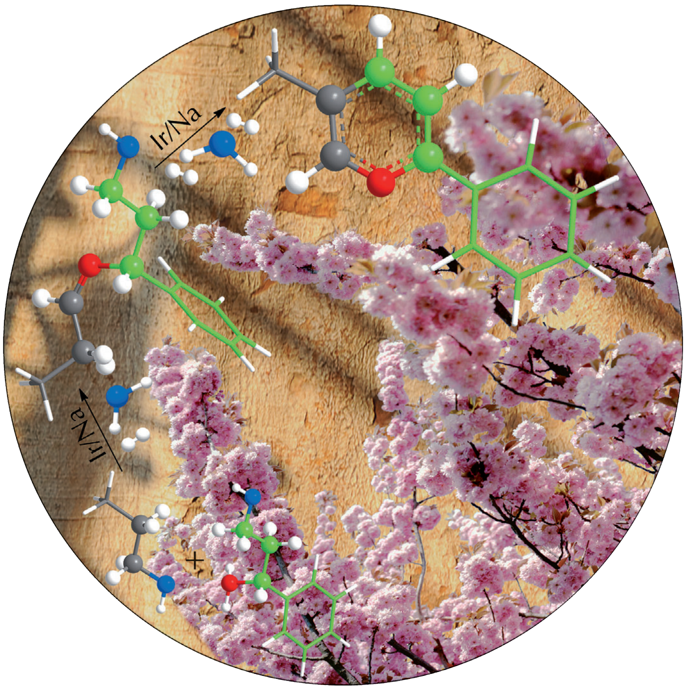
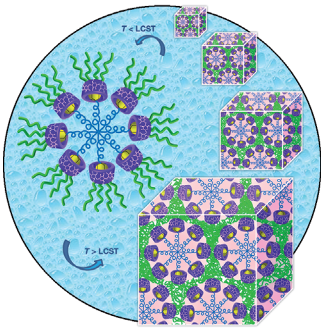
In the sustainable Ir-catalyzed synthesis …

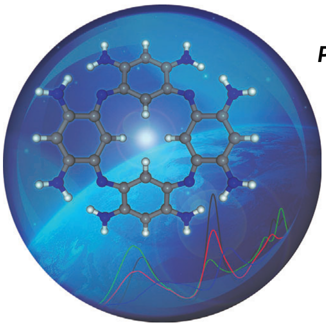


… of pyridine derivatives described by R. Kempe and S. Michlik in their Communication on page 6326 ff., alcohols and 1,3-amino alcohols are deoxygenated and selectively linked in C–N and C–C bond-forming steps. Three equivalents of hydrogen gas are liberated per generated pyridine unit (see reaction scheme). The wood and blossoms in the background underline the fact that the starting materials can be obtained from renewable resources.

Supramolecular Hydrogel

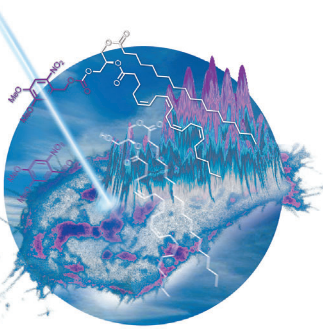
In their Communication on page 6180 ff., J. Li et al. describe a novel star–star supramolecular architecture that self-aggregates into a 3D network in response to temperature change, forming a thermo-responsive reversible hydrogel.





Porphyrin Analogues

The unusual bis-zwitterionic character of the isostructural, isoelectronic “pyrrol-free” analogue of porphyrin is one of the topics discussed by D. Jacquemin, O. Siri, and co-workers in their Communication on page 6250 ff.



Photoactivation

In their Communication on page 6330 ff., C. Schultz and co-workers demonstrate that regionally limited photoactivation simultaneously leads to a local protein kinase C and a global calcium response.

How to contact us:

Editorial Office:
E-mail: angewandte@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-315

Reprints, E-Prints, Posters, Calendars:
Carmen Leitner
E-mail: chem-reprints@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-327

Copyright Permission:
Bettina Loycke
E-mail: rights-and-licences@wiley-vch.de
Fax: (+49) 6201–606-332
Telephone: (+49) 6201–606-280

Online Open:
Margitta Schmitt, Carmen Leitner
E-mail: angewandte@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-315

Subscriptions:
www.wileycustomerhelp.com
Fax: (+49) 6201–606-184
Telephone: 0800 1800536 (Germany only)
+44(0) 1865476721 (all other countries)

Advertising:
Marion Schulz
E-mail: mschulz@wiley-vch.de
jspiess@wiley-vch.de
Fax: (+49) 6201–606-550
Telephone: (+49) 6201–606-565

Courier Services:
Boschstrasse 12, 69469 Weinheim

Regular Mail:
Postfach 101161, 69451 Weinheim

Angewandte Chemie International Edition is a journal of the Gesellschaft Deutscher Chemiker (GDCh), the largest chemistry-related scientific society in continental Europe. Information on the various activities and services of the GDCh, for example, cheaper subscription to *Angewandte Chemie International Edition*, as well as applications for membership can be found at **www.gdch.de** or can be requested from GDCh, Postfach 900440, D-60444 Frankfurt am Main, Germany.

GDCh
GESELLSCHAFT
DEUTSCHER CHEMIKER

Service

Author Profile

"My biggest motivation is the excitement of discovery. My favorite piece of research is a discovery that you had not intended to make in the first place …"
This and more about Peter J. Sadler can be found on page 6136.

News

M. J. Rosseinsky

J.-Q. Yu

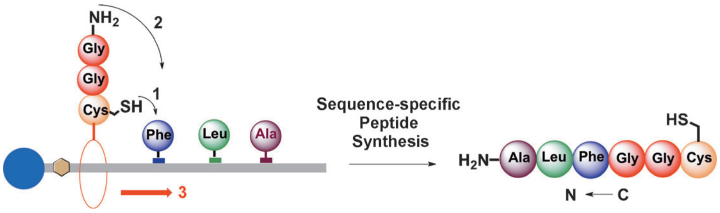
M. S. Sanford

A. Brik

Books

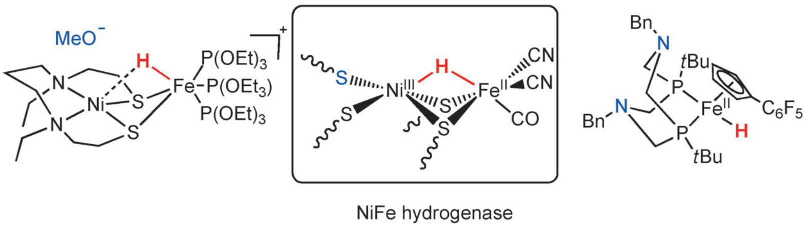
Highlights

Molecular Machines



Line up for synthesis! In a recent report the Leigh group described a rotaxane-based setup for the sequence-specific synthesis of small peptides, which runs automatically once started. This molecular machine combines elements from both chemical and biochemical peptide (bio-)syntheses, which are discussed in this Highlight.

Hydrogenase Mimics

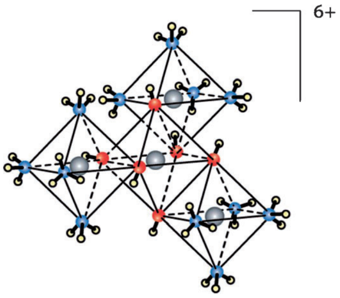


One metal or two? Recent results in the design of hydrogenase mimics have resulted in NiFe- and Fe-based complexes (see picture) that split molecular H_2 into electrons and protons. Although these compounds are still far from technological application they improve our understanding of how nature exploits abundant metals to achieve complex reactions.

Essays

History of Chemistry

Numerous honors were bestowed on Alfred Werner, who in 1913 was the first Swiss scientist to be awarded the Nobel Prize in Chemistry. This Essay gives an overview of Werner's scientific work and its significance beyond coordination chemistry. Picture: gray Co, red O, blue N, yellow H.



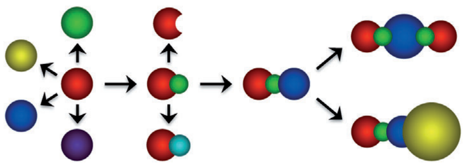
For the USA and Canada: ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. Annual subscription price for institutions: US$ 11.738/10.206 (valid for print and 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.

Reviews

Nanostructures

M. R. Buck, R. E. Schaak* ___ **6154–6178**

Emerging Strategies for the Total Synthesis of Inorganic Nanostructures



Nanoscale total synthesis: Diverse nanoparticle reaction libraries can be applied sequentially and predictably to construct complex multicomponent nanoscale architectures, in analogy to the total synthesis concept used to construct large and complex molecules.

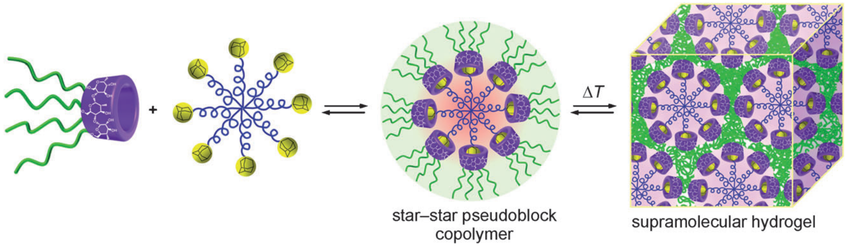
Communications

Supramolecular Hydrogel

Z.-X. Zhang, K. L. Liu, J. Li* **6180–6184**

A Thermoresponsive Hydrogel Formed from a Star–Star Supramolecular Architecture

Frontispiece



Smart stars: A novel star–star supramolecular architecture was self-assembled from a star-shaped adamantyl-terminated 8-arm poly(ethylene glycol) and a star-shaped poly(*N*-isopropylacrylamide) with a β-cyclodextrin core through inclusion complexation. The star–star supramolecules further self-aggregated into a 3D network in response to temperature change, forming a thermoresponsive reversible "smart" hydrogel.

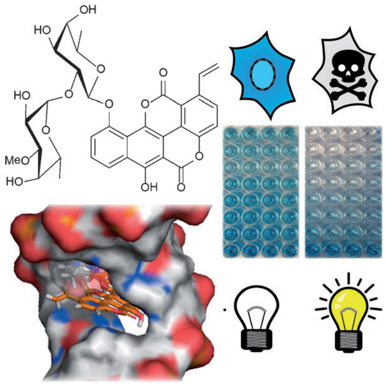
Antitumor Agents

N. Ueberschaar, H.-M. Dahse,
T. Bretschneider,
C. Hertweck* ___ **6185–6189**

Rational Design of an Apoptosis-Inducing Photoreactive DNA Intercalator

Inside Cover

Light on DNA intercalators: Molecular modeling and mutasynthesis were employed to rationally tailor the antitumoral agent chartreusin into a vinyl-substituted derivative. Exposure with visible light dramatically improved antiproliferative activities owing to covalent binding with DNA and induction of apoptosis. The results hold promise for a more efficient chemotherapy, in particular for selectively treating tumors with light probes.



GDCh

GESELLSCHAFT DEUTSCHER CHEMIKER

www.gdch.de

Call for Nominations

GDCh Awards

The Gesellschaft Deutscher Chemiker – GDCh (German Chemical Society) will confer the following awards in 2014:

Alfred-Stock-Gedächtnispreis (gold medal)

For recognition of outstanding work in the field of inorganic chemistry. The prize is endowed with € 7,500 Euro.

NEW Albrecht-Kossel-Preis

For recognition of outstanding achievements in the field of biochemistry. The prize is endowed with € 7,500.

August-Wilhelm-von-Hofmann-Denkmünze (gold medal)

Awarded preferably to non-German scientists, who have made significant contributions to chemistry.

Carl-Duisberg-Gedächtnispreis

For recognition of outstanding junior faculty members in the chemical sciences. The prize is endowed with € 5,000,- for the recipient + € 2,500,- for the recipient's research group. The award is bestowed upon someone who is active in a German university or who as a German is active in a university or research institution abroad. Moreover, the nominee should not be older than 40 or already hold a C4/W3 professorship or a similar position.

NEW Carl-Roth-Förderpreis

The prize sponsored by the Carl Roth GmbH + Co. KG addresses the younger generation of Molecular Scientists and is awarded for outstanding contributions in the fields of resource-friendly synthesis or innovative application of chemicals. The value of the award is € 5,000. In addition the group of the award winner is granted a € 3,000 voucher for items from the Carl Roth catalogue. Self-nomination is allowed.

Emil-Fischer-Medaille (gold medal)

For recognition of outstanding work in the field of organic chemistry. The prize is endowed with € 7,500.

GDCh-Preis für Journalisten und Schriftsteller (GDCh Prize for journalists and writers)

Awarded to journalists and writers in recognition of their contributions to the public understanding and awareness of chemistry. The prize is endowed with € 7,500 Euro.

Gmelin-Beilstein-Denkmünze (silver medal)

For recognition of special contributions to chemical literature, chemical information, or the history of chemistry. The prize is endowed with € 7,500.

Hermann-Staudinger-Preis (gold medal)

For recognition of contributions in the field of macromolecular chemistry. The prize is endowed with € 7,500.

Liebig-Denkmünze (silver medal)

For recognition of outstanding achievements in chemistry. The prize is endowed with € 7,500.

Awarding of Prizes

The GDCh Board has appointed Selection Committees for each prize who will present their suggestions to the Board for the final decision. The award ceremonies take place at the Chemiedozententagung (Conference of University Chemistry Docents), the EuCheMS Chemistry Congress, the Assembly of the Gesellschaft Deutscher Naturforscher und Ärzte (GDNÄ – Association of German Natural Scientists and Physicians) and at GDCh Division meetings. The Carl-Roth-Förderpreis will be awarded on the occasion of the JCF Spring Symposium.

Nomination Procedures

Members and non-members of the GDCh are welcome to make proposals. Self-nomination except for the Carl Roth Förderpreis is not allowed. Proposals shall consist of a letter of nomination (one page), CV, publication list and a link to the homepage of the nominated person.

The GDCh Prizes acknowledge outstanding achievements for and within chemistry. Accordingly, the achievements of the prize winner, rather than experience or age of the nominee, will be decisive in the decision-making process. As progress in science can often follow unusual pathways, nominations that cross interdisciplinary borders, open up surprising new perspectives, or which at first glance are difficult to classify, are particularly welcome.

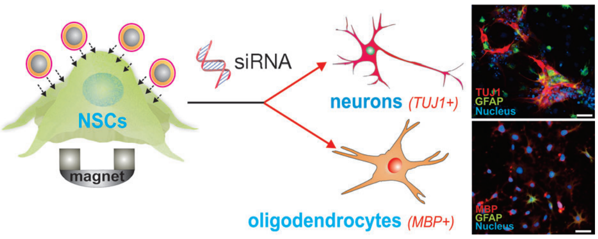
Prof. Dr. Barbara Albert
President

Please submit your proposal by
October 15, 2013 to

Gesellschaft Deutscher Chemiker e.V.
Preise und Auszeichnungen
P.O. Box 90 04 40
60444 Frankfurt am Main
Germany

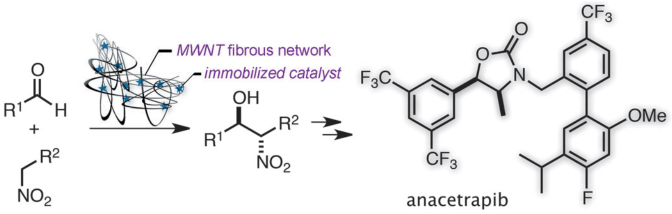
Tel.: 0049 (0)69 7917-323
Fax: 0049 (0)69 7917-1323
E-mail: b.koehler@gdch.de

Nanoparticles for Stem Cells



Special delivery! The title system, composed of a highly magnetic core surrounded by a thin uniform gold shell, has been synthesized and applied to the magnetically facilitated delivery of genetic material (siRNA or plasmid DNA) into neural stem cells (NSCs) for controlling their neural differentiation in a spatiotemporally controlled, biocompatible manner.

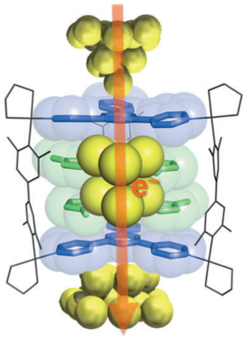
Asymmetric Heterogeneous Catalysis



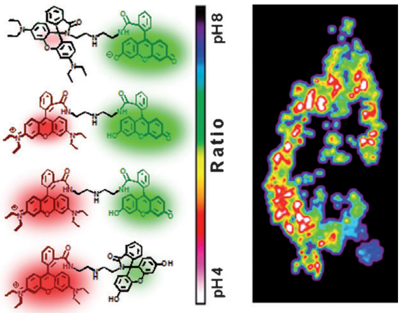
Confined cat works better: A self-assembling heterobimetallic catalyst, comprised of a Nd/Na/amide ligand confined in an entangled multiwalled carbon nanotube (MWNT) network, outperforms the unconfined catalyst in *anti*-selective catalytic asymmetric nitroaldol reactions. The confined catalyst could be used repeatedly through simple filtration, and was applied to a concise enantioselective synthesis of anacetrapib.

Single-Molecule Conductance

Ion nanowire: Electron transport through discrete gold-ion arrays within coordination cages was directly measured between Au nanogap electrodes (see picture) using STM. Precise calibration of the electron transport distance demonstrates that Au-ion arrays exhibit good conductance and only moderate loss with increasing transport length.



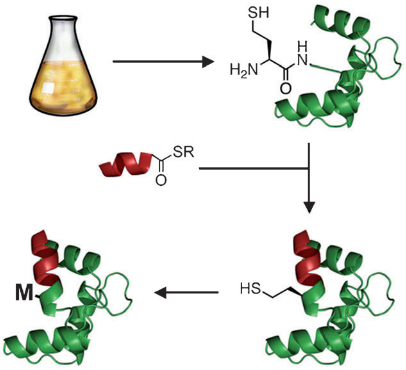
Analytical Methods



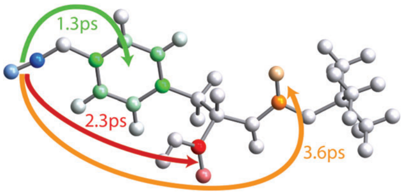
High-tech pH paper: A “chameleon” pH probe composed of rhodamine (red, see scheme) and fluorescein (green) units emits at wavelengths of 580 nm and 512 nm, where the intensities show a contrary response to pH changes. Confocal microscopy of HeLa cells with this probe reveals red and green spots; the ratio of these signals can be calibrated to give the pH value of the respective organelle.

Protein Semi-Synthesis

A useful handle: One major limitation of protein semi-synthesis is the need for Cys at the ligation site in native chemical ligation reactions. It is shown that a transferase enzyme can deliver homocysteine to the N-terminus of an expressed protein (see scheme). Homocysteine can be used in a ligation reaction and then converted to Met. This allows one to use the MetArg or MetLys motif as a point of disconnection in semi-synthesis.



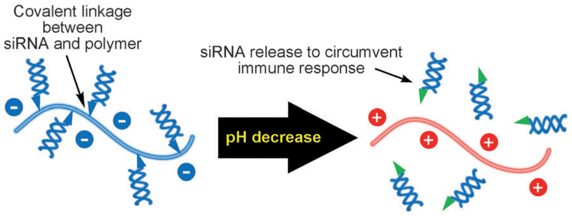
IR Spectroscopy



Distance matters: Interpretation of infrared spectra regularly involves the assignment of absorption bands to certain functional groups of the molecule. Distance-dependent vibrational energy transfer can be used for exact band assignment in molecules in which assignment is difficult and quantum chemical computations are contradictory.

---

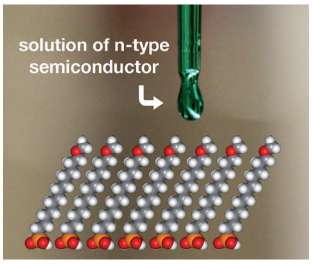
siRNA Conjugates



An siRNA conjugate is based on an acid-labile maleic acid amide linkage for programmed transfer of siRNA from the endosome to the cytosol and siRNA release in the cell interior. The procedure relies on reversible stability in response to endosomal acidic pH value. The complexed polyionic conjugate achieved gene silencing in cultured cancerous cells with negligible side effects.

Self-Assembled Monolayers

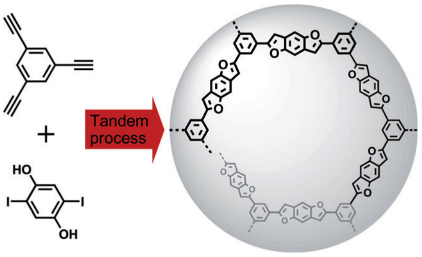
Add an O: A new strategy for preparing solution-processed organic thin-film transistors (OTFTs) is based on enhancing the surface energy of self-assembled monolayers (SAMs) by inserting polar oxygen atoms into the long alkyl chain of phosphonic acids. SAMs of these phosphonic acids on a high-*k* metal oxide layer lead to solution-processed n-channel OTFTs with average field effect mobilities of up to 2.5 $cm^2 V^{-1} s^{-1}$ and low operational voltages.



Porous Organic Materials

N. Kang, J. H. Park, K. C. Ko, J. Chun, E. Kim, H.-W. Shin, S. M. Lee, H. J. Kim, T. K. Ahn,* J. Y. Lee,* S. U. Son* ______ **6228 – 6232**

Tandem Synthesis of Photoactive Benzodifuran Moieties in the Formation of Microporous Organic Networks

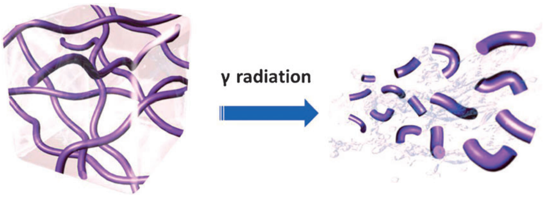


Tiny pores: Benzodifuran moieties were introduced into microporous organic networks (MONs) through a tandem process consisting of Sonogashira coupling of 1,3,5-triethynylbenzene and 2,5-diiodo-1,4-hydroquinone and intramolecular cyclization. The resultant benzodifuran-containing MON showed promising photocatalytic activities in the oxidative conversion of primary amines into imines.

Stimuli-Responsive Gels

W. Cao, X. Zhang, X. Miao, Z. Yang,* H. Xu* ______ **6233 – 6237**

γ-Ray-Responsive Supramolecular Hydrogel Based on a Diselenide-Containing Polymer and a Peptide

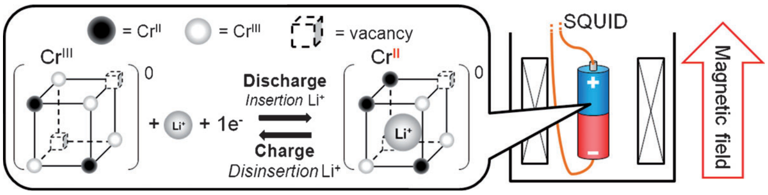


An overwhelming response: The exposure of a supramolecular hydrogel based on a diselenide-containing polymer and a peptide amphiphile containing a drug moiety to γ radiation led to a gel–sol transition owing to the oxidative cleavage of diselenide bonds in the polymer main chain (see picture). The hydrogel can also act as a UV-mediated drug self-delivery system and suggests a new avenue for combined radio- and chemotherapy.

Electrochemistry

T. Yamada, K. Morita, H. Wang, K. Kume, H. Yoshikawa,* K. Awaga* _ **6238 – 6241**

In situ Seamless Magnetic Measurements for Solid-State Electrochemical Processes in Prussian Blue Analogues

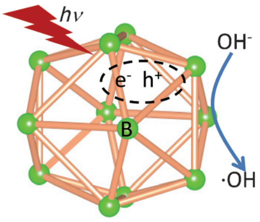


Seamless observation: Magnetic measurements in a solid-state electrochemical environment have been developed and applied to a mixed-valent chromium Prussian blue analogue (PBA) ferrimagnet. Battery cells containing PBA as a cathode active material were inserted into a SQUID and the PBA reduction during battery discharge was controlled. Magnetic changes were revealed that can be understood by the redox-induced spin changes of the Cr ions.

Elemental Photocatalysts

G. Liu, L.-C. Yin, P. Niu, W. Jiao, H.-M. Cheng* ______ **6242 – 6245**

Visible-Light-Responsive β-Rhombohedral Boron Photocatalysts



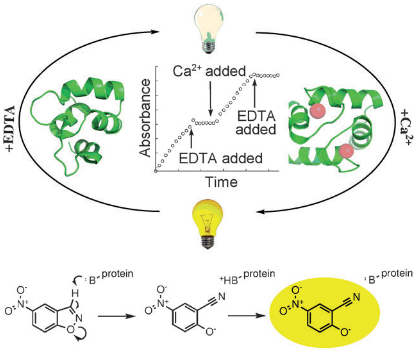
It's elemental! β-Rhombohedral boron was investigated as an elemental photocatalyst. Boron crystals were found to be photocatalytically active in the generation of $^{\bullet}$OH radicals under irradiation with visible light (see picture); however, the presence of an amorphous oxide layer on the surface of the crystals impaired their photocatalytic activity.

Protein Design

O. V. Moroz, Y. S. Moroz, Y. Wu, A. B. Olsen, H. Cheng, K. L. Mack, J. M. McLaughlin, E. A. Raymond, K. Zhezherya, H. Roder, I. V. Korendovych* ________ **6246 – 6249**

A Single Mutation in a Regulatory Protein Produces Evolvable Allosterically Regulated Catalyst of Nonnatural Reaction

It only takes one mutation: A strategically placed single mutation in a non-enzymatic protein scaffold produced AlleyCat, a small, allosterically regulated catalyst of Kemp elimination. In only seven rounds of directed evolution the enzymatic efficiency of the original 74 amino acid residue catalyst was improved more than 220-fold to achieve a k_{cat} value higher than that of catalytic antibodies for the same reaction, still preserving allosteric regulation.

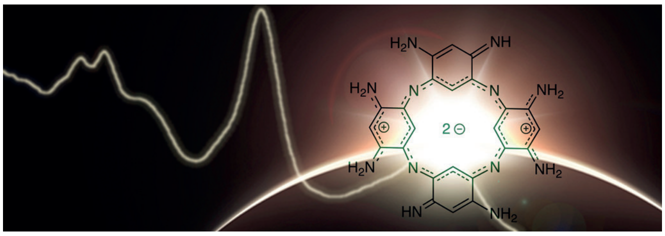


Porphyrin Analogues

Z. Chen, M. Giorgi, D. Jacquemin,* M. Elhabiri, O. Siri* ______ **6250 – 6254**

Azacalixphyrin: The Hidden Porphyrin Cousin Brought to Light

Inside Back Cover

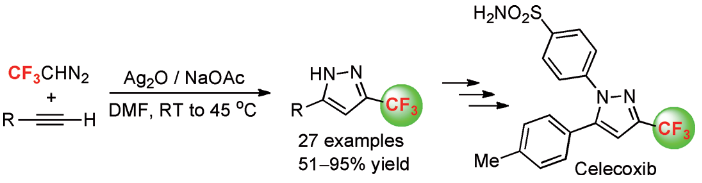


No pyrrol: Azacalixphyrin (see picture), a novel isostructural and isoelectronic "pyrrol-free" analogue of porphyrins is easily prepared in two straightforward steps. The azacalixphyrin is aromatic, absorbs in the entire visible region, and is highly stable (even in the presence of water under air) owing to its unusual bis-zwitterionic character.

Synthetic Methods

F. Li, J. Nie, L. Sun, Y. Zheng, J.-A. Ma* ______________ **6255 – 6258**

Silver-Mediated Cycloaddition of Alkynes with CF_3CHN_2: Highly Regioselective Synthesis of 3-Trifluoromethylpyrazoles

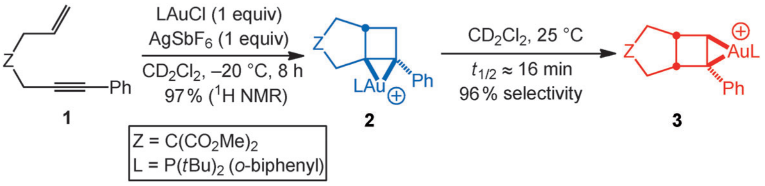


Silver screen: The title reaction provides a convenient and efficient method for the construction of 5-substituted 3-trifluoromethylpyrazoles under mild reaction conditions. By using this protocol, the marketed drug Celecoxib (antiarthritic) could be easily synthesized (see scheme; DMF = *N*,*N*-dimethylformamide).

Cycloaddition

R. E. M. Brooner, T. J. Brown, R. A. Widenhoefer* ________ **6259 – 6261**

Direct Observation of a Cationic Gold(I)–Bicyclo[3.2.0]hept-1(7)-ene Complex Generated in the Cycloisomerization of a 7-Phenyl-1,6-enyne

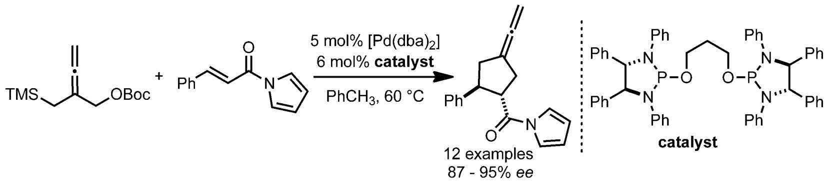


The reaction of enyne 1 with a 1:1 mixture of [LAuCl] and $AgSbF_6$ in CD_2Cl_2 at −20 °C gave the gold complex **2** in 97% yield (NMR spectroscopy). Warming a solution of **2** at 25 °C led to 1,3-H migration ($t_{1/2}$≈16 min) to form the gold complex **3** with 96% selectivity. ^{13}C NMR analysis of **2** and **3** showed predominant metallacyclopropane character of the gold–bicyclo[3.2.0]heptene bond.

Asymmetric Catalysis

B. M. Trost,* A. Maruniak —— **6262 – 6264**

Enantioselective Construction of Highly Substituted Vinylidenecylopentanes by Palladium-Catalyzed Asymmetric [3+2] Cycloaddition Reaction

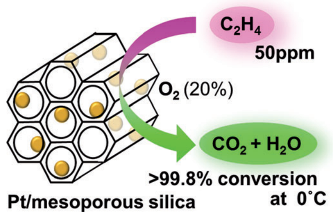


A new cycloadduct: The title reaction of methylene-trimethylenemethane (TMM) with α,β-unsaturated *N*-acyl pyrroles is an efficient method for the construction of vinylidenecyclopentanes. An asymmetric protocol using this unique donor forms cycloadducts in excellent yield and enantioselectivity, making use of a bisdiamidophosphite ligand derived from *trans*-1,2-stilbenediamine.

Ethylene Oxidation

C. X. Jiang, K. Hara,
A. Fukuoka* —————— **6265 – 6268**

Low-Temperature Oxidation of Ethylene over Platinum Nanoparticles Supported on Mesoporous Silica

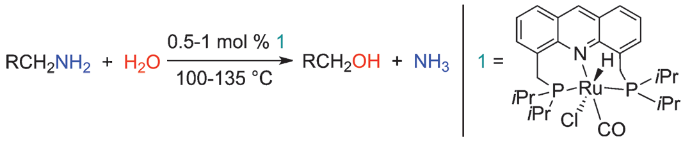


Fresh fruit not rotting vegetables: Ethylene released from fruits and vegetables accelerates their spoiling even in refrigerators. To oxidatively remove traces of ethylene from a gas mix, supported metal nanoparticles were tested. A Pt catalyst supported on mesoporous silica gave complete conversion of 50 ppm ethylene even at 0 °C. IR experiments suggest the facile oxidation of CO over Pt on the silica supports is the key to the catalytic activity.

Cleaving Amines by Water

J. R. Khusnutdinova, Y. Ben-David,
D. Milstein* —————— **6269 – 6272**

Direct Deamination of Primary Amines by Water To Produce Alcohols

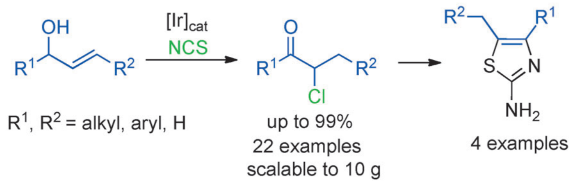


Just add water! The title reaction is catalyzed by an acridine-based pincer complex (**1**, see scheme). This one-step transformation uses water as the only reagent in the absence of additional bases, oxidants, or reductants. Cyclization of 1,4-diaminobutane and 1,6-diaminohexane catalyzed by **1** leads to the formation of pyrrolidine and azepane, respectively.

Synthetic Methods

N. Ahlsten, A. Bermejo Gómez,
B. Martín-Matute* ———— **6273 – 6276**

Iridium-Catalyzed 1,3-Hydrogen Shift/Chlorination of Allylic Alcohols

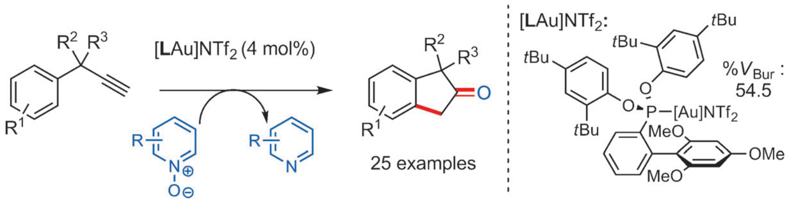


Tandem: Allylic alcohols react with *N*-chlorosuccinimide (NCS) in a tandem 1,3-H shift/C–Cl bond formation leading to α-chloroketones and α-chloroaldehydes. The reactions proceed with complete selectivity to give single constitutional isomers of monochlorinated carbonyl compounds. The utility of the transformation is illustrated by the straightforward synthesis of 4,5-disubstituted 2-aminothiazoles from allylic alcohols.

Homogeneous Catalysis

G. Henrion, T. E. J. Chavas, X. Le Goff, F. Gagosz* ______ **6277 – 6282**

Biarylphosphonite Gold(I) Complexes as Superior Catalysts for Oxidative Cyclization of Propynyl Arenes into Indan-2-ones



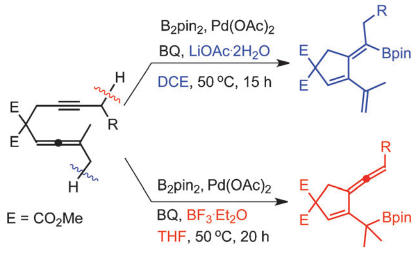
Striking gold: A series of variously functionalized propynyl arenes was smoothly converted into indan-2-ones by a new gold(I)-catalyzed oxidative cyclization process. [LAu]NTf$_2$ (Tf = trifluoromethanesulfonyl) is a superior catalyst both in terms of yield and kinetics for the present transformation.

Synthetic Methods

Y. Deng, T. Bartholomeyzik, J.-E. Bäckvall* ______ **6283 – 6287**

Control of Selectivity in Palladium-Catalyzed Oxidative Carbocyclization/Borylation of Allenynes

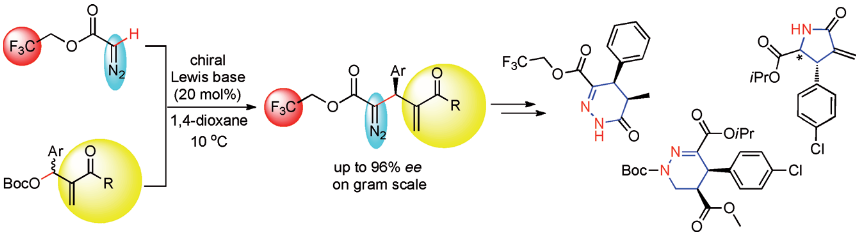
In control: A highly selective carbocyclization/borylation of allenynes with bis(pinacolato)diboron (B$_2$pin$_2$) under palladium catalysis and with *p*-benzoquinone (BQ) as the oxidant was developed. The use of either LiOAc·2 H$_2$O with 1,2-dichloroethane (DCE) as the solvent or BF$_3$·Et$_2$O together with THF is crucial for the selective formation of borylated trienes and vinylallenes, respectively.



Organocatalysis

H. Mao, A. Lin, Y. Shi, Z. Mao, X. Zhu, W. Li, H. Hu, Y. Cheng, C. Zhu* ______ **6288 – 6292**

Construction of Enantiomerically Enriched Diazo Compounds Using Diazo Esters as Nucleophiles: Chiral Lewis Base Catalysis

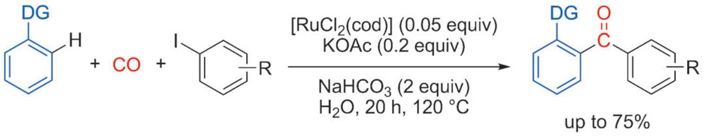


Amazing diazo: The title reaction leads to highly functionalized diazo compounds in good yields with excellent enantioselectivities (see scheme; Boc = *tert*-butoxycarbonyl). The utility of the products was demonstrated by the rapid synthesis of a number of optically pure nitrogen heterocycles. The key to this process was the use of 2,2,2-trifluoroethyl diazoacetate as a superior nucleophilic reagent.

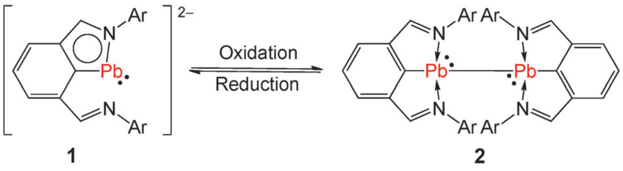
Synthetic Methods

A. Tlili, J. Schranck, J. Pospech, H. Neumann, M. Beller* ______ **6293 – 6297**

Ruthenium-Catalyzed Carbonylative C–C Coupling in Water by Directed C–H Bond Activation



First things first: The title reaction of arenes bearing *ortho*-directing groups (DG) in the presence of a ruthenium catalyst and aryl iodide is presented. The reaction is general for variously substituted aryl iodides to give ketones in moderate to good yields, and water serves as the solvent. The system is highly selective towards the mono-carbonylative arylation by *ortho* C–H functionalization. cod = cyclo-1,5-octadiene.



The aromatic low-valent lead analogue of an indenyl anion (see scheme; **1**) undergoes oxidation with $SnCl_2$ to form the base-stabilized lead(I) dimer **2**. Reduction of **2** with lithium regenerates **1**. These compounds were characterized by NMR spectroscopy and X-ray crystallography.

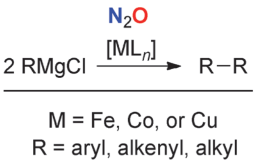
Lead Chemistry

S.-P. Chia, H.-W. Xi, Y. Li, K. H. Lim,
C.-W. So* ______________ **6298 – 6301**

A Base-Stabilized Lead(I) Dimer and an Aromatic Plumbylidenide Anion

---

Catalysis with laughing gas: N_2O in combination with transition-metal catalysts allow the oxidative homo- and cross-coupling of Grignard reagents. The reactions can be performed under mild conditions despite the inert character of N_2O.

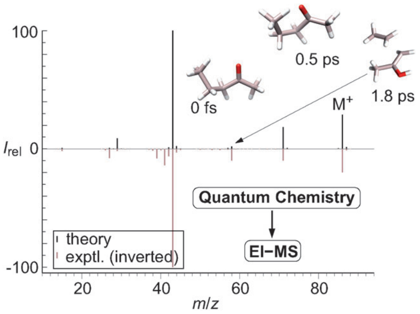


Nitrous Oxide

G. Kiefer, L. Jeanbourquin,
K. Severin* ______________ **6302 – 6305**

Oxidative Coupling Reactions of Grignard Reagents with Nitrous Oxide

---



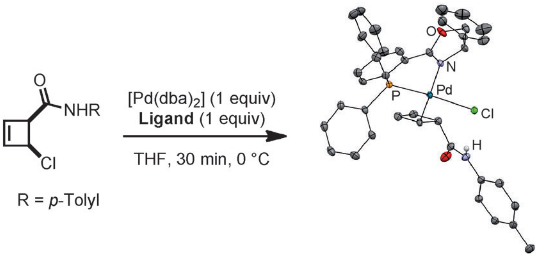
The routine calculation of EI mass spectra is based on a combination of fast quantum chemical methods, molecular dynamics, and the stochastic preparation of "hot" primary ions. All basic elementary processes are considered with minor empiricism and realistic potential free energy surfaces are employed. Reasonable spectra are generated along with detailed information on the corresponding decomposition and reaction mechanisms.

Theoretical Mass Spectrometry

S. Grimme* ______________ **6306 – 6312**

Towards First Principles Calculation of Electron Impact Mass Spectra of Molecules

---



Caught in the act: A series of unique η^1-allyl palladium complexes of four-membered cyclic systems bearing β-hydrogens were prepared (see structure). Their unusual structure, reactivity, and unprecedented propensity for undergoing pericyclic reactions were uncovered.

Palladium Complexes

D. Audisio, G. Gopakumar, L. Xie,
L. G. Alves, C. Wirtz, A. M. Martins,
W. Thiel, C. Farès,
N. Maulide* ______________ **6313 – 6316**

Palladium-Catalyzed Allylic Substitution at Four-Membered-Ring Systems: Formation of η^1-Allyl Complexes and Electrocyclic Ring Opening

Biomimetic Mineralization

S. S. Wang, A. Picker, H. Cölfen,*
A. W. Xu* ______ **6317 – 6321**

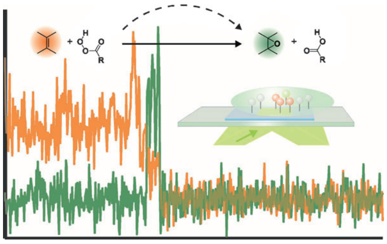
Heterostructured Calcium Carbonate Microspheres with Calcite Equatorial Loops and Vaterite Spherical Cores

It takes two different functional additives to produce the title structures. The proposed mechanism based on the nonclassical particle-mediated crystallization of calcium carbonate demonstrates the individual and cooperative effects of the polymer poly(sodium 4-styrenesulfonate) and small folic acid molecules on the formation of heterostructures at different reaction stages.

Single-Molecule Chemistry

A. Rybina, C. Lang, M. Wirtz,
K. Grußmayer, A. Kurz, F. Maier,
A. Schmitt, O. Trapp, G. Jung,
D.-P. Herten* ______ **6322 – 6325**

Distinguishing Alternative Reaction Pathways by Single-Molecule Fluorescence Spectroscopy



Focus on chemical transitions: Epoxidation of a double bond in conjugation to a fluorescent dye was studied at single-molecule level. Direct observation of oxirane formation, indicated as a spectral shift from substrate to product state, revealed an alternative reaction pathway for the epoxidation reaction.

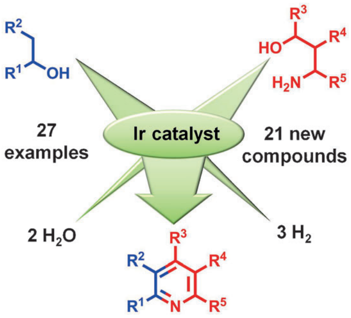
Homogeneous Catalysis

S. Michlik, R. Kempe* ______ **6326 – 6329**

Regioselectively Functionalized Pyridines from Sustainable Resources

Front Cover

Make the most of it! An Ir-catalyzed dehydrogenative condensation of alcohols and 1,3-amino alcohol was used to construct pyridine derivatives regioselectively. This method provides access to unsymmetrically substituted pyridines and tolerates a wide variety of functional groups. Three equivalents of H_2 are generated per pyridine unit formed and the alcohol substrates become completely deoxygenated.

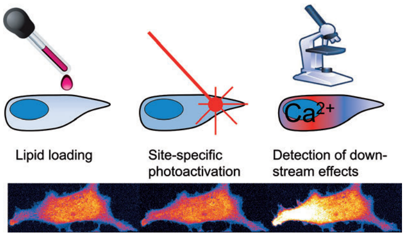


Photoactivatable Lipids

A. Nadler, G. Reither, S. Feng, F. Stein,
S. Reither, R. Müller,
C. Schultz* ______ **6330 – 6334**

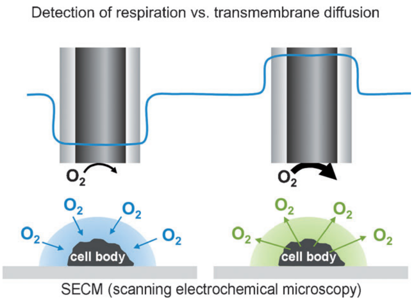
The Fatty Acid Composition of Diacylglycerols Determines Local Signaling Patterns

Back Cover



Caged compounds are designed to release biologically active signaling molecules with temporal, spatial, and even subcellular resolution. But how localized does the signal stay? Using the example of diacylglycerol, some signal responses (PKC) are shown to remain spatially distinct while other signals ($[Ca^{2+}]_i$) spread across the entire cell. Surprisingly, this distribution patterns depend on the fatty acid composition of the lipid species.

SECM at Living Cells



The influence of the reaction rate at the SECM tip on the overall imaging result is often neglected during respiration studies performed by SECM. The effect of the driving force of the tip reaction is elucidated using a potential pulse profile implemented into a constant-distance mode. Time-dependent data acquisition allows visualization of the transition between a tip behaving as a passive observer and a tip actively inducing transmembrane diffusion of oxygen.

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).

This article is available online free of charge (Open Access).

This article is accompanied by a cover picture (front or back cover, and inside or outside).