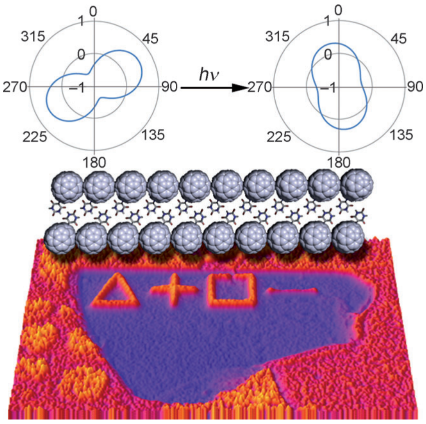
Reviews



As easy as π systems found it to bond with cations, they concealed their attraction to anions until they were spotted together in too many crystal structures for it to be mere coincidence. Today, the anion–π relationship has an established place in the repertory of noncovalent interactions. Extensive theoretical and experimental studies illuminate the physical nature of the interaction and its utility in the design of hosts, and the engineering of solid-state structures.

Communications

Turning light: A crystalline fullerene material based on H-bonding interactions exhibits highly polarized fluorescence emission, whose angle of polarization can be turned using light (see picture). This process can be used to write optical information onto the material, which can be read through the polarization component of the luminescence emitted by the material.



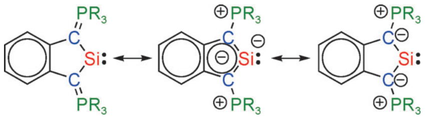
Contents

Silicon Chemistry

M. Asay, S. Inoue,
M. Driess* ______________ 9589 – 9592

Aromatic Ylide-Stabilized Carbocyclic Silylene

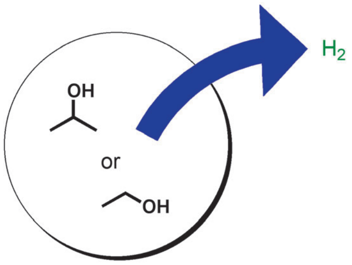
New ring on the block: A new type of silylene (see scheme) has been synthesized and is stabilized by the ylidic carbon centers which serve as π-donor substituents while attenuating the σ-withdrawing effects of the nitrogen groups. The electronic and structural features of this neutral silaaromatic system were probed using DFT calculations.



Renewable Energy

M. Nielsen, A. Kammer, D. Cozzula,
H. Junge, S. Gladiali,
M. Beller* ______________ 9593 – 9597

Efficient Hydrogen Production from Alcohols under Mild Reaction Conditions

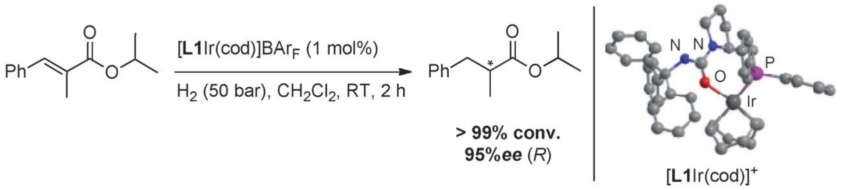


Run out of gas? A protocol for the title transformation under mild reaction conditions has been developed. Highest activities are found with an in situ catalyst system consisting of a 1:1 mixture of an *H*PNP^{iPr} ligand and [RuH$_2$(PPh$_3$)$_3$CO]. A turnover frequency of up to 14 145 h^{-1} and turnover number of more than 40 000 have been achieved for production of hydrogen gas from isopropyl alcohol.

Asymmetric Catalysis

D. Rageot, D. H. Woodmansee, B. Pugin,
A. Pfaltz* ______________ 9598 – 9601

Proline-Based P,O Ligand/Iridium Complexes as Highly Selective Catalysts: Asymmetric Hydrogenation of Trisubstituted Alkenes



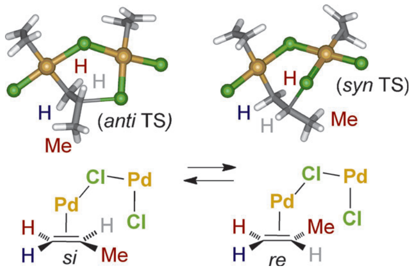
P,O joins the mix: P,O ligands (**L1**) form efficient iridium catalysts for the asymmetric hydrogenation of olefins. The proline-derived ligands lead to high enantioselectivities with several classes of alkenes, most notably with α,β-unsaturated carboxylic esters and ketones, where they match or even surpass the *ee* values reported for the best N,P and C,N ligands.

Reaction Mechanisms

E. H. P. Tan, G. C. Lloyd-Jones,*
J. N. Harvey,* A. J. J. Lennox,
B. M. Mills ______________ 9602 – 9606

[(RCN)$_2$PdCl$_2$]-Catalyzed *E*/*Z* Isomerization of Alkenes: A Non-Hydride Binuclear Addition–Elimination Pathway

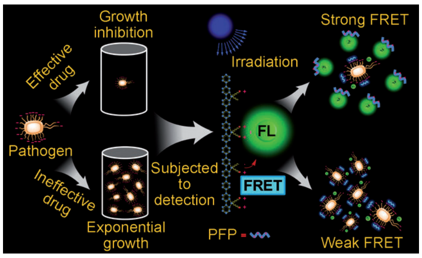
A crepuscular catalyst: Alkene migration catalyzed by [(RCN)$_2$PdCl$_2$] complexes proceeds through an in situ generated Pd-H species. Addition of a 1,5-diene inhibits migration and allows the slower background catalysis of *E*/*Z* interconversion to be studied. Experimental and computational results suggest this interconversion proceeds through a conformational equilibrium in dipalladacycles (see picture).



Antibiotic Screening

C. Zhu, Q. Yang,* L. Liu,
S. Wang* ______ 9607 – 9610

Rapid, Simple, and High-Throughput Antimicrobial Susceptibility Testing and Antibiotics Screening

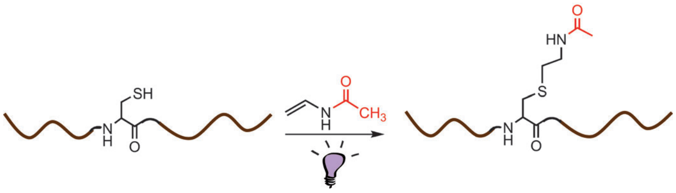


Lightning bugs: The emergence of antibiotic-resistant pathogens necessitates rapid, simple, and high-throughput antimicrobial susceptibility assessment and new antibiotics screening. A new method exploiting fluorescence resonance energy transfer (see picture) meets these demands and should ease new antibiotics discovery and point-of-care treatment applications.

Protein Acetylation

F. Li, A. Allahverdi, R. Yang, G. B. J. Lua,
X. Zhang, Y. Cao, N. Korolev,
L. Nordenskiöld, C. F. Liu* ______ 9611 – 9614

A Direct Method for Site-Specific Protein Acetylation

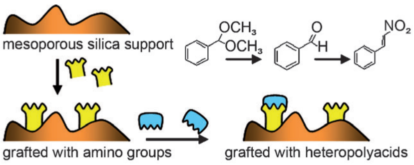


Radicals at work: Radical-mediated thiol-ene addition of the thiol group of Cys to *N*-vinylacetamide gives acetyl-thialysine (K_SAc), a near-perfect mimic of acetyl-lysine (see picture). The reaction is highly efficient with near quantitative conversion obtained in short reaction times. The generated K_SAc is functionally identical or similar to its native counterpart.

Bifunctional Catalysis

N. R. Shiju,* A. H. Alberts, S. Khalid,
D. R. Brown,
G. Rothenberg* ______ 9615 – 9619

Mesoporous Silica with Site-Isolated Amine and Phosphotungstic Acid Groups: A Solid Catalyst with Tunable Antagonistic Functions for One-Pot Tandem Reactions

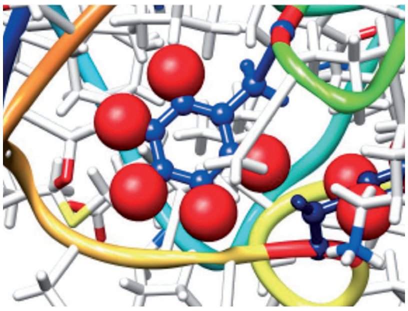


Coniuga et impera: A bifunctional solid catalyst is prepared by combining acid and base functions on mesoporous silica supports (see picture). The co-existence of these functions is shown by a two-step reaction sequence in one pot. Excellent product yields, which cannot be obtained by separated acid and base functions in one pot, show the validity of our concept.

Conformation Analysis

A. B. Sahakyan, W. F. Vranken, A. Cavalli,
M. Vendruscolo* ______ 9620 – 9623

Using Side-Chain Aromatic Proton Chemical Shifts for a Quantitative Analysis of Protein Structures

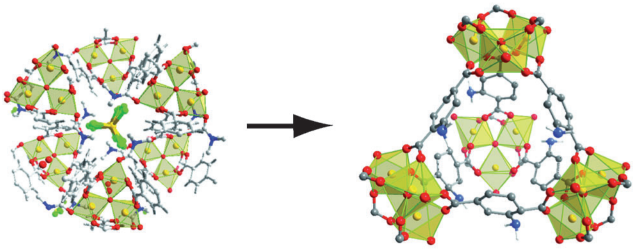


Predicting chemical shifts: A method for the structure-based prediction of side-chain aromatic ^1H chemical shifts of proteins is presented (see picture; blue structures: aromatic side chains, red spheres: aromatic hydrogen atoms). Its ability to differentiate correct structural models from incorrect ones is also demonstrated, together with its use to detect differences caused by cofactor or ligand binding, or by sequence alterations between structures.

MOF Crystallization

E. Stavitski,* M. Goesten, J. Juan-Alcañiz,
A. Martinez-Joaristi, P. Serra-Crespo,
A. V. Petukhov, J. Gascon,*
F. Kapteijn ______ **9624 – 9628**

Kinetic Control of Metal–Organic Framework Crystallization Investigated by Time-Resolved In Situ X-Ray Scattering

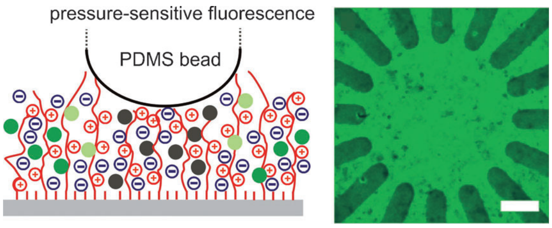


MOFs scattering away: The mechanism behind the multistep synthesis of two metal–organic frameworks sharing the same metal and organic precursors was revealed by in situ time-resolved small- and wide-angle X-ray scattering. Key factors governing the crystal assembly could be established (see picture: C gray, H white, N blue, O red, Al yellow, Cl green), including solvent, temperature, and precursor concentration.

Pressure-Responsive Polymers

J. Bünsow, J. Erath, P. M. Biesheuvel,
A. Fery,* W. T. S. Huck* ______ **9629 – 9632**

Direct Correlation between Local Pressure and Fluorescence Output in Mechanoresponsive Polyelectrolyte Brushes

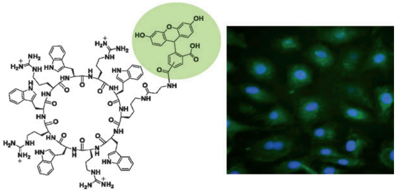


Gentle touch: Mechanoresponsive polyelectrolyte brushes show a strong correlation between local fluorescence intensity and local pressures (see picture; PDMS = polydimethylsiloxane). The response of the surface to mechanical stimuli was completely reversible and provided a sensitivity under 10 kPa, similar to human skin.

Drug Delivery

D. Mandal, A. Nasrolahi Shirazi,
K. Parang* ______ **9633 – 9637**

Cell-Penetrating Homochiral Cyclic Peptides as Nuclear-Targeting Molecular Transporters

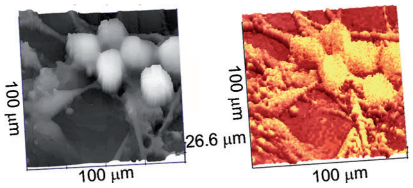


Going round in circles: Amphipathic L-cyclic peptides facilitate the cellular uptake of fluorescently labeled lamivudine and a phosphopeptide. A corresponding fluorescently labeled conjugate F-[W_5R_4K] showed a highly efficient translocation in the nucleus of colon adenocarcinoma, breast carcinoma, and human ovarian adenocarcinoma (see picture).

Scanning Probe Microscopy

Y. Takahashi, A. I. Shevchuk, P. Novak,
Y. Zhang, N. Ebejer, J. V. Macpherson,
P. R. Unwin, A. J. Pollard, D. Roy,
C. A. Clifford, H. Shiku, T. Matsue,
D. Klenerman,
Y. E. Korchev* ______ **9638 – 9642**

Multifunctional Nanoprobes for Nanoscale Chemical Imaging and Localized Chemical Delivery at Surfaces and Interfaces

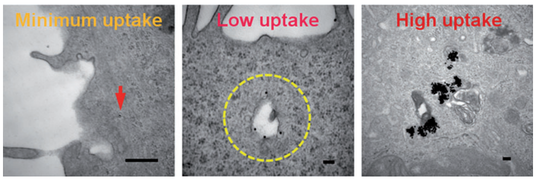


Double take: Double-barrel carbon nanoprobes with integrated distance control for simultaneous nanoscale electrochemical and ion conductance microscopy can be fabricated with a wide range of probe sizes in less than two minutes. The nanoprobes allow simultaneous noncontact topographical (left image) and electrochemical imaging (right) of living neurons, as well as localized K^+ delivery and simultaneous neurotransmitter detection.

Nanoparticle Hybrids

H. Yang, S. Y. Fung, M. Liu* **9643 – 9646**

Programming the Cellular Uptake of Physiologically Stable Peptide–Gold Nanoparticle Hybrids with Single Amino Acids



Uptake of gold nanoparticles by cancer cells can be manipulated by tuning the surface chemical modalities using hexapeptide ligands. This remarkable tuning was achieved by introducing only 5% of tryptophan- or serine-ended peptide in the ligand mixture during surface modification. Uptake was governed by the aromatic ring structure of the end amino acids rather than their hydrophobicity.

The Cluster of Excellence “Unifying Concepts in Catalysis” unicat

offers in open competition the

Clara Immerwahr Award

The Clara Immerwahr Award will be conferred annually to a young female scientist at an early stage of her career (postdoctoral fellow, junior researcher) for outstanding results in Catalysis Research. It is associated with a financial support of 15.000 Euro for a research stay at UniCat and thought to pave the way for setting up an independent research group in the consortium or for establishing close collaborative links with UniCat. The award is sponsored by the TU Berlin and BASF SE.

The Clara Immerwahr Award winner 2012 will be announced in December 2011 and will be honored during a public ceremony involving a guest lecture held by an internationally renowned female scientist in February 2012 at TU Berlin.

Application Documents
We expect applications of postgraduate female researchers with no restrictions to nationality or home institution who are not older than 35 years. The application must include: An application letter, a curriculum vitae, a letter containing a one page summary of the candidate‘s achievements, a project description (2 pages), a publication list, PDF files of 3 of the published papers and two letters of recommendation. The application and all submitted documents must be in English.

Application deadline: November 15, 2011

more details: www.unicat.tu-berlin.de/clara-immerwahr-award

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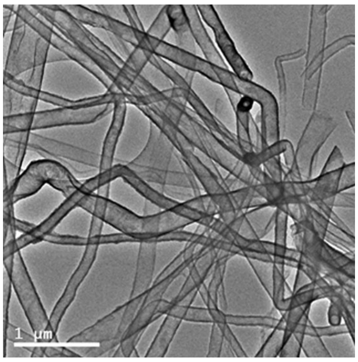
Germanium Nanotubes

M.-H. Park, Y. Cho, K. Kim, J. Kim, M. Liu, J. Cho* ———— **9647 – 9650**

Germanium Nanotubes Prepared by Using the Kirkendall Effect as Anodes for High-Rate Lithium Batteries

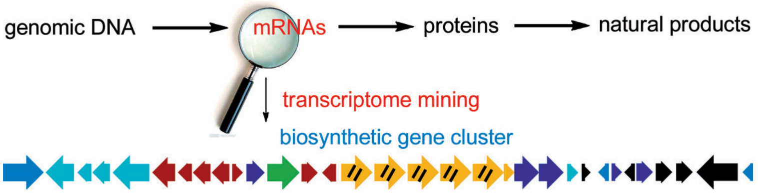


Ultralong germanium nanotubes (Ge NTs; see picture) are synthesized in high yield from core–shell Ge–Sb nanowires by utilizing the Kirkendall effect at 700 °C. The Ge NTs have an exceptionally high rate capability (40 Ag^{-1}) while maintaining a reversible capacity of more than 1000 $mAhg^{-1}$ over 400 cycles, with minimal capacity fading when paired with a $LiCoO_2$ cathode in a lithium-ion cell.

Natural Products

X. Qu, C. Lei, W. Liu* ———— **9651 – 9654**

Transcriptome Mining of Active Biosynthetic Pathways and Their Associated Products in *Streptomyces flaveolus*

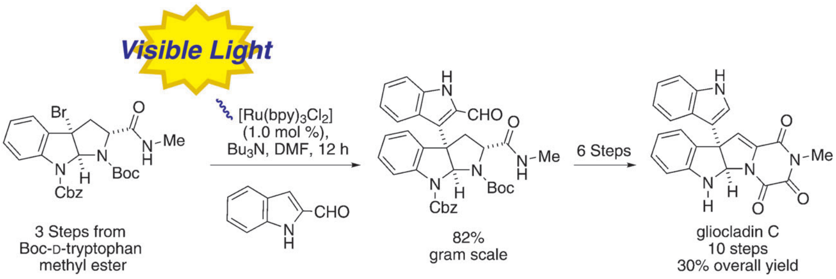


Missing link: Biosynthetic pathways and the production of related (known and unknown) natural products can be probed at the transcriptional level in *Streptomyces flaveolus* by a transcriptome-screening strategy (see picture). The approach complements recent advances in genome mining and potentially benefits natural product discovery from strains whose genomes have not been sequenced.

Total Synthesis

L. Furst, J. M. R. Narayanam, C. R. J. Stephenson* ———— **9655 – 9659**

Total Synthesis of (+)-Gliocladin C Enabled by Visible-Light Photoredox Catalysis



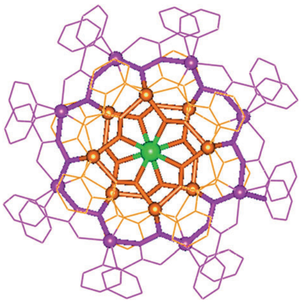
Lighting the way: In a 10-step total synthesis of the title compound, visible-light photoredox catalysis enabled the construction of the key bond by facilitating the direct coupling of a pyrroloindoline-derived radical with a substituted indole (see scheme; Boc = *tert*-butyloxycarbonyl, Cbz = benzyloxycarbonyl, DMF = *N*,*N*′-dimethylformamide). This represents the first implementation of visible-light photoredox catalysis in a total synthesis.

Metallamacrocycles

J. Jankolovits, C. M. Andolina, J. W. Kampf, K. N. Raymond,* V. L. Pecoraro* ———— **9660 – 9664**

Assembly of Near-Infrared Luminescent Lanthanide Host(Host–Guest) Complexes With a Metallacrown Sandwich Motif

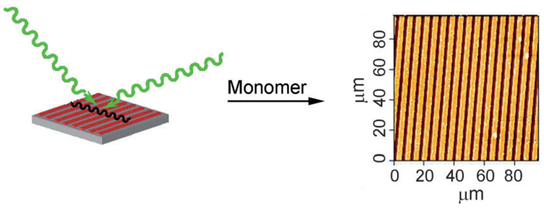
Oscillators omitted: A self-assembled inclusion complex between a $Ln^{III}[12\text{-metallacrown-}4]_2^{3+}$ sandwich motif (green and bronze) and a [24-metallacrown-8] (purple) is stable in methanol. The Yb^{III} complex has a large quantum yield (0.89 %) and luminescent lifetime (14 µs) in methanol, which are attributed to the exclusion of high-energy oscillators from within 6.7 Å of the emitting Yb^{III} ion by the metallacrown topology.



Polymerization Catalysts

J. Huber, B. Scheinhardt, T. Geldhauser, J. Boneberg, S. Mecking* —— **9665 – 9667**

Polymerization Catalyst Laser-Interference Patterning



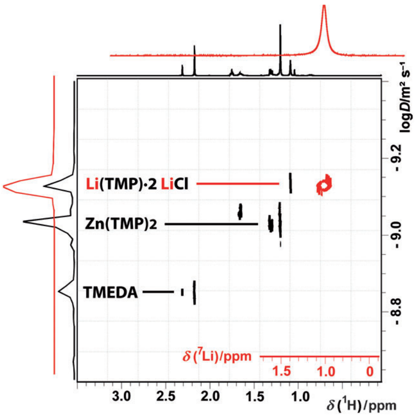
Spatially resolved patterns of a polymerization catalyst are generated by laser interference (see picture). Polymerization leads to a functional polymer replica of the catalyst pattern, as illustrated for polyacetylene as an example of a polymer not amenable to postpolymerization processing.

Lithium Zincate Reagents

P. García-Álvarez,* R. E. Mulvey,* J. A. Parkinson —— **9668 – 9671**

“LiZn(TMP)$_3$”, a Zincate or a Turbo-Lithium Amide Reagent? DOSY NMR Spectroscopic Evidence

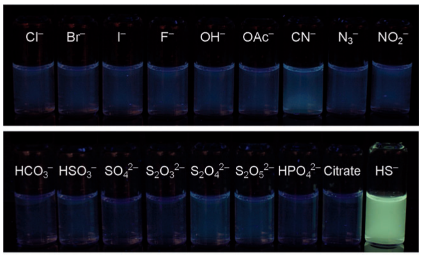
LiCl counts! DOSY NMR studies (see picture; TMP = 2,2,6,6-tetramethylpiperidide; TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) reveal the true nature of the synthetically useful basic mixture formed by reacting three equivalents of LiTMP with one of (TMEDA)·ZnCl$_2$ in THF. Surprisingly, Zn(TMP)$_2$ is just a spectator of the mutual interactions shown between LiTMP and the LiCl coproduct released from the transmetalation/“salt elimination” reaction.



Fluorescent Probes

H. Peng, Y. Cheng, C. Dai, A. L. King, B. L. Predmore, D. J. Lefer, B. Wang* —— **9672 – 9675**

A Fluorescent Probe for Fast and Quantitative Detection of Hydrogen Sulfide in Blood

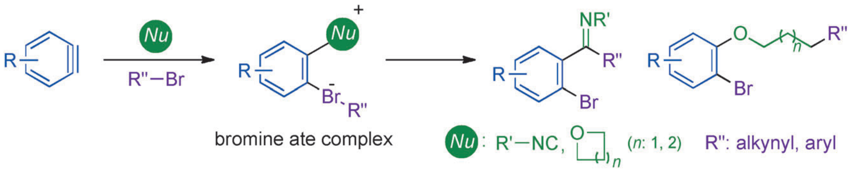


The dose makes the poison: Hydrogen sulfide is an important gasotransmitter for which rapid detection agents are needed. A hydrogen sulfide probe, which allows for fast (within seconds), selective, and quantitative detection in buffer solution, serum, and whole blood is designed, synthesized, and used for detection of hydrogen sulfide (see picture).

Multicomponent Reactions

H. Yoshida,* Y. Asatsu, Y. Mimura, Y. Ito, J. Ohshita, K. Takaki —— **9676 – 9679**

Three-Component Coupling of Arynes and Organic Bromides



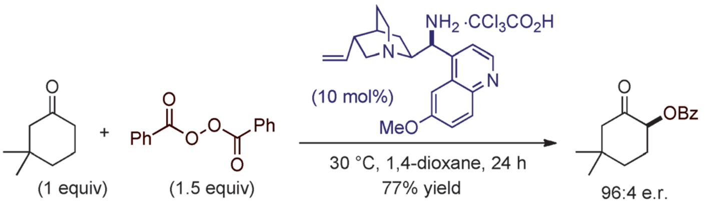
Magic trio: Arynes are easily coupled with neutral nucleophiles and organic bromides to afford functionalized bromoarenes depending upon the nucleophile (Nu). The three-component coupling proceeds through the formation of bromine ate complexes, and can be applied to the synthesis of multisubstituted isoquinolines and benzo[*b*]oxepines having pharmacological activity.

Contents

Organocatalysis

O. Lifchits, N. Demoulin,
B. List* ———————— **9680 – 9683**

Direct Asymmetric α Benzoyloxylation of Cyclic Ketones

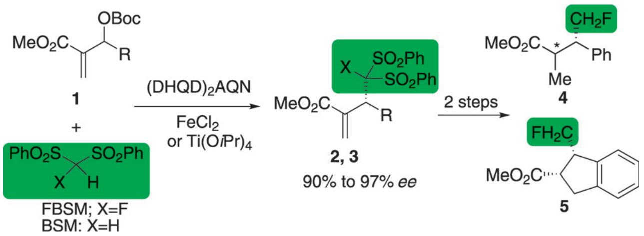


It's amine business: A readily available cinchona-derived primary amine is an effective catalyst for the direct asymmetric α benzoyloxylation of cyclic ketones (see scheme; Bz = benzoyl). This efficient and highly enantioselective method uses inexpensive benzoyl peroxide as the oxygen source and stoichiometric amounts of the ketone, and expands the current set of methodologies to directly access valuable protected 2-hydroxyketone derivatives.

Organocatalysis

T. Furukawa, J. Kawazoe, W. Zhang,
T. Nishimine, E. Tokunaga, T. Matsumoto,
M. Shiro, N. Shibata* ———— **9684 – 9688**

Asymmetric Allylic Monofluoromethylation and Methylation of Morita–Baylis–Hillman Carbonates with FBSM and BSM by Cooperative Cinchona Alkaloid/FeCl$_2$ Catalysis

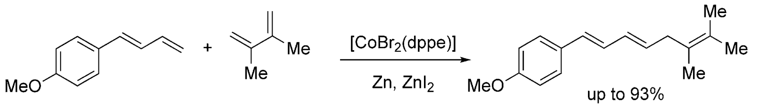


Working together: The title reactions were achieved in high yields with high *ee* values (see scheme, (DHQD)$_2$AQN = hydroquinidine(anthraquinone-1,4-diyl) diether). The cooperative catalysis of bis(cinchona alkaloid) and Lewis acid, particularly FeCl$_2$, was effective for these transformations and gave the monofluoromethylation products with over 90% *ee* and methylation products with up to 97% *ee*.

Synthetic Methods

M. A. Bohn, A. Schmidt, G. Hilt,*
M. Dindaroğlu,
H.-G. Schmalz ———————— **9689 – 9693**

Cobalt-Catalyzed 1,4-Hydrobutadienylation of 1-Aryl-1,3-dienes with 2,3-Dimethyl-1,3-butadiene

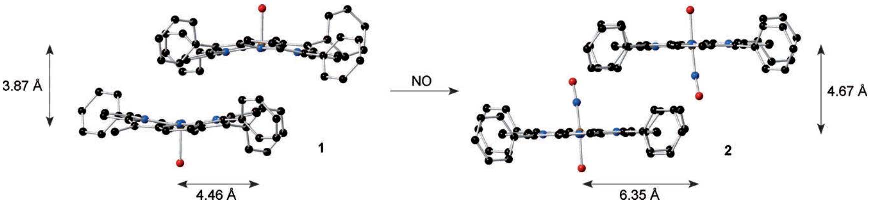


Round and round the olefin goes! A cobalt-catalyzed 1,4-hydrobutadienylation of a 1-aryl-substituted 1,3-diene with 2,3-dimethyl-1,3-butadiene yields 1,3,6-triene derivatives in excellent yield and chemoselectivity. The application of a bulky ligand (SchmalzPhos) leads to the selective formation of a single regio- and stereoisomer.

Iron Porphyrinoids

N. Xu,* D. R. Powell,
G. B. Richter-Addo* ———— **9694 – 9696**

Nitrosylation in a Crystal: Remarkable Movements of Iron Porphyrins Upon Binding of Nitric Oxide

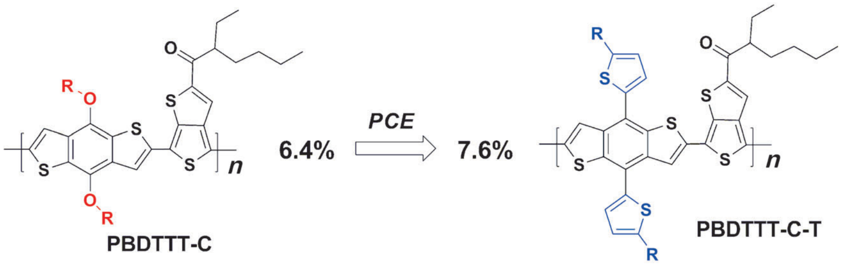


Bustin' a move: Diffusion of NO gas into crystals of [(TPP)Fe(H$_2$O)]SO$_3$CF$_3$ (**1**) results in nitrosylation of half the number of molecules to generate [(TPP)Fe(NO)(H$_2$O)]SO$_3$CF$_3$ (**2**). This nitrosylation reaction in the solid phase produces a dramatic movement of the porphyrins to accommodate the NO ligands. The presence of both molecules in the same crystal allows a reliable comparison of their geometric data. TPP = tetraphenylporphyrin; C black, N blue, O red.

Solar Cells

L. Huo, S. Zhang, X. Guo, F. Xu, Y. Li,* J. Hou* ——— **9697 – 9702**

Replacing Alkoxy Groups with Alkylthienyl Groups: A Feasible Approach To Improve the Properties of Photovoltaic Polymers

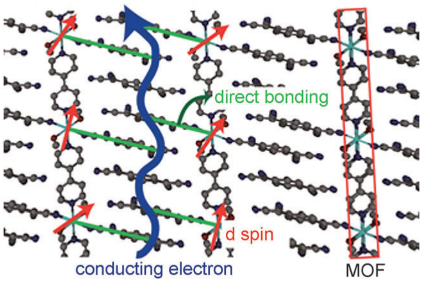


Another dimension: Two newly designed two-dimensional (2D) conjugated polymers, PBDTTT-E-T (see scheme; left) and PBDTTT-C-T, were prepared and their properties compared to those of the alkoxy-substituted analogues (right). PBDTTT-E-T and PBDTTT-C-T exhibited smaller band gaps, lower-energy HOMO levels, better thermal stabilities, and much better photovoltaic properties. Therefore, the 2D structures are feasible for the design of photovoltaic polymers.

Conducting Materials

M. Ballesteros-Rivas, A. Ota, E. Reinheimer, A. Prosvirin, J. Valdés-Martinez, K. R. Dunbar* ——— **9703 – 9707**

Highly Conducting Coordination Polymers Based on Infinite M(4,4′-bpy) Chains Flanked by Regular Stacks of Non-Integer TCNQ Radicals

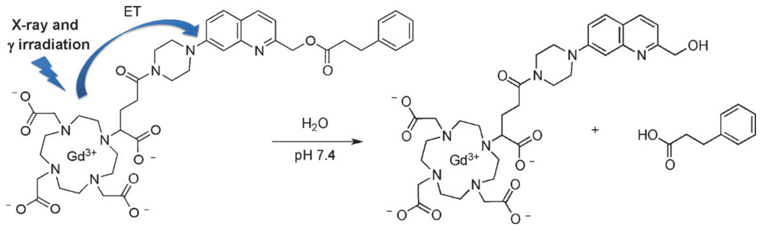


All coordinated: Highly conducting coordination polymers of the type $[M(4,4'\text{-bpy})(\eta^1\text{-TCNQ})_2(CH_3OH)_2]TCNQ$ (M = Mn, Zn) have been realized by using TCNQ (7,7,8,8-tetracyanoquinodimethane) as a building block (see picture). Regularly spaced stacks of TCNQ are connected to a Mn^{II}–4,4′-bipyridine spine by two η^1-TCNQ ligands involved in a stacked column with free TCNQ radicals.

Molecular Probes

M. Petit, G. Bort, B.-T. Doan, C. Sicard, D. Ogden, D. Scherman, C. Ferroud, P. I. Dalko* ——— **9708 – 9711**

X-ray Photolysis To Release Ligands from Caged Reagents by an Intramolecular Antenna Sensitive to Magnetic Resonance Imaging



Sensitive to light: A metal-complex-sensitized organic probe was developed to release ligands on excitation by X-ray or γ irradiation (see picture). This overcomes a current limitation in permitting use of photolysis as an experimental tool in otherwise inaccessible materials that are not penetrated by light (ET = electron transfer).

Synthetic Methods

M. Batuecas, L. Escalante, M. A. Esteruelas,* C. García-Yebra, E. Oñate, C. Saá* ——— **9712 – 9715**

Dehydrative Cyclization of Alkynals: Vinylidene Complexes with the C_β Incorporated into Unsaturated Five- or Six-Membered Rings

A nice ring: The title compounds are easily prepared by dehydrative cyclization of terminal alkynals in the presence of osmium, iridium, and rhodium precursors (see scheme).

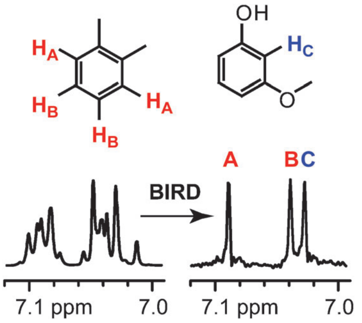
Contents

NMR Spectroscopy

J. A. Aguilar, M. Nilsson,
G. A. Morris* ____________ **9716 – 9717**

Simple Proton Spectra from Complex Spin Systems: Pure Shift NMR Spectroscopy Using BIRD

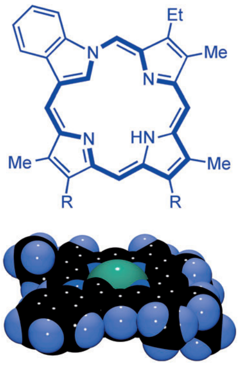
Turning multiplets into singlets: Bilinear rotation decoupling (BIRD) allows broadband homonuclear decoupling of proton NMR spectra even when spins are very strongly coupled, as in the two aromatics shown.



Porphyrin Isomers

T. D. Lash,* A. D. Lammer,
G. M. Ferrence ____________ **9718 – 9721**

Neo-Confused Porphyrins, a New Class of Porphyrin Isomers

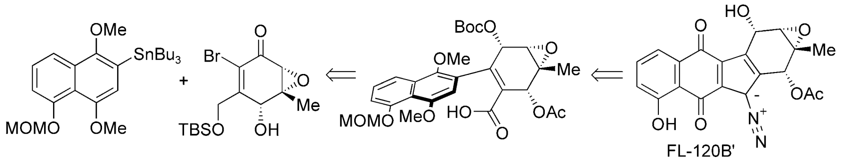


Confused yet still diatropic: A new type of porphyrin isomer is reported where a pyrrole nitrogen is connected to one of the *meso*-bridges. This system retains porphyrin-like characteristics and reacts with nickel(II) acetate to generate a stable organometallic complex.

Natural Product Synthesis

S. S. Scully, J. A. Porco, Jr.* **9722 – 9726**

Asymmetric Total Synthesis of the Epoxykinamycin FL-120 B′

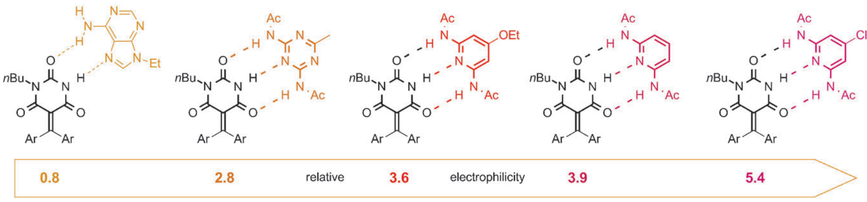


Turn up the heat: The synthesis of the title compound was achieved and a route to epoxide-containing diazobenzofluorenes, which could potentially serve as monomers to the dimeric lomaiviticins, was established. Key steps to construct the FL-120B′ core structure include Sharpless asymmetric epoxidation, Stille coupling, and intramolecular Friedel–Crafts acylation of atropisomeric carboxylic acids at elevated temperatures.

Electrophilicity

M. Bauer, S. Spange* _____ **9727 – 9730**

Adjustable Electrophilicity by Cooperative Hydrogen Bonds

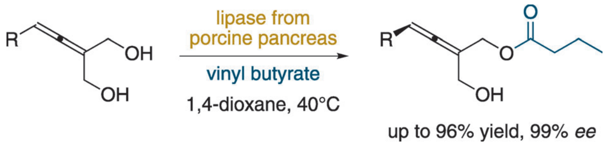


Control of reactivity: A gradual adjustment of the electrophilicity of a barbiturate merocyanine is achievable using cooperative hydrogen bonds (see scheme). Substituent effects at the receptor are directly transmitted to the reactive center of the electrophilic substrate so that an almost infinitely variable adjustment of its reactivity is possible.

Axial Chirality

C. Manzuna Sapu, J.-E. Bäckvall, J. Deska* ——— **9731 – 9734**

Enantioselective Enzymatic Desymmetrization of Prochiral Allenic Diols

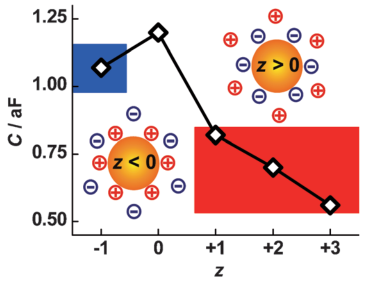


Crude lipase from porcine pancreas acts as a highly efficient biocatalyst in the enantioselective transesterification of prochiral allendiols. Following a simple synthetic protocol, highly functionalized axially chiral allenes are obtained in high yields and excellent enantiopurity (see scheme).

Nanoparticles in Ionic Liquids

S. F. L. Mertens,* C. Vollmer, A. Held, M. H. Aguirre, M. Walter,* C. Janiak,* T. Wandlowski* ——— **9735 – 9738**

“Ligand-Free” Cluster Quantized Charging in an Ionic Liquid



On a charge: The experimental capacitance per cluster (*C*) as a function of charge state (*z*, see picture) confirms the quantized charging of “ligand-free” metal clusters in an ionic liquid. DFT calculations indicate a switch in orientation of the ionic shell around the clusters when the sign of the charge changes, and explain the maximum capacitance at zero charge.

Nucleobase Variations

D. Globisch, D. Pearson, A. Hienzsch, T. Brückl, M. Wagner, I. Thoma, P. Thumbs, V. Reiter, A. C. Kneuttinger, M. Müller, S. A. Sieber, T. Carell* ——— **9739 – 9742**

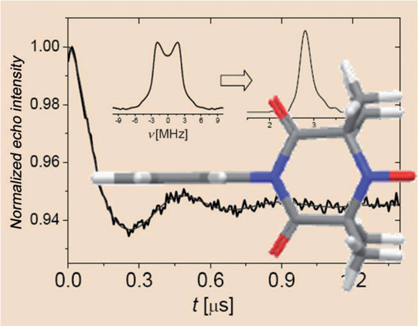
Systems-Based Analysis of Modified tRNA Bases

Quantification of modified tRNA nucleosides in 16 species reveals evolutionary development of modification levels corresponding to phylogenetic branching. Comparison of modification profiles additionally allows characterization of species and differentiation between a number of pathogenic and harmless bacterial strains.

Spin Labels

S. Stoller, G. Sicoli,* T. Y. Baranova, M. Bennati, U. Diederichsen* ——— **9743 – 9746**

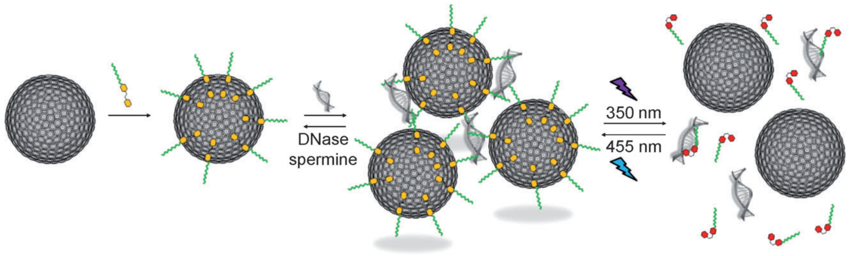
TOPP: A Novel Nitroxide-Labeled Amino Acid for EPR Distance Measurements



A new tool: The amino acid 4-(3,3,5,5-tetramethyl-2,6-dioxo-4-oxylpiperazin-1-yl)-L-phenylglycine (TOPP), which has a rigid nitroxide spin label, can be used for EPR-based distance measurements in peptides. The key feature of the design is the defined orientation of the nitroxide in space with respect to the peptide backbone. EPR measurements provide evidence for the low conformational flexibility of the TOPP label.

Contents

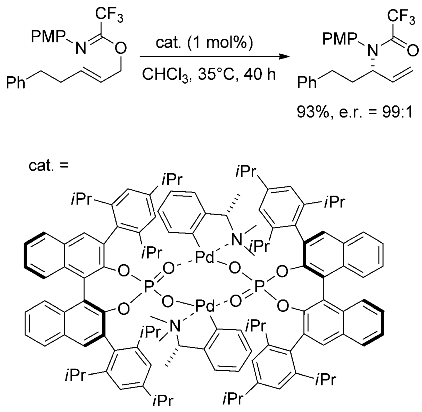
Photoresponsive Systems



The wavelength determines whether DNA is captured in a light-responsive ternary supramolecular complex or released (see scheme). The reversible binding of DNA is triggered by a photoisomerization, which switches the complex from a multivalent to a monovalent binding mode.

Asymmetric Catalysis

The chiral TRIP anion combined with a simple commercially available palladacycle furnishes a highly active catalyst for the enantioselective rearrangement of allylic imidates to the corresponding amide products in high yields (see scheme). The stereoselectivity is induced entirely by the chiral phosphate anion although the catalyst complex contains a chiral palladacycle (see scheme).



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