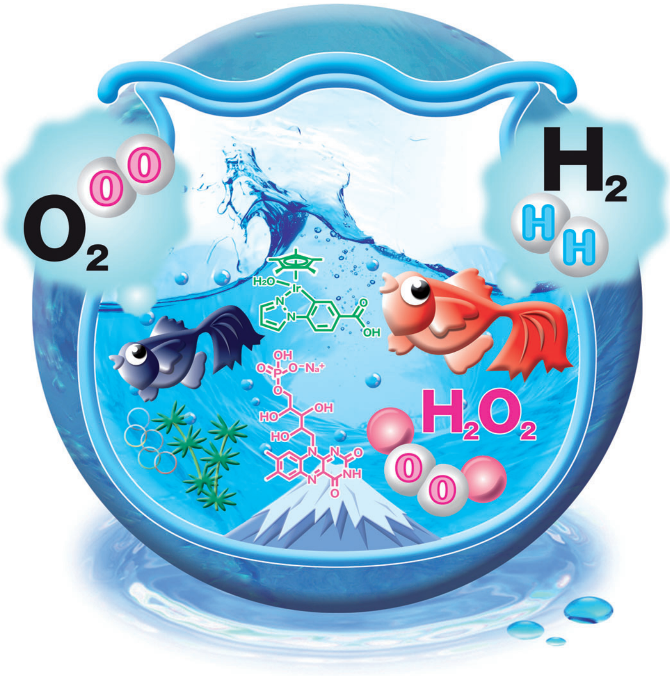
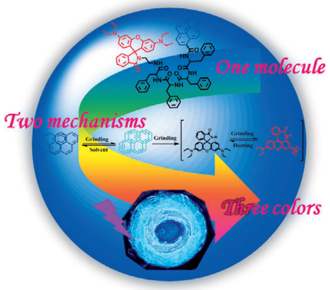
A homogeneous catalytic system …

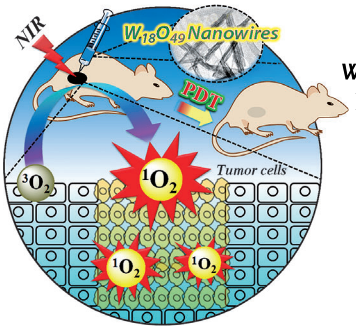


… for the direct synthesis of hydrogen peroxide is presented by S. Fukuzumi and co-workers in their Communication on page 12327 ff. In the presence of an organoiridium complex in combination with flavin mononucleotide (FMN), nontoxic hydrogen and oxygen gases react with each other in water under normal pressure at room temperature to selectively form hydrogen peroxide, a chemical fuel expected to be utilized in future fuel cells.

Mechanochromic Fluorescence

X. R. Jia and co-workers describe in their Communication on page 12268 ff. a single organic molecule containing pyrene and rhodamine B chromophores separated by a peptide spacer that shows tunable multicolored emission on grinding.



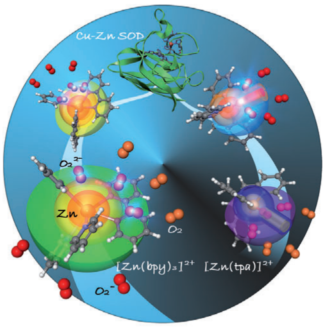


$W_{18}O_{49}$ Nanowires

In their Communication on page 12332 ff., K. C. Hwang et al. report on photodynamic therapy mediated by $W_{18}O_{49}$ nanowires, which leads to the complete destruction of solid tumors in mice.

Enzyme Models

Synthetic Zn^{II} complexes were investigated as models of copper–zinc superoxide dismutase by H. Masuda et al. in their Communication on page 12293 ff. Superoxide undergoes a unique disproportionation reaction in the electrostatic sphere of the complexes.



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

Spotlight on Angewandte's Sister Journals — *12216 – 12219*

Author Profile

Zhong Lin Wang — **12220**

“My biggest inspiration is my love and passion for science. My favorite saying is “doing an experiment is magic, you never know what you will find out next, just do it”. …”
This and more about Zhong Lin Wang can be found on page 12220.

News

Otto Roelen Medal:
B. Cornils — **12221**

Liebig Lectureship:
L. Brunsveld — **12221**

Honorary Professorships:
P. Gregory — **12221**

ChemPubSoc Europe Medal:
E.-E. Wille — **12221**

B. Cornils

L. Brunsveld

P. Gregory

E.-E. Wille

Books

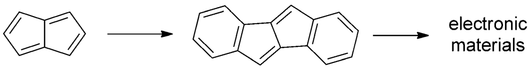
Asymmetric Domino Reactions — Hélène Pellissier — *reviewed by J. Franzén* — **12222**

Highlights

Hydrocarbon Chemistry

H. Hopf* **12224 – 12226**

Pentalenes—From Highly Reactive Antiaromatics to Substrates for Material Science



Antimatter: Once studied primarily for their antiaromatic properties, pentalenes are rapidly becoming important π-systems for novel electronic materials (see scheme). Recent developments in this area are summarized.

Essays

History of Science

W. H. E. Schwarz* **12228 – 12238**

100th Anniversary of Bohr's Model of the Atom

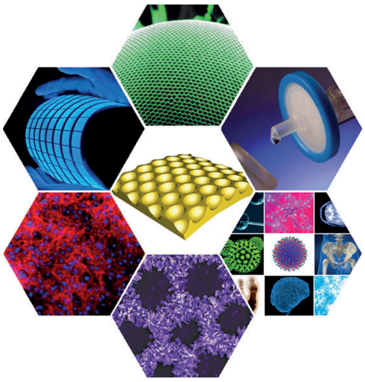
In the fall of 1913 Niels Bohr formulated his atomic models at the age of 27. This Essay traces Bohr's fundamental reasoning regarding atomic structure and spectra, the periodic table of the elements, and chemical bonding. His enduring insights and superseded suppositions are also discussed.

Minireviews

Porous Films

H. Bai, C. Du, A. Zhang, L. Li* **12240 – 12255**

Breath Figure Arrays: Unconventional Fabrications, Functionalizations, and Applications



Every breath you take: A breath figure (BF) is the water droplet array that forms when moisture comes in contact with a cold substrate. Several unconventional BF methods have been established to prepare BF array films with unique morphologies or primary materials, and various newly developed functionalization techniques have significantly improved the performance of BF array films, leading to some novel applications.

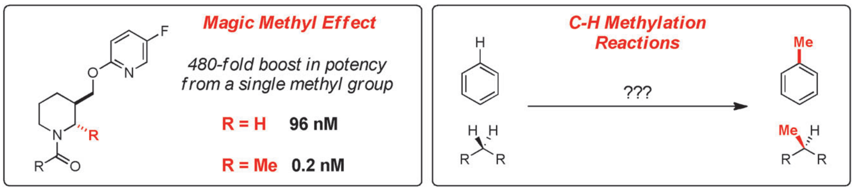
For the USA and Canada: ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. 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

Methylation

H. Schönherr, T. Cernak * 12256 – 12267

Profound Methyl Effects in Drug Discovery and a Call for New C–H Methylation Reactions



It's a kind of magic: The methyl group is one of the most prominent functional groups in bioactive small molecules and appears in more than 67 % of the top-selling drugs. This Review highlights examples of the magic methyl effect, whereby the installation of a single methyl group boosts potency by more than two orders of magnitude. New C–H activation reactions are required to facilitate the direct introduction of methyl groups.

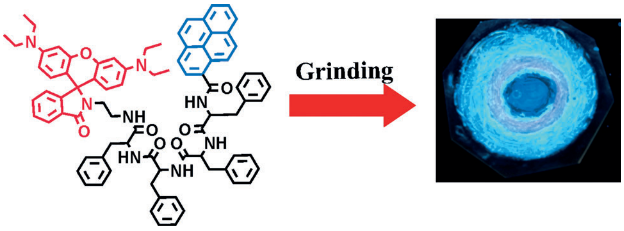
Communications

Mechanochromic Fluorescence

Z. Y. Ma, M. J. Teng, Z. J. Wang, S. Yang, X. R. Jia* 12268 – 12272

Mechanically Induced Multicolor Switching Based on a Single Organic Molecule

Frontispiece

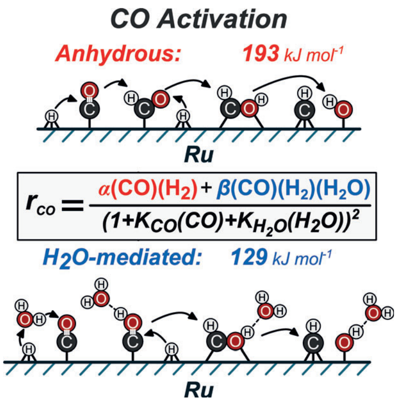


Asserting its independence: A single organic molecule containing pyrene and rhodamine B chromophores separated by a peptide spacer (see structure) formed a mechanochromic material whose fluorescence could be switched from blue to bluish-green and reddish by grinding. Modulation of the overlapped packing pattern of the pyrene excimer for blue emission was crucial for the reversible tricolored switching observed.

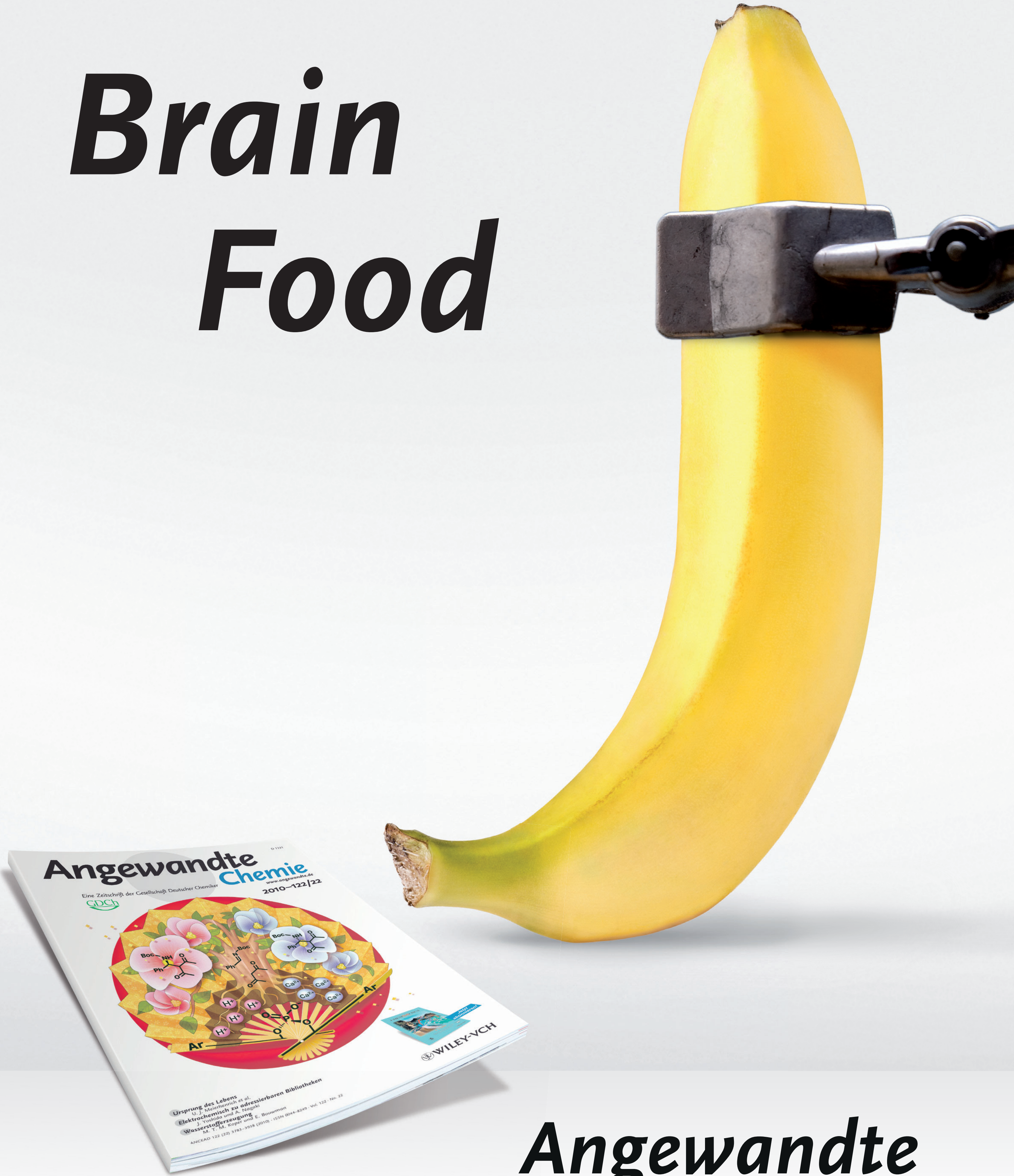
Heterogeneous Catalysis

D. D. Hibbitts, B. T. Loveless, M. Neurock,* E. Iglesia * 12273 – 12278

Mechanistic Role of Water on the Rate and Selectivity of Fischer–Tropsch Synthesis on Ruthenium Catalysts



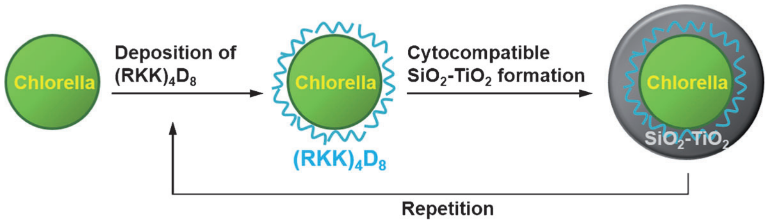
Water increases Fischer–Tropsch synthesis (FTS) rates on Ru through H-shuttling processes. Chemisorbed hydrogen (H*) transfers its electron to the metal and protonates the O-atom of CO* to form COH*, which subsequently hydrogenates to *HCOH* in the kinetically relevant step. H_2O also increases the chain length of FTS products by mediating the H-transfer steps during reactions of alkyl groups with CO* to form longer-chain alkylidynes and OH*.


Brain
Food
Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker
www.angewandte.de
2010–122/22
WILEY-VCH

Bioinspired Mineralization

E. H. Ko, Y. Yoon, J. H. Park, S. H. Yang, D. Hong, K.-B. Lee, H. K. Shon, T. G. Lee, I. S. Choi* ———— **12279 – 12282**

Bioinspired, Cytocompatible Mineralization of Silica–Titania Composites: Thermoprotective Nanoshell Formation for Individual *Chlorella* Cells



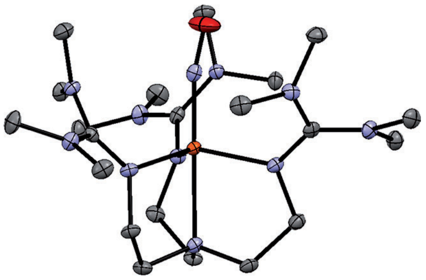
Hard-shell case: Using a $(RKK)_4D_8$ peptide allows mineralization to occur under cytocompatible conditions. Thus individual *Chlorella* cells could be encapsulated within a SiO_2–TiO_2 nanoshell with high cell viability (87%). The encapsulated *Chlorella* showed an almost threefold increase in their thermo-tolerance after 2 h at 45 °C.

Nitroxyl Complexes

A. L. Speelman, N. Lehnert* ———— **12283 – 12287**

Characterization of a High-Spin Non-Heme $\{FeNO\}^8$ Complex: Implications for the Reactivity of Iron Nitroxyl Species in Biology

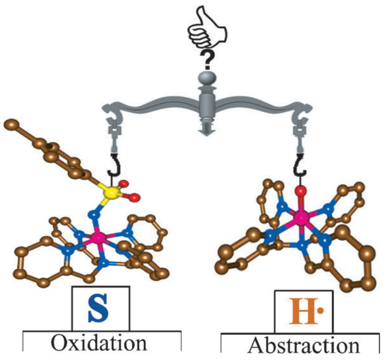
Stable but able: Chemical and electrochemical reduction of a five-coordinate high-spin non-heme $\{FeNO\}^7$ complex (see structure: N blue, Fe orange, and O red) generated the first stable high-spin ($S=1$) non-heme $\{FeNO\}^8$ model complex. The finding that the reduction is metal-centered and causes a decrease in Fe–NO covalency indicates that in biological systems, reduction activates stable non-heme Fe–NO units for further transformations.



Iron(IV)–Imido Complexes

A. K. Vardhaman, P. Barman, S. Kumar, C. V. Sastri,* D. Kumar,* S. P. de Visser* ———— **12288 – 12292**

Comparison of the Reactivity of Nonheme Iron(IV)–Oxo versus Iron(IV)–Imido Complexes: Which is the Better Oxidant?



Which is better? The first detailed comparison of the reactivity of nonheme iron(IV)–imido versus nonheme iron(IV)-oxo intermediates with substrates is presented. The iron(IV)–imido variant reacts with sulfides five times faster than iron(IV)–oxo, whereas the reverse trend is observed for hydrogen atom abstraction. These observed trends are analyzed and explained.

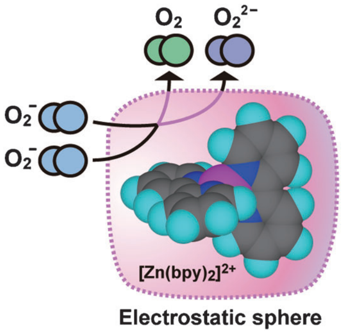
Enzyme Models

A. Wada, K. Jitsukawa, H. Masuda* ———— **12293 – 12297**

Superoxide Disproportionation Driven by Zinc Complexes with Various Steric and Electrostatic Properties

Back Cover

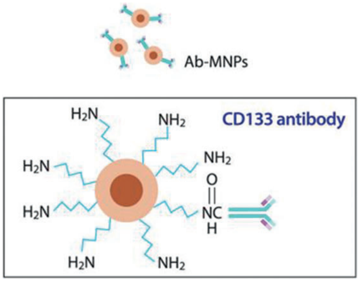
Attractive models: Synthetic Zn^{II} complexes were investigated as models of copper–zinc superoxide dismutase. Superoxide underwent a unique disproportionation reaction in the electrostatic sphere of the complexes (see picture; bpy = 2,2′-bipyridyl). The effectiveness of the Zn^{II} complexes in inducing the disproportionation of superoxide depended on both the Lewis acidity and the coordination geometry of the Zn center.



Magnetic-Tagged Stem Cells

C. N. P. Lui, Y. P. Tsui, A. S. L. Ho,
D. K. Y. Shum,* Y. S. Chan,* C. T. Wu,
H. W. Li,* S. C. E. Tsang,*
K. K. L. Yung* ______ **12298 – 12302**

Neural Stem Cells Harvested from Live Brains by Antibody-Conjugated Magnetic Nanoparticles

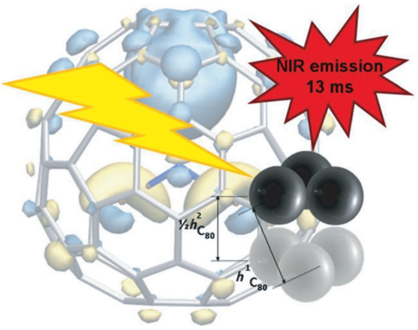


It stems from the magnetism: The extraction of stem/progenitor cells from the brain of live animals is possible using antibodies conjugated to magnetic nanoparticles (Ab-MNPs). The Ab-MNPs are introduced to a rat's brain with a superfine micro-syringe. The stem cells attach to the Ab-MNPs and are magnetically isolated and removed. They can develop into neurospheres and differentiate into different types of cells outside the subject body. The rat remains alive and healthy.

Photophysics

K. Toth, J. K. Molloy, M. Matta,
B. Heinrich, D. Guillon, G. Bergamini,
F. Zerbetto,* B. Donnio,* P. Ceroni,*
D. Felder-Flesch* ______ **12303 – 12307**

A Strongly Emitting Liquid-Crystalline Derivative of $Y_3N@C_{80}$: Bright and Long-Lived Near-IR Luminescence from a Charge Transfer State

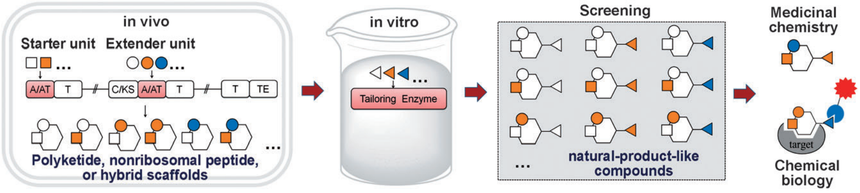


Great balls of fire: C_{60} and $Y_3N@C_{80}$ were connected to the same oligo(phenylene-ethynylene) unit to investigate their structural and photophysical properties. NMR investigations revealed a fulleroid structure for the $Y_3N@C_{80}$ derivative, and both dyads gave rise to columnar phases with core-shell cylinders. The black and gray spheres represent the fullerene core units of the $Y_3N@C_{80}$ derivative, which is an ideal candidate to be involved in energy and electron transfer processes.

Combinatorial Biosynthesis

Y. Yan, J. Chen, L. Zhang, Q. Zheng,
Y. Han, H. Zhang, D. Zhang, T. Awakawa,
I. Abe, W. Liu* ______ **12308 – 12312**

Multiplexing of Combinatorial Chemistry in Antimycin Biosynthesis: Expansion of Molecular Diversity and Utility

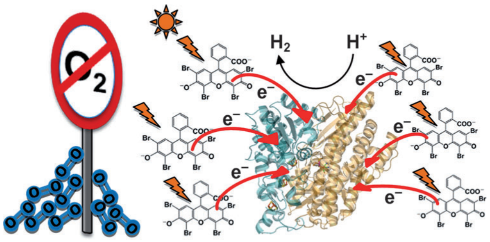


Diversity-oriented biosynthesis of a library of antimycin-like compounds (380 altogether) was accomplished by using multiplex combinatorial biosynthesis. The core strategy depends on the use of combinatorial chemistry at different biosynthetic stages. This approach is applicable for the diversification of polyketides, nonribosomal peptides, and the hybrids that share a similar biosynthetic logic.

Photocatalysis

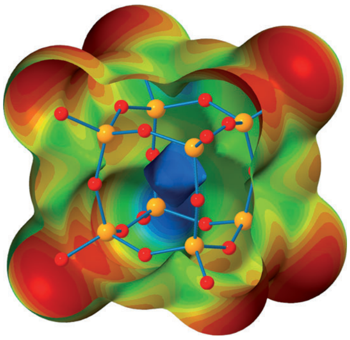
T. Sakai, D. Mersch,
E. Reisner* ______ **12313 – 12316**

Photocatalytic Hydrogen Evolution with a Hydrogenase in a Mediator-Free System under High Levels of Oxygen



Take a breath: An oxygen-tolerant hydrogenase can be employed with a dye in a photocatalytic scheme for the generation of H_2. The homogeneous system does not require a redox mediator and visible-light irradiation yields high amounts of H_2 even in the presence of air.

The w(hole) picture: A tetrel bond is a directional noncovalent interaction between a covalently bonded atom of Group IV and a negative site, for example, the lone pair of a Lewis base or an anion. It involves a region of positive electrostatic potential (σ hole), and energetically, they are comparable to hydrogen bonds and other σ-hole-based interactions.

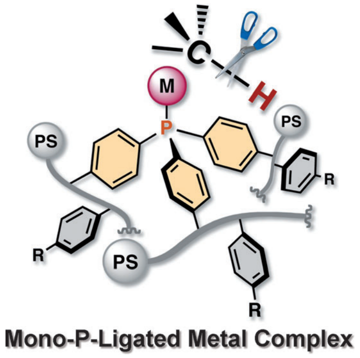


Supramolecular Chemistry

A. Bauzá, T. J. Mooibroek,
A. Frontera* ———— 12317 – 12321

Tetrel-Bonding Interaction: Rediscovered Supramolecular Force?

Covalently bound polystyrene–phosphane hybrids were prepared by a method based on radical emulsion polymerization of styrenes in the presence of a tris(*p*-vinylphenyl)phosphane cross-linker. These hybrids favor mono-P-ligation to transition-metal complexes and are useful for challenging catalysis, such as Pd-catalyzed C−C/C−N couplings with unactivated chloroarenes and Ir- or Rh-catalyzed C(sp^3)−H borylations.

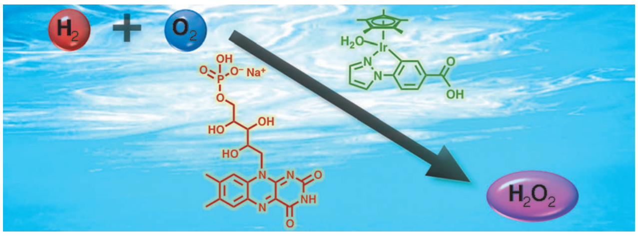


Heterogeneous Catalysis

T. Iwai, T. Harada, K. Hara,
M. Sawamura* ———— 12322 – 12326

Threefold Cross-Linked Polystyrene–Triphenylphosphane Hybrids: Mono-P-Ligating Behavior and Catalytic Applications for Aryl Chloride Cross-Coupling and C(sp^3)−H Borylation

---



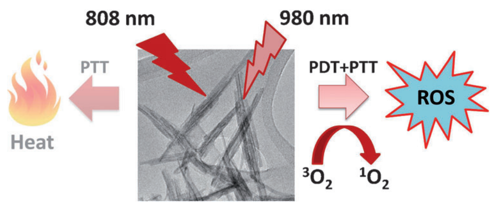
H_2, O_2 to H_2O_2: The direct synthesis of hydrogen peroxide from hydrogen and oxygen in water has been made possible by using an iridium(III) complex, [Ir^{III}-(Cp*)(4-(1*H*-pyrazol-1-yl-κ*N*^{2})benzoic acid-κ*C*^{3})(H$_2$O)]$_2$SO$_4$, and flavin mononucleotide. This method gives hydrogen peroxide with a high turnover number (847) and yield (19.2%) under normal pressure and at room temperature.

Homogeneous Catalysis

S. Shibata, T. Suenobu,
S. Fukuzumi* ———— 12327 – 12331

Direct Synthesis of Hydrogen Peroxide from Hydrogen and Oxygen by Using a Water-Soluble Iridium Complex and Flavin Mononucleotide

Front Cover



Upon excitation with near-infrared light (980 nm), PEGylated W$_{18}$O$_{49}$ nanowires can sensitize the formation of singlet oxygen and thus reactive oxygen species (ROS). The resulting photodynamic therapy (PDT) effect can cause the destruction of tumors in the absence of organic photosensitizers. PEG = poly(ethylene glycol), PTT = photothermal therapy.

Photodynamic Therapy

P. Kalluru, R. Vankayala, C.-S. Chiang,
K. C. Hwang* ———— 12332 – 12336

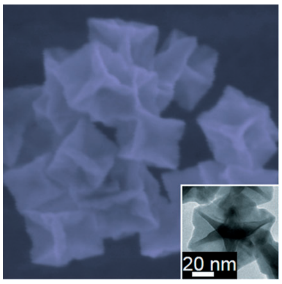
Photosensitization of Singlet Oxygen and In Vivo Photodynamic Therapeutic Effects Mediated by PEGylated W$_{18}$O$_{49}$ Nanowires

Inside Back Cover

Concave Nanocrystals

B. Y. Xia, H. B. Wu, X. Wang,*
X. W. Lou* ______ 12337 – 12340

Highly Concave Platinum Nanoframes with High-Index Facets and Enhanced Electrocatalytic Properties



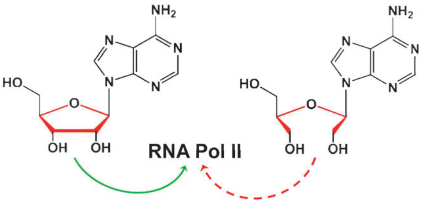
Deeply excavated: Platinum nanoframes with highly concave {740} facets (see picture) are synthesized directly by a facile oleylamine-assisted solvothermal method. Because of the unique structure and exposed high-index facets, the as-prepared Pt nanoframes exhibit very high electrocatalytic activity and remarkable stability for the oxygen reduction reaction and the oxidation of methanol and formic acid.

Nucleic Acid Analogues

L. Xu, S. W. Plouffe, J. Chong, J. Wengel,
D. Wang* ______ 12341 – 12345

A Chemical Perspective on Transcriptional Fidelity: Dominant Contributions of Sugar Integrity Revealed by Unlocked Nucleic Acids

Transcription unlocked: A synthetic chemical biology approach involving unlocked nucleic acids was used to dissect the contribution of sugar backbone integrity to the RNA Polymerase II (Pol II) transcription process. An unexpected dominant role for sugar-ring integrity in Pol II transcriptional efficiency and fidelity was revealed.

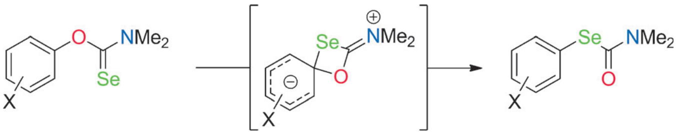


Inside Cover

Synthetic Methods

A. Sørensen, B. Rasmussen, S. Agarwal,
M. Schau-Magnussen, T. I. Sølling,
M. Pittelkow* ______ 12346 – 12349

Conversion of Phenols into Selenophenols: Seleno Newman–Kwart Rearrangement

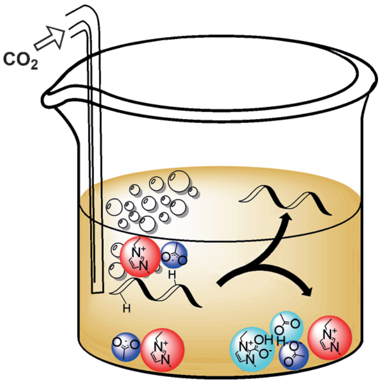


A ‘Se’lling point: The first thermally induced $O_{Ar} \rightarrow Se_{Ar}$ migration reaction is reported, and it can be used to prepare aryl selenols in three steps from the corresponding phenols. *O*-aryl selenocarbamates rearrange to *Se*-aryl carbamates via a four-membered transition state (see scheme). The aryl selenols (isolated as the diselenides) can be prepared by hydrolysis of the *Se*-aryl selenocarbamates.

Ionic Liquids

P. S. Barber, C. S. Griggs, G. Gurau, Z. Liu,
S. Li, Z. Li, X. Lu, S. Zhang,*
R. D. Rogers* ______ 12350 – 12353

Coagulation of Chitin and Cellulose from 1-Ethyl-3-methylimidazolium Acetate Ionic-Liquid Solutions Using Carbon Dioxide

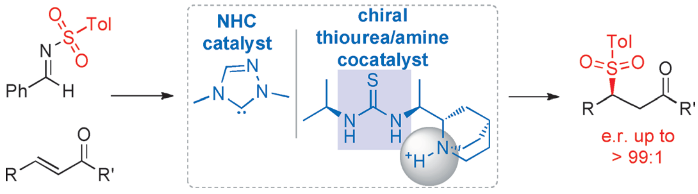


Chemisorption of carbon dioxide by 1-ethyl-3-methylimidazolium acetate ($[C_2mim][OAc]$) provides a route to coagulate chitin and cellulose from $[C_2mim][OAc]$ solutions without the use of high-boiling antisolvents (e.g., water or ethanol). The use of CO_2 chemisorption as an alternative coagulating process has the potential to provide an economical and energy-efficient method for recycling the ionic liquid.

Asymmetric Synthesis

Z. Jin, J. Xu, S. Yang,* B.-A. Song,
Y. R. Chi* ——— 12354 – 12358

Enantioselective Sulfonation of Enones with Sulfonyl Imines by Cooperative N-Heterocyclic-Carbene/Thiourea/Tertiary-Amine Multicatalysis

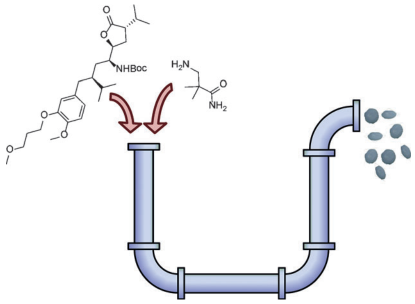


Many hands make light work: In an organocatalytic asymmetric sulfonation of enones, the activation of a sulfonyl imine by an N-heterocyclic carbene (NHC) catalyst led to the release of a sulfinic anion, which underwent nucleophilic addition to the enone. The enantioselectivity of the process was controlled by a chiral thiourea/amine co-catalyst through anion recognition and hydrogen-bonding interactions. Tol = *p*-tolyl.

Continuous Drug Manufacturing

S. Mascia, P. L. Heider, H. Zhang,
R. Lakerveld, B. Benyahia, P. I. Barton,
R. D. Braatz, C. L. Cooney, J. M. B. Evans,
T. F. Jamison, K. F. Jensen, A. S. Myerson,
B. L. Trout* ——— 12359 – 12363

End-to-End Continuous Manufacturing of Pharmaceuticals: Integrated Synthesis, Purification, and Final Dosage Formation

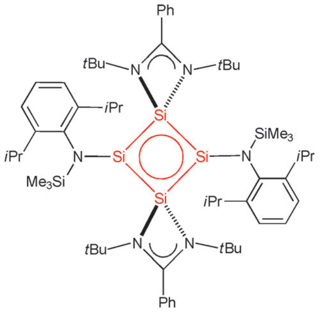


A series of tubes: The continuous manufacture of a finished drug product starting from chemical intermediates is reported. The continuous pilot-scale plant used a novel route that incorporated many advantages of continuous-flow processes to produce active pharmaceutical ingredients and the drug product in one integrated system.

Silicon Compounds

S.-H. Zhang, H.-W. Xi, K. H. Lim,
C.-W. So* ——— 12364 – 12367

An Extensive n, π, σ-Electron Delocalized Si_4 Ring

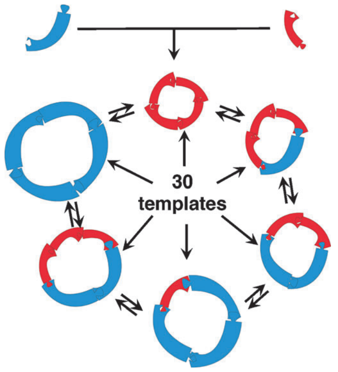


The tetrasilacyclobutadiene $[LSi(\mu\text{-}SiL')_2SiL]$ ($L = PhC(NtBu)_2$, $L' = 2,6\text{-}iPr_2C_6H_3NSiMe_3$) consists of an aromatic silicon-containing four-membered ring in which two π, two σ, and two lone-pair electrons are cyclically delocalized. The electron delocalization was illustrated by theoretical studies and reactivity with elemental sulfur to form the allylic zwitterionic cyclic compound $[(LSi)_2(\mu\text{-}SiL')(\mu\text{-}Si(S)L')]$ with 2π-electron delocalization along the Si_3 skeleton.

Molecular Recognition

S. Hamieh, V. Saggiomo, P. Nowak,
E. Mattia, R. F. Ludlow,
S. Otto* ——— 12368 – 12372

A "Dial-A-Receptor" Dynamic Combinatorial Library

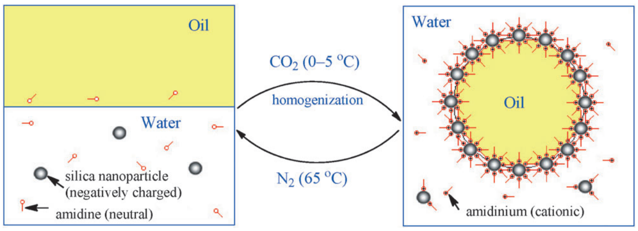


Making receptors to order: A small dynamic combinatorial library (DCL), formed from two dithiols in water, provides a continuous range of six receptors of different sizes. The majority of the 30 tested amines and ammonium ions amplified receptors from this library, thus spanning the complete receptor-size range and showing that this DCL provides a generic platform for the development of receptors for this important class of compounds.

Switchable Emulsions

J. Jiang, Y. Zhu, Z. Cui,*
B. P. Binks* ________ **12373 – 12376**

Switchable Pickering Emulsions Stabilized by Silica Nanoparticles Hydrophobized In Situ with a Switchable Surfactant

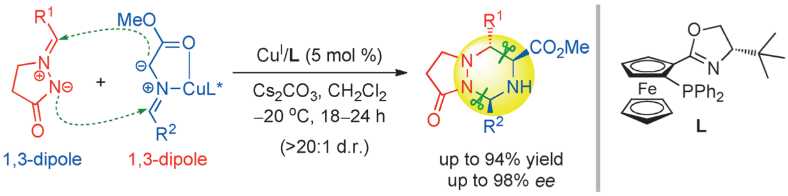


Back and forth: The CO$_2$/N$_2$ trigger of a switchable surfactant (neutral amidine/cationic amidinium) was transferred to mineral nanoparticles through in situ hydrophobization in water. Switchable oil-in-water Pickering emulsions that entail a CO$_2$/N$_2$ trigger were obtained by using negatively charged silica nanoparticles and a trace amount of the switchable surfactant as the stabilizer.

Asymmetric Catalysis

M.-C. Tong, X. Chen, H.-Y. Tao,
C.-J. Wang* ________ **12377 – 12380**

Catalytic Asymmetric 1,3-Dipolar Cycloaddition of Two Different Ylides: Facile Access to Chiral 1,2,4-Triazinane Frameworks

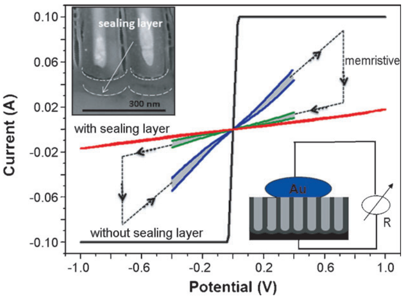


Ylides at a crossing: An unprecedented 1,3-dipolar cycloaddition (cross-cycloaddition) between two different ylides (see scheme) was realized by using the chiral Cu^I/*t*Bu-Phosferrox complex as the catalyst under mild reaction conditions. This catalytic system provides an expeditious approach to the construction of highly functionalized 1,2,4-triazinane derivatives in good yields with excellent diastereoselectivities and enantioselectivities.

Electrodeposition

N. Liu, K. Lee,
P. Schmuki* ________ **12381 – 12384**

Reliable Metal Deposition into TiO$_2$ Nanotubes for Leakage-Free Interdigitated Electrode Structures and Use as a Memristive Electrode

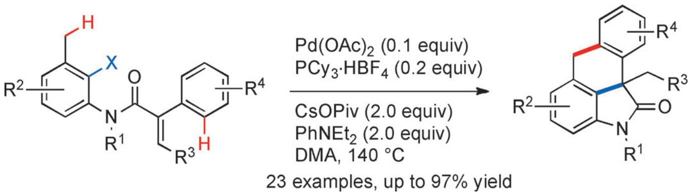


Nearly 100 % filling of TiO$_2$ nanotubes with metals, including Ag, Cu, Au, and Pt, was achieved by defect-sealing treatment at the bottom of the nanotubes, followed by metal deposition using nuclei formation/coalescence. The resulting short-circuit-free interdigitated electrode configurations can, for example, be used to fabricate memristive electrodes.

Synthetic Methods

T. Piou, A. Bunescu, Q. Wang, L. Neuville,
J. Zhu* ________ **12385 – 12389**

Palladium-Catalyzed Through-Space C(sp^3)–H and C(sp^2)–H Bond Activation by 1,4-Palladium Migration: Efficient Synthesis of [3,4]-Fused Oxindoles

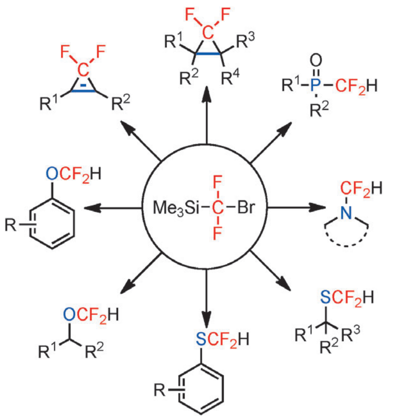


Palladium two step: Linear anilides were converted into the title compounds in good to excellent yields through a palladium-catalyzed domino carbopalladation/1,4-palladium shift sequence. The C(sp^3)-H activation involves a seven-membered palladacycle, and is chemoselective in the presence of competitive C(sp^2)–H bonds. DMA = *N*,*N*-dimethylacetamide, OPiv = pivalate.

Synthetic Methods

L. Li, F. Wang, C. Ni,
J. Hu* ______ 12390 – 12394

Synthesis of *gem*-Difluorocyclopropa(e)nes and O-, S-, N-, and P-Difluoromethylated Compounds with $TMSCF_2Br$

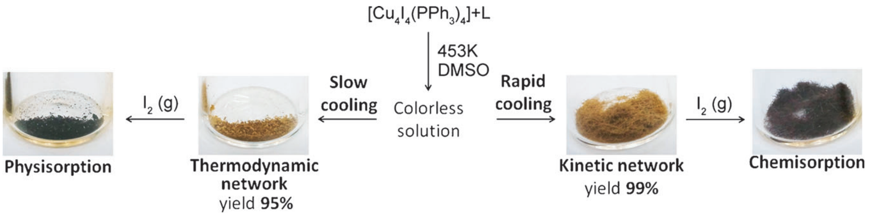


Two-in-one: Me_3SiCF_2Br is an efficient difluorocarbene source and is compatible with both neutral and aqueous basic conditions. Bromide-ion-initiated [2+1] cycloaddition with alkenes/alkynes and hydroxide ion promoted α-addition with (thio)phenols, (thio)alcohols, sulfinates, heterocyclic amines, and H-phosphine oxides give the corresponding *gem*-difluorinated compounds with broad functional-group tolerance.

Porous Coordination Networks

H. Kitagawa, H. Ohtsu,
M. Kawano* ______ 12395 – 12399

Kinetic Assembly of a Thermally Stable Porous Coordination Network Based on Labile CuI Units and the Visualization of I_2 Sorption

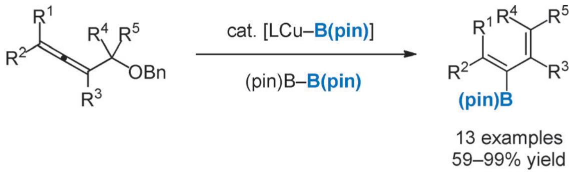


A net gain: A kinetically assembled, but thermally stable network is obtained using the labile metal species $[Cu_4I_4(PPh_3)_4]$. The network uniquely adsorbs I_2 by chemisorption through I_3^- formation. The chemisorbed I_2 readily desorbs above 380 K owing to the dynamic motion of the framework. A thermodynamically assembled network physisorbs I_2, which is an exact fit for the channel.

Synthetic Methods

K. Semba, T. Fujihara, J. Terao,
Y. Tsuji* ______ 12400 – 12403

Copper-Catalyzed Borylation of α-Alkoxy Allenes with Bis(pinacolato)diboron: Efficient Synthesis of 2-Boryl 1,3-Butadienes

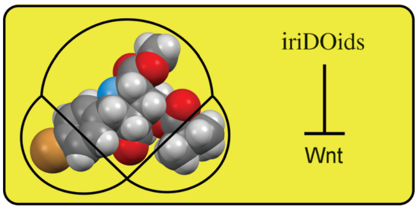


Something solid to build on: 2-Boryl 1,3-butadienes with various substitution patterns were formed in good to high yields in a copper-catalyzed borylation of α-alkoxy allenes with bis(pinacolato)diboron (see scheme; Bn = benzyl, pin = pinacolate, L is an N-heterocyclic carbene ligand). The products were found to be useful intermediates for the synthesis of cyclic vinyl boranes, α,β-unsaturated ketones, and functionalized multisubstituted dienes.

Biology-Oriented Synthesis

H. Takayama, Z.-J. Jia, L. Kremer,
J. O. Bauer, C. Strohmann, S. Ziegler,
A. P. Antonchick,*
H. Waldmann* ______ 12404 – 12408

Discovery of Inhibitors of the Wnt and Hedgehog Signaling Pathways through the Catalytic Enantioselective Synthesis of an Iridoid-Inspired Compound Collection



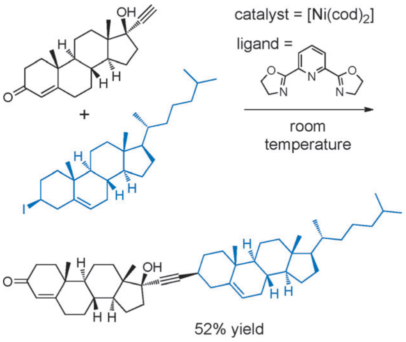
Cousins you can count on: An iridoid-inspired compound collection was synthesized efficiently by the resolution of cyclic enones in an asymmetric cycloaddition with azomethine ylides. The collection contained novel potent inhibitors of the Wnt and Hedgehog signaling pathways.

Cross-Coupling

J. Yi, X. Lu, Y.-Y. Sun, B. Xiao,
L. Liu* ———— 12409 – 12413

Nickel-Catalyzed Sonogashira Reactions of Non-activated Secondary Alkyl Bromides and Iodides

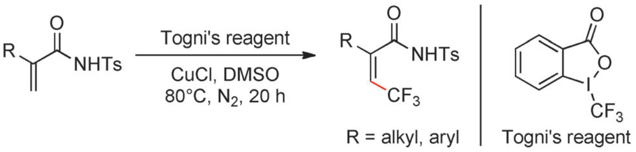
A nicked reaction: The title reaction of terminal alkynes with non-activated secondary alkyl iodides and bromides was accomplished for the first time. This reaction provides a new and practical approach for the synthesis of substituted alkynes (see scheme; cod = cyclo-1,5-octadiene).



Trifluoromethylation

C. Feng, T.-P. Loh* ———— 12414 – 12417

Directing-Group-Assisted Copper-Catalyzed Olefinic Trifluoromethylation of Electron-Deficient Alkenes

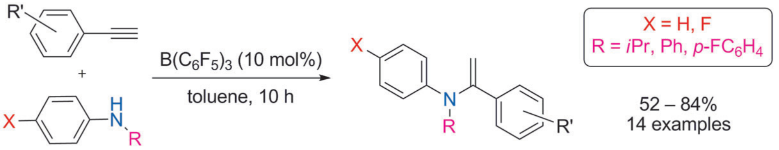


Assistance provided: The directing group in the title reaction not only activates the substrates but also allows the stereospecific formation of *cis*-trifluoromethylated products. The reaction is operationally simple and tolerates a wide variety of functional groups, thus providing an efficient method for the stereoselective synthesis of β-CF_3-functionalized acrylamide derivatives.

Hydroamination

T. Mahdi, D. W. Stephan* 12418 – 12421

Frustrated Lewis Pair Catalyzed Hydroamination of Terminal Alkynes

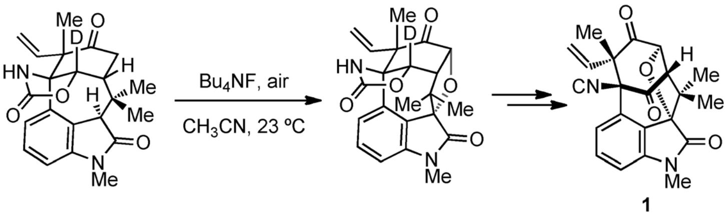


Catalytic amounts of the Lewis acid $B(C_6F_5)_3$ enable the hydroamination of terminal alkynes by aryl amines to the corresponding enamines. In accord with the results of stoichiometric reactions, the mechanism of this reaction involves a frustrated Lewis pair (FLP). The hydroamination can be followed by an FLP-catalyzed hydrogenation, resulting in a one-pot stepwise synthesis of amine derivatives.

Natural Product Synthesis

E. D. Styduhar, A. D. Huters, N. A. Weires,
N. K. Garg* ———— 12422 – 12425

Enantiospecific Total Synthesis of *N*-Methylwelwitindolinone D Isonitrile

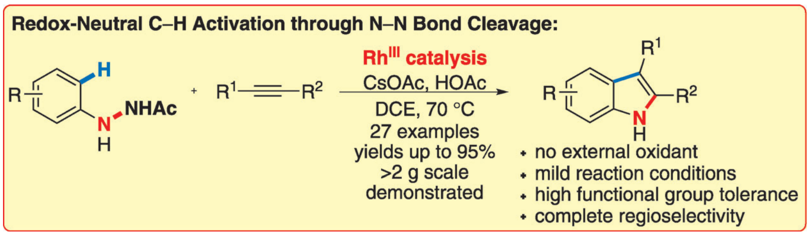


The total synthesis of *N*-methylwelwitindolinone D isonitrile (**1**) has been achieved in 17 steps from a readily available carvone derivative. The route features a double C–H functionalization event involving a keto oxindole substrate to introduce the tetrahydrofuran ring of the natural product.

Heteroarenes

D. Zhao, Z. Shi,
F. Glorius* ____ 12426 – 12429

Indole Synthesis by Rhodium(III)-Catalyzed Hydrazine-Directed C–H Activation: Redox-Neutral and Traceless by N–N Bond Cleavage

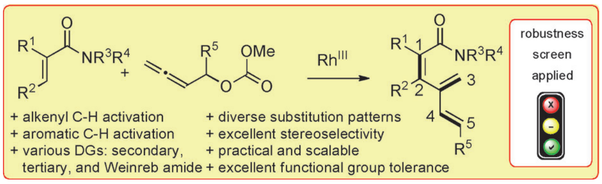


Fishing for complements! There is an alternative to the useful Fischer indole synthesis. The new method utilizes the same retrosynthetic disconnection but is based on a Rh^{III}-catalyzed directed C–H activation step and a successive coupling with alkynes.

C–H Activation

H. Wang, B. Beiring, D.-G. Yu,
K. D. Collins, F. Glorius* ____ 12430 – 12434

[3]Dendralene Synthesis: Rhodium(III)-Catalyzed Alkenyl C–H Activation and Coupling Reaction with Allenyl Carbinol Carbonate

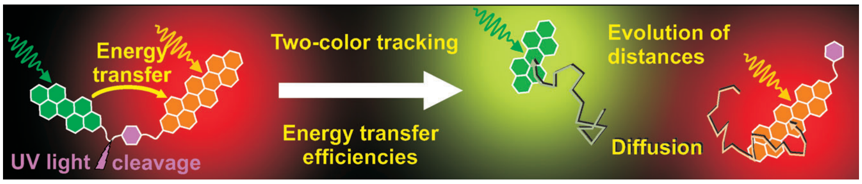


[3]DendrAl(l)ene! A new synthesis of [3]dendralenes is based on a Rh^{III}-catalyzed alkenyl C–H activation and coupling reaction with allenyl carbinol carbonates (see scheme; DG = directing group). A variety of [3]dendralenes with diverse substitution patterns are accessible with good efficiency. The reaction is highly stereoselective and compatible with different directing groups and numerous functional groups.

Fluorescence Microscopy

M. Dill, M. C. Baier, S. Mecking,
D. Wöll* ____ 12435 – 12438

Enhanced Accuracy of Single-Molecule Diffusion Measurements with a Photocleavable Energy-Transfer Dyad

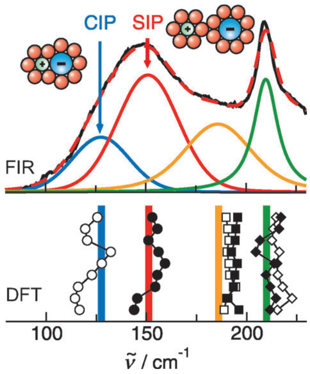


A photocleavable energy-transfer dyad was synthesized, characterized, and applied to single-molecule fluorescence microscopy. After photocleavage, a combination of independent two-color single-molecule tracking and analysis of single-molecule energy-transfer efficiencies allows the determination of the temporal evolution of the relative distances between both fragments from the nm to the μm scale. This gives access to a broad range of diffusion coefficients.

Ion Pairing

K. Fumino, P. Stange, V. Fossog,
R. Hempelmann,
R. Ludwig* ____ 12439 – 12442

Equilibrium of Contact and Solvent-Separated Ion Pairs in Mixtures of Protic Ionic Liquids and Molecular Solvents Controlled by Polarity



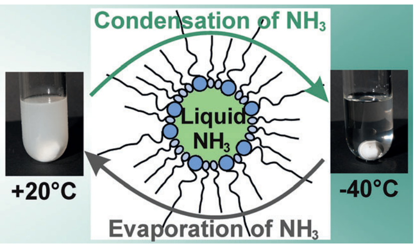
Polarity controls the equilibrium constants and free energies of contact ion pairs (CIPs) and solvent-separated ion pairs (SIPs) in mixtures of protic ionic liquids and molecular solvents. The subtle balance between the ionic species was studied by far-infrared difference spectra and related DFT-calculated properties for solvents of low and high polarity and for different solvent concentrations.

Nanoparticle Synthesis

F. Gyger, P. Bockstaller, D. Gerthsen, C. Feldmann* ———— **12443 – 12447**

Ammonia-in-Oil-Microemulsions and Their Application

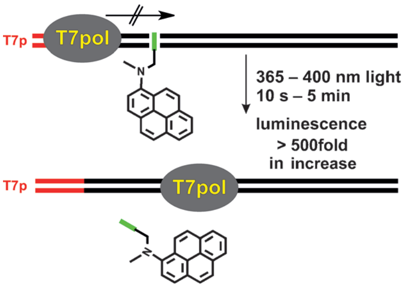
Liquid ammonia on the nanoscale: Ammonia-in-oil microemulsions are used to synthesize Bi, Re, CoN, and GaN nanoparticles, which can be obtained without further thermal treatment. These microemulsions are as reproducible and simple as their water-in-oil conterparts, with the exception of the required low temperature of −40 °C.



Photoprotected Genes

T. Stafforst,* J. M. Stadler **12448 – 12451**

Photoactivation of a Psoralen-Blocked Luciferase Gene by Blue Light



A single psoralen cross-link completely blocks expression of a gene. An aminopyrene derivative has been found that allows the efficient light-triggered activation of cross-linked genes by UV or blue light. This paves the way to apply such psoralen cross-links for the photocleavable protection of nucleic acids.

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).

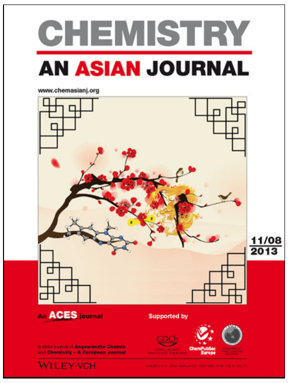
This article is available online free of charge (Open Access).

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

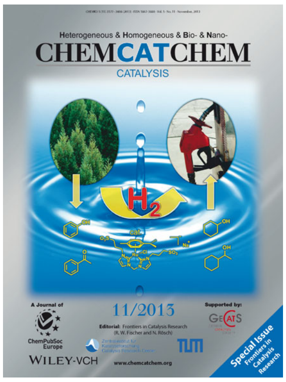
The Very Important Papers, marked VIP, have been rated unanimously as very important by the referees.

The Hot Papers are articles that the Editors have chosen on the basis of the referee reports to be of particular importance for an intensely studied area of research.

Check out these journals:

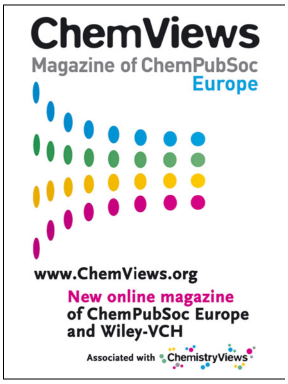


www.chemasianj.org



www.chemcatchem.org

www.chempluschem.org



www.chemviews.org