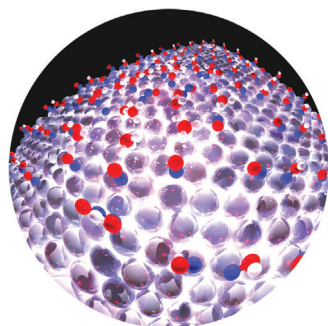
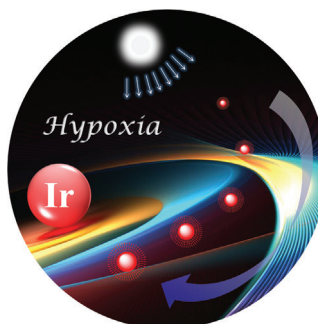




... were described by Aristotle as early as the fourth century B.C. In their Communication on page 8124 ff., I. V. Yampolsky, J. I. Gitelson, and co-workers unveil the structure of fungal luciferin, a compound that is responsible for fungal bioluminescence.

Cancer Diagnostics

A hypoxia-sensitive sensor for tracking cancer metastasis is reported by X. Q. Jiang et al. on page 8094 ff. After systemic administration of the sensor, cancer cells metastasizing to the lungs or to the lymph nodes are detected by whole-body optical imaging.



NO Electroreduction

The crucial role of water in determining the mechanism of NO electroreduction to ammonia on Pt(111) surfaces is investigated by J. Greeley et al. in their Communication on page 8255 ff. Water facilitates proton transfer to adsorbed surface intermediates with very low kinetic barriers.

Porphyrinoids

M. Bröring et al. present the first free-base corrole radical in their Communication on page 8213 ff. Loss of an inner hydrogen atom from the air-stable, easy-to-handle porphyrinoid gives a planar molecule that can, for example, bind Zn^{2+} .



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"... There is more than what meets the eye. After 25 years of optical experiments on single molecules, it is time to reflect on the insights and the present or potential applications that single-molecule optics, and more generally single-molecule chemistry, have brought to us. Subtle and detailed information can be gleaned from the wealth of signals single molecules relay to us from their nanometer-scale environment ..."

Read more in the Editorial by Michel Orrit.

Editorial

M. Orrit* _____ 8004–8005

Single-Molecule Chemistry is More than
Superresolved Fluorescence Microscopy

Spotlight on Angewandte's Sister Journals

Service

8024–8027



"I admire dedication and true achievement—in all areas of life.

My favorite way to spend a holiday is motorcycling (or skiing, depending on the season) in the Alps ..."

This and more about Albrecht Berkessel can be found on page 8028.

Author Profile

Albrecht Berkessel _____ 8028



K. Matyjaszewski



E. P. Balskus



W. Min



D. A. Nicewicz



J. A. Prescher

News

Dreyfus Prize:

K. Matyjaszewski _____ 8029

Camille Dreyfus Teacher-Scholar Awards:

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and J. A. Prescher _____ 8029

Books

Methods and Applications of
Cycloaddition Reactions in Organic
Synthesis

Nagatoshi Nishiwaki

reviewed by B. Witulski* _____ 8030

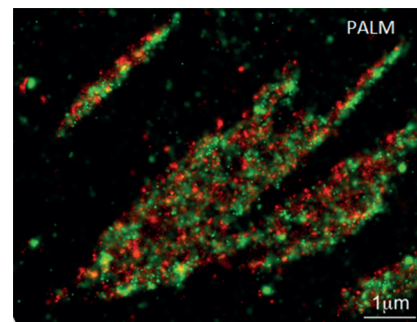
Nobel Lectures

Super-Resolution Microscopy

E. Betzig* _____ 8034 – 8053

Single Molecules, Cells, and Super-
Resolution Optics (Nobel Lecture)

The resolution of a microscope is determined by the diffraction limit in classical microscopy, whereby objects that are separated by half a wavelength can no longer be visually separated. To go below the diffraction limit required several tricks and discoveries. In his Nobel Lecture, E. Betzig describes the developments that have led to modern super high-resolution microscopy.



Super-Resolution Microscopy

S. W. Hell* _____ 8054 – 8066

Nanoscopy with Focused Light (Nobel
Lecture)

A picture is worth a thousand words—This doesn't only apply to everyday life but also to the natural sciences. It is, therefore, probably not by chance that the historical beginning of modern natural sciences very much coincides with the invention of light microscopy. S. W. Hell shows in his Nobel Lecture that the diffraction resolution barrier has been overcome by using molecular state transitions (e.g. on/off) to make nearby molecules transiently discernible.

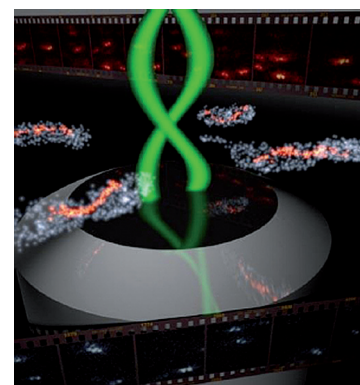


Super-Resolution Microscopy

W. E. Moerner* _____ 8067 – 8093

Single-Molecule Spectroscopy, Imaging,
and Photocontrol: Foundations for Super-
Resolution Microscopy (Nobel Lecture)

In the early 90s, many fascinating physical effects were observed when ensemble averaging was removed to allow study of individual molecules. The imaging of single molecules as well as observations of spectral diffusion, optical switching, and the ability to select different single molecules in the same focal volume by tuning the pumping laser frequency provided important forerunners of the later super-resolution microscopy with single molecules.



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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.

Communications

Cancer Diagnostics

X. C. Zheng, H. Tang, C. Xie, J. L. Zhang, W. Wu, X. Q. Jiang* — 8094–8099

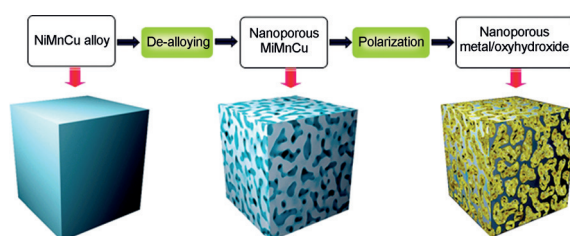
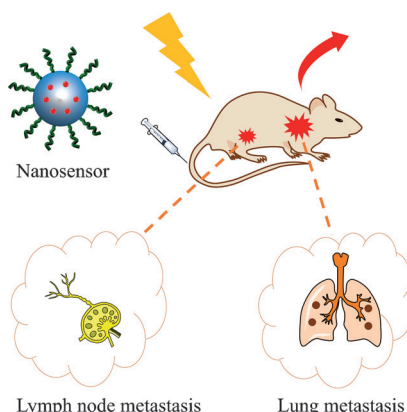
Tracking Cancer Metastasis In Vivo by Using an Iridium-Based Hypoxia-Activated Optical Oxygen Nanosensor



Frontispiece



Tracking down cancer: A hypoxia-sensitive optical oxygen nanosensor is reported for tracking cancer metastasis in vivo. After systemic administration of the nanosensor, cancer cells metastasizing to the lungs through the blood stream or to the lymph node through lymphatics can be effectively detected by whole-body optical imaging.



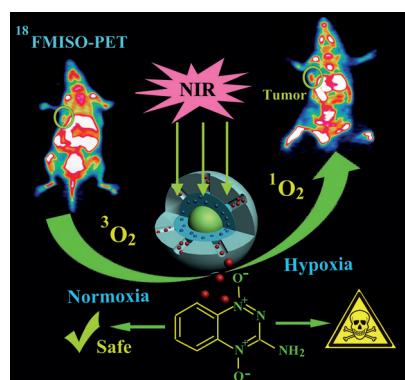
Electrochemical polarization of a de-alloyed nanoporous NiCuMn alloy was employed to synthesize a novel multicomponent mixed-valence oxyhydroxide based electrode. The oxyhydroxide/metal electrode possesses both high specific

capacitance (627 F cm^{-3}) at a current density of 0.25 A cm^{-3} and a wide working-potential window (1.8 V) in aqueous electrolyte, thereby resulting in a high energy and power densities with excellent cyclic stability.

Electrochemistry

J. L. Kang, A. Hirata, L. Y. Chen, S. L. Zhu, T. Fujita, M. W. Chen* — 8100–8104

Extraordinary Supercapacitor Performance of a Multicomponent and Mixed-Valence Oxyhydroxide



Synergistic therapy: Strong hypoxia created by upconversion photodynamic therapy (UC-PDT) activates bioreductive pro-drugs co-delivered to form cytotoxic species, thereby potentiating the synergistic anticancer efficacy of UC-PDT. This process was accomplished by using upconversion-based nanoparticles designed to simultaneously deliver photosensitizer molecules and bioreductive pro-drugs in silica layers.

Nanotechnology

Y. Liu, Y. Liu, W. Bu,* C. Cheng, C. Zuo, Q. Xiao, Y. Sun, D. Ni, C. Zhang, J. Liu, J. Shi* — 8105–8109

Hypoxia Induced by Upconversion-Based Photodynamic Therapy: Towards Highly Effective Synergistic Bioreductive Therapy in Tumors

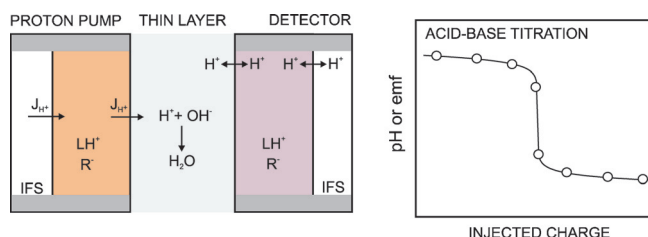


Electrochemistry

M. G. Afshar, G. A. Crespo,
E. Bakker* 8110–8113



Thin-Layer Chemical Modulations by
a Combined Selective Proton Pump and
pH Probe for Direct Alkalinity Detection



A chemically selective electrochemical proton pump creates a concentration perturbation in a thin-layer sample that is detected by a pH probe placed opposite. The proposed methodology is applicable

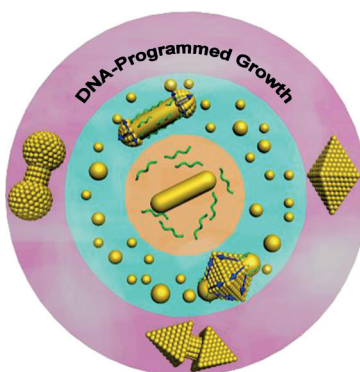
for a range of ions and is demonstrated here for direct alkalinity measurements. L = ionophore; R⁻ = cation exchanger; J_{H+} = proton flux; IFS = inner filling solution.

Gold Nanoparticles

T. Song, L. Tang, L. H. Tan, X. Wang,
N. S. R. Satyavolu, H. Xing, Z. Wang, J. Li,
H. Liang,* Y. Lu* 8114–8118



DNA-Encoded Tuning of Geometric and
Plasmonic Properties of Nanoparticles
Growing from Gold Nanorod Seeds



Controlling nanoparticle morphology was achieved by tuning the overgrowth of gold nanorods using DNA as a capping ligand. Kinetic studies show two representative pathways for the shape control. Furthermore, the geometric and plasmonic properties of the gold nanoparticles could be precisely controlled by adjusting the base composition of the DNA sequences or by introducing phosphorothioate modifications in the DNA.

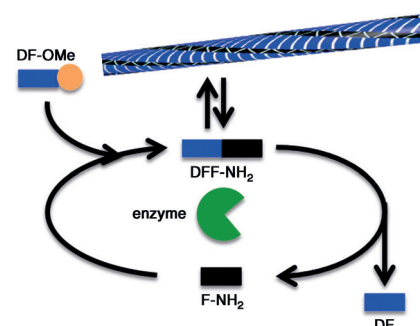
Biocatalytic Self-Assembly

C. G. Pappas, I. R. Sasselli,
R. V. Uljin* 8119–8123



Biocatalytic Pathway Selection in
Transient Tripeptide Nanostructures

Off the beaten track: Sequence-dependent kinetic pathway selection in chemically fueled catalytic self-assembly of tripeptides is demonstrated, in which the control of the lifetime of the nanostructures is dictated by chemical design. Mimicking the unique features of these systems may open up opportunities to create supramolecular systems for non-equilibrium motility and shape control.



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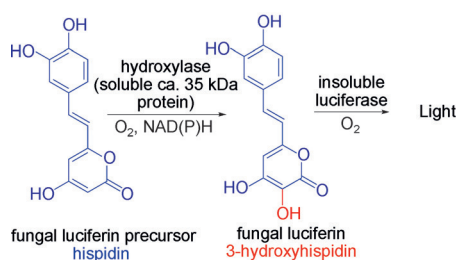
We create chemistry

Bioluminescence

K. V. Purtov, V. N. Petushkov,
M. S. Baranov, K. S. Mineev,
N. S. Rodionova, Z. M. Kaskova,
A. S. Tsarkova, A. I. Petunin, V. S. Bondar,
E. K. Rodicheva, S. E. Medvedeva, Y. Oba,
Y. Oba, A. S. Arseniev, S. Lukyanov,
J. I. Gitelson,*
I. V. Yampolsky* ————— 8124–8128



The Chemical Basis of Fungal
Bioluminescence



Getting the green light: Hispidin is shown to be a luciferin precursor in at least four evolutionary distant genera of luminous fungi. However, its biosynthesis alone does not result in fungal biolumines-

cence. Two enzymes are required: first a hydroxylase converts the hispidin into 3-hydroxyhispidin, which acts as the luciferin, which undergoes a subsequent oxidation in the presence of a luciferase.

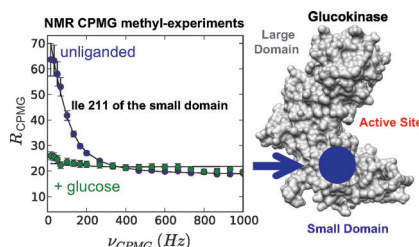
Front Cover

Protein Dynamics

M. Larion, A. L. Hansen, F. Zhang,
L. Bruschweiler-Li, V. Tugarinov,
B. G. Miller,
R. Bruschweiler* ————— 8129–8132



Kinetic Cooperativity in Human
Pancreatic Glucokinase Originates from
Millisecond Dynamics of the Small
Domain



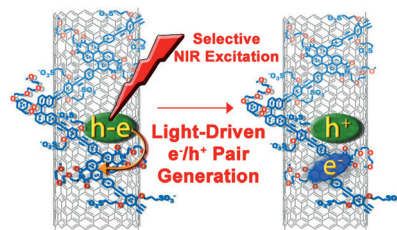
Distant but decisive: Kinetic cooperativity is an intrinsic property of glucokinase that enables it to maintain whole-body glucose homeostasis. The small-domain dynamics of glucokinase on the millisecond timescale have now been quantified by NMR spectroscopic experiments and found to be responsible for this effect by interfering with the turnover rate constant and generating non-Michaelis–Menten kinetics (see picture).

Semiconducting Nanostructures

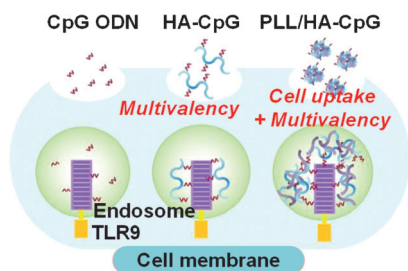
J.-H. Olivier, J. Park, P. Deria, J. Rawson,
Y. Bai, A. S. Kumbhar,
M. J. Therien* ————— 8133–8138



Unambiguous Diagnosis of Photoinduced
Charge Carrier Signatures in
a Stoichiometrically Controlled
Semiconducting Polymer-Wrapped
Carbon Nanotube Assembly



Nanohybrid compositions based on (6,5) chirality-enriched SWNTs and a chiral n-type polymer (S-PBN(b)-Ph₄PDI) that exploits a perylenediimide-containing repeat unit undergo light-driven electron–hole pair generation. Rigorously controlled SWNT:electron acceptor stoichiometry and organization enable spectroscopic characterization of the photoinduced charge carrier signatures and evaluation of the associated charge separation and charge migration dynamics by pump-probe transient absorption spectroscopy.



Enhanced immunostimulation: A multivalent polymer nanocomplex for the effective intracellular delivery and subsequent multivalent display of immunostimulatory cytosine-phosphate-guanine oligodeoxynucleotides (CpG ODNs) in antigen-presenting cells is described. Mice vaccinated with dendritic cells treated with the nanocomplex exhibited tumor growth inhibition as well as a strong antitumor memory response. HA = hyaluronic acid, PLL = poly-(L-lysine).

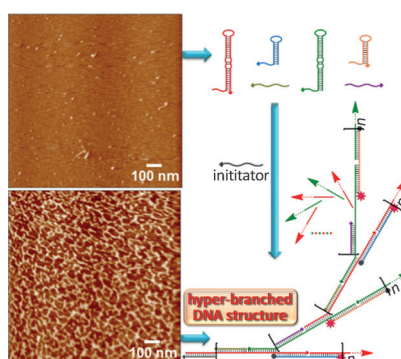
Multivalent Polymer Nanocomplex

S.-Y. Kim, M. B. Heo, G.-S. Hwang, Y. Jung, D. Y. Choi, Y.-M. Park,* Y. T. Lim* **8139–8143**

Multivalent Polymer Nanocomplex Targeting Endosomal Receptor of Immune Cells for Enhanced Antitumor and Systemic Memory Response



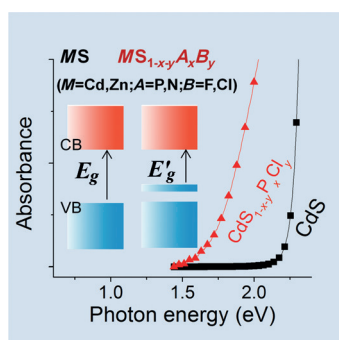
DNA branches out: A hyperbranched hybridization chain reaction is reported for the self-assembly of dendritic DNA structures triggered by an initiator DNA strand. By using this method, ultrasensitive detection of target DNA was achieved and three-input concatenated logic circuits have been constructed which can operate as keypad locks for biocomputing security systems at the molecular level.



DNA Self-Assembly

S. Bi,* M. Chen, X. Jia, Y. Dong, Z. Wang **8144–8148**

Hyperbranched Hybridization Chain Reaction for Triggered Signal Amplification and Concatenated Logic Circuits



Anionic doping: Cosubstitution of CdS and ZnS by P, Cl and N, F brings about remarkable changes in the electronic structure of these materials as the electronic band gaps are significantly decreased (E_g = band-gap energy). The effect of both P, Cl and N, F in CdS and ZnS were studied by DFT calculations, and the changes were measured by high-resolution X-ray photoelectron spectroscopy.

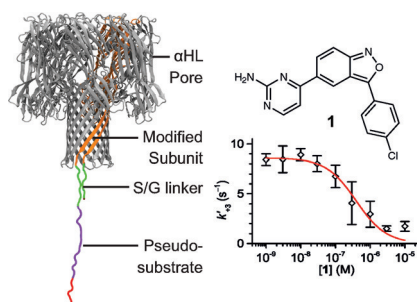
Photocatalysis

S. Kouser, S. R. Lingampalli, P. Chithaiah, A. Roy, S. Saha, U. V. Waghmare, C. N. R. Rao* **8149–8153**

Extraordinary Changes in the Electronic Structure and Properties of CdS and ZnS by Anionic Substitution: Cosubstitution of P and Cl in Place of S



Unbiased selection: A kinase inhibitor screening approach was developed that uses a radically different basis of detection than existing methods. Engineered protein nanopores allow the label-free determination of inhibition constants, are scalable to high-throughput, and circumvent biases inherent in prevailing technologies.



Drug Screening

L. Harrington, L. T. Alexander, S. Knapp, H. Bayley* **8154–8159**

Pim Kinase Inhibitors Evaluated with a Single-Molecule Engineered Nanopore Sensor

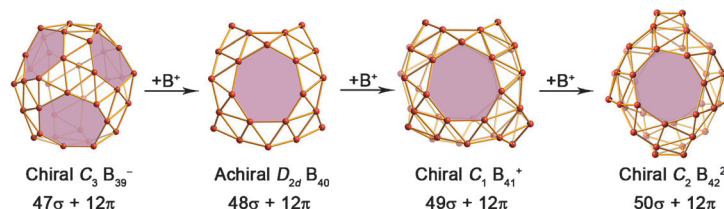


Inside Cover



Chiral Borospherenes

Q. Chen, S.-Y. Zhang, H. Bai, W.-J. Tian,
T. Gao, H.-R. Li, C.-Q. Miao, Y.-W. Mu,
H.-G. Lu,* H.-J. Zhai,*
S.-D. Li* 8160–8164



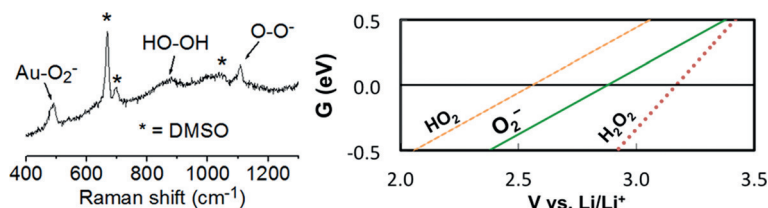
Cage-Like B_{41}^+ and B_{42}^{2+} : New Chiral Members of the Borospherene Family

Chiral cations: Following the recently observed $C_3/C_2 B_{39}^-$ and $D_{2d} B_{40}$, two new chiral members $C_1 B_{41}^+$ and $C_2 B_{42}^{2+}$ are introduced to the borospherene family. These chiral borospherene cations are composed of twelve interwoven boron

double chains with six hexagonal and heptagonal faces and exhibit σ plus π double delocalization, which can be viewed as cuborenes analogous to cubane (C_8H_8).

Lithium–Air Battery

Z. Peng,* Y. Chen, P. G. Bruce,
Y. Xu* 8165–8168



Direct Detection of the Superoxide Anion as a Stable Intermediate in the Electroreduction of Oxygen in a Non-Aqueous Electrolyte Containing Phenol as a Proton Source

Stable superoxide found in gold ORR: An in situ spectroscopic study of the oxygen reduction reaction (ORR) on gold in a DMSO electrolyte containing phenol as a proton source shows that the ORR can

begin with $1e^-$ transfer to O_2 . Thus O_2^- , not HO_2 , is the first stable intermediate during the ORR to hydrogen peroxide. The unusual stability of O_2^- is explained using DFT calculations.

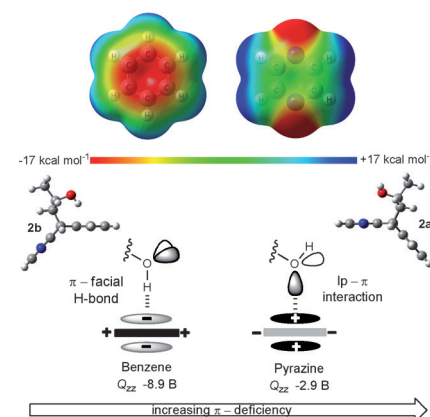
Conformational Analysis

I. Pavlakos, T. Arif, A. E. Aliev,*
W. B. Motherwell,* G. J. Tizzard,
S. J. Coles 8169–8174



Noncovalent Lone Pair... (No- π !)-Heteroarene Interactions: The Janus-Faced Hydroxy Group

Fatal attraction: The noncovalent interaction of a hydroxy group with pyrazines and quinoxalines involves a lone pair (lp)-heteroarene attraction which is stronger and solvent independent when measured relative to the π -facial hydrogen bond to a benzene ring. Organic fluorides also prefer the heteroarene ring over benzene. The attraction between a quinoxaline and a terminal alkyne is stronger than an OH-arene interaction.

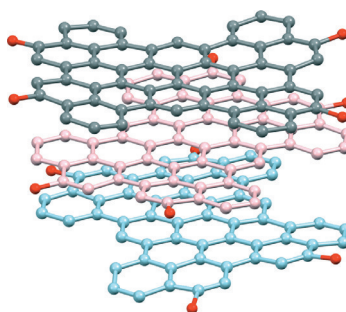


Polycycles

A. Matsumoto, M. Suzuki, D. Kuzuhara,
H. Hayashi, N. Aratani,*
H. Yamada* 8175–8178

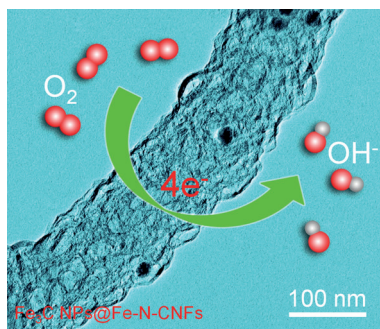


Tetrabenzoperipentacene: Stable Five-Electron Donating Ability and a Discrete Triple-Layered β -Graphite Form in the Solid State



Triple the fun: Synthesis of an all-carbon conjugated tetrabenzoperipentacene was achieved. The single-crystal X-ray structure revealed that the molecules form a triple-layered cluster-like β -graphite. The remarkably rigid carbon framework results in a small Stokes shift and fully reversible five-electron oxidation potentials.

Nanocomposite electrocatalyst: A high-performance electrocatalyst for the oxygen reduction reaction (ORR) is based on Fe₃C nanoparticles encapsulated in mesoporous Fe-N-doped carbon nanofibers. It can be synthesized from low-cost and abundant precursors and exhibits excellent electrocatalytic performance for the ORR in both alkaline and acidic media.



Electrocatalysis

Z. Y. Wu, X. X. Xu, B. C. Hu, H. W. Liang, Y. Lin, L. F. Chen, S. H. Yu* **8179–8183**

Iron Carbide Nanoparticles Encapsulated in Mesoporous Fe-N-Doped Carbon Nanofibers for Efficient Electrocatalysis



Chemical gardens: Self-assembling membranes in iron sulfide and iron hydroxide reaction systems were studied. The electrical potential and current generated by precipitation of the inorganic membranes were measured. The battery-like properties of the chemical gardens were demonstrated by linking multiple experiments in series, which produced sufficient electrical power to light an external light-emitting diode.



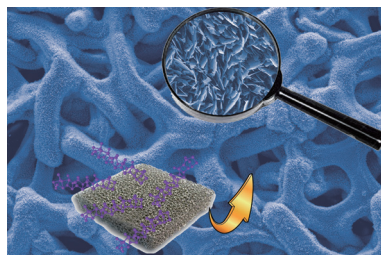
Inorganic Membranes

L. M. Barge,* Y. Abedian, M. J. Russell, I. J. Doloboff, J. H. E. Cartwright, R. D. Kidd, I. Kanik **8184–8187**

From Chemical Gardens to Fuel Cells: Generation of Electrical Potential and Current Across Self-Assembling Iron Mineral Membranes



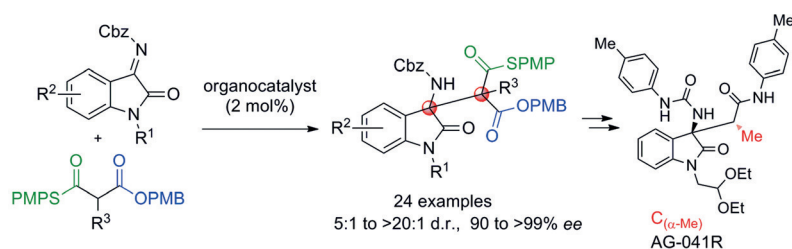
Hydrogen generation on self-supported three-dimensional nickel phosphide nanosheet array cathodes is reported. The nanosheets have been fabricated by direct phosphorization of commercial nickel foams and show superior electrocatalytic activity and stability in acidic medium toward H₂ generation.



Electrocatalysis

X. G. Wang, Y. V. Kolen'ko, X. Q. Bao, K. Kovnir, L. F. Liu* **8188–8192**

One-Step Synthesis of Self-Supported Nickel Phosphide Nanosheet Array Cathodes for Efficient Electrocatalytic Hydrogen Generation



Asymmetric Synthesis

O. D. Engl, S. P. Fritz, H. Wennemers* **8193–8197**

Stereoselective Organocatalytic Synthesis of Oxindoles with Adjacent Tetrasubstituted Stereocenters



Crowd around: Oxindoles with adjacent fully substituted stereogenic centers were formed by mild organocatalytic addition reactions with high diastereo- and enantioselectivities. The synthetic versatility of

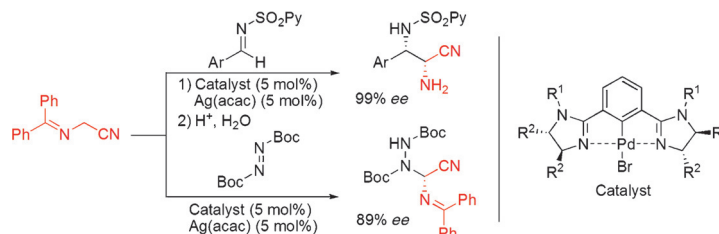
the products with orthogonally addressable functional moieties was showcased in the synthesis of derivatives of the bioactive oxindole AG-041R.

Asymmetric Synthesis

M. Kondo, T. Nishi, T. Hatanaka,
Y. Funahashi, S. Nakamura* **8198–8202**



Catalytic Enantioselective Reaction of α -Aminoacetonitriles Using Chiral Bis(imidazoline) Palladium Catalysts



Good yields and diastereo- and enantioselectivities were observed for the title reaction with various imines using chiral bis(imidazoline)/Pd catalysts. The reaction of α -aminonitriles with di-*tert*-butyl

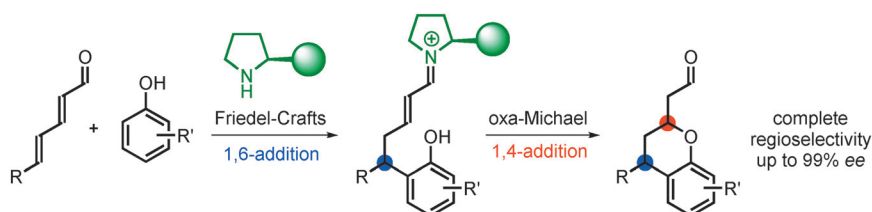
azodicarboxylate afforded chiral α,α -diaminonitrile in high yield with high enantioselectivity. acac = acetylacetonate, Boc = *tert*-butoxycarbonyl.

Asymmetric Synthesis

P. H. Poulsen, K. S. Feu, B. M. Paz,
F. Jensen, K. A. Jørgensen* **8203–8207**



Organocatalytic Asymmetric 1,6-Addition/1,4-Addition Sequence to 2,4-Dienals for the Synthesis of Chiral Chromans



One six one four: Based on a 1,6-Friedel-Crafts/1,4-oxa-Michael sequence, an organocatalyst directs the reaction of hydroxyarenes with a vinylogous iminium-

ion intermediate to give only one out of four possible regioisomers. The reaction provides optically active chromans in high yields with up to 99% *ee*.

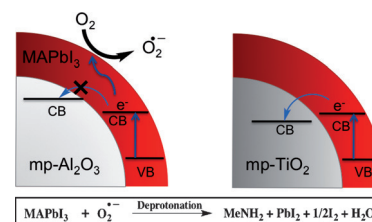
Perovskites

N. Aristidou, I. Sanchez-Molina,
T. Chotchuangchutaval, M. Brown,
L. Martinez, T. Rath,
S. A. Haque* **8208–8212**



The Role of Oxygen in the Degradation of Methylammonium Lead Trihalide Perovskite Photoactive Layers

The influence of light and oxygen on the stability of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite-based photoactive layers is investigated. Upon exposure to both light and dry air, the mesoporous (mp) $\text{Al}_2\text{O}_3/\text{CH}_3\text{NH}_3\text{PbI}_3$ layers decompose to methylamine, PbI_2 , and I_2 . This degradation is initiated by the reaction of superoxide (O_2^-) with the methylammonium moiety of the perovskite absorber. MA = methyl ammonium, CB = conduction band, VB = valence band.

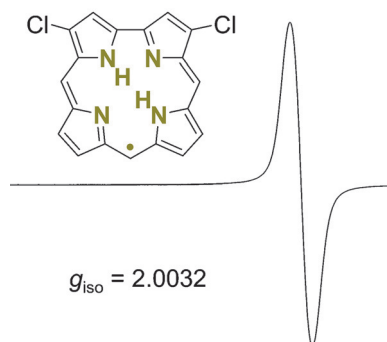


Porphyrinoids

P. Schweyen, K. Brandhorst, R. Wicht,
B. Wolfram, M. Bröring* **8213–8216**

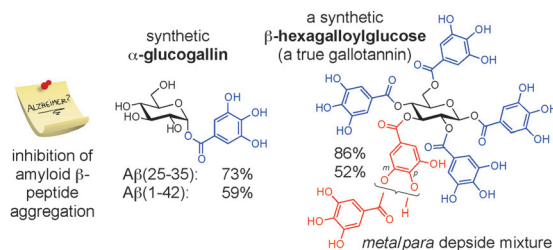


The Corrole Radical



Surprisingly radical was the outcome of an attempt to prepare sterically protected tungsten corroles. Instead of a heavy-metal chelate, a chlorinated corrole radical (see picture) was formed as an air-stable and easy-to-handle open-shell 17π ($4n+1$) porphyrinoid. The loss of one inner H atom results in a planar molecular structure with the ability to bind divalent metal ions, such as zinc(II).

Back Cover



Hexa- and decagalloylglucoses, which belong to the gallotannin plant polyphenols, were chemically synthesized for the first time, and a method for the selective synthesis of the monogalloylglucoses α -

and β -glucogallin was developed. An in vitro evaluation showed that the non-natural α -glucogallin and a natural β -hexagalloylglucose are potent inhibitors of amyloid β -peptide aggregation.

Plant Polyphenols

T. Sylla, L. Pouységou,* G. Da Costa, D. Deffieux, J.-P. Monti,* S. Quideau* ————— **8217–8221**

Gallotannins and Tannic Acid: First Chemical Syntheses and In Vitro Inhibitory Activity on Alzheimer's Amyloid β -Peptide Aggregation



Reuse and recycle: A tripodal nitroxide ligand is used in the separation of Nd and Dy and gives good recoveries from $Nd/Dy(OTf)_3$ mixtures. The separation factor $S_{Nd/Dy} = 359$ achieved is an

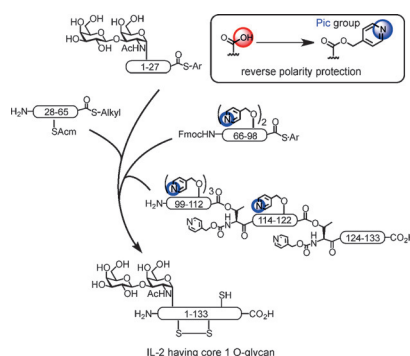
improvement over conventional separation methods involving liquid–liquid extractions. This method will contribute to incentivizing recycling of Nd/Dy permanent magnetic materials.

Rare-Earth Elements

J. A. Bogart, C. A. Lippincott, P. J. Carroll, E. J. Schelter* ————— **8222–8225**

An Operationally Simple Method for Separating the Rare-Earth Elements Neodymium and Dysprosium

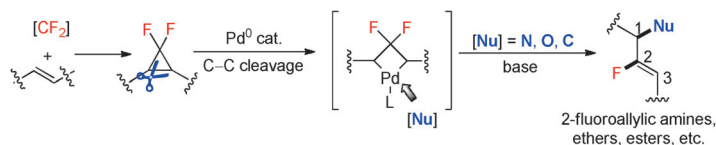
Take your Pic: Total synthesis of the glycosylated human interleukin-2 (IL-2) has been achieved. The poor solubility of the C-terminal half during purification and ligation was overcome by using the reverse polarity protection of the carboxylic acid by a picolyl (Pic) ester. Together with a new prolyl thioester synthesis for the (28–65) segment, the desired IL-2, having full biological activity, was successfully prepared.



Glycoproteins

Y. Asahina, S. Komiya, A. Ohagi, R. Fujimoto, H. Tamagaki, K. Nakagawa, T. Sato, S. Akira, T. Takao, A. Ishii, Y. Nakahara, H. Hojo* ————— **8226–8230**

Chemical Synthesis of O-Glycosylated Human Interleukin-2 by the Reverse Polarity Protection Strategy



C–C bond cleavage under Pd catalysis induces a regioselective activation of *gem*-difluorinated cyclopropanes. The reaction provides access to a variety of 2-fluoroallylic scaffolds with high Z-selectivity and

represents the first general application of *gem*-difluorinated cyclopropanes as reaction partners in transition-metal-catalyzed cross-coupling reactions.

Synthetic Methods

J. Xu, E.-A. Ahmed, B. Xiao, Q.-Q. Lu, Y.-L. Wang, C.-G. Yu, Y. Fu* ————— **8231–8235**

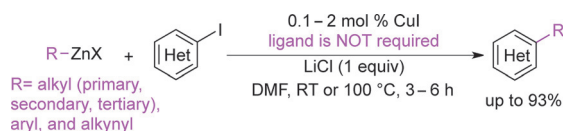
Pd-Catalyzed Regioselective Activation of *gem*-Difluorinated Cyclopropanes: A Highly Efficient Approach to 2-Fluorinated Allylic Scaffolds

Cross-Coupling

S. Thapa, A. Kafle, S. K. Gurung,
A. Montoya, P. Riedel,
R. Giri* ————— 8236–8240



Ligand-Free Copper-Catalyzed Negishi
Coupling of Alkyl-, Aryl-, and Alkynylzinc
Reagents with Heteroaryl Iodides



Simply copper: Primary, secondary, and tertiary alkylzinc reagents couple with heteroaryl iodides in the presence of ligand-free CuI without complications arising from β -hydride elimination and

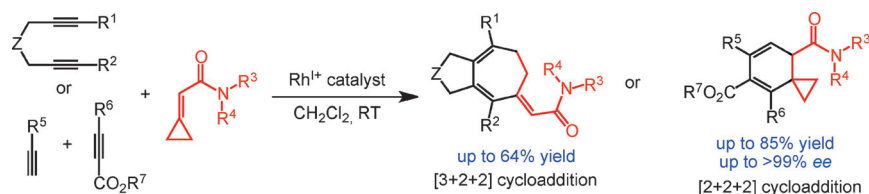
rearrangement. The reactions can also be extended to the coupling of aryl- and alkynylzinc reagents. DMF = *N,N*-dimethylformamide.

Asymmetric Catalysis

T. Yoshida, Y. Tajima, M. Kobayashi,
K. Masutomi, K. Noguchi,
K. Tanaka* ————— 8241–8244



Rhodium-Catalyzed [3+2+2] and [2+2+2]
Cycloadditions of Two Alkynes with
Cyclopropylideneacetamides



'Cat nap': The cationic Rh^I/H_8 -binap complex catalyzes the [3+2+2] cycloaddition of 1,6-diynes with cyclopropylideneacetamides to produce cycloheptadienes. In contrast, the cationic $Rh^I/(S)$ -

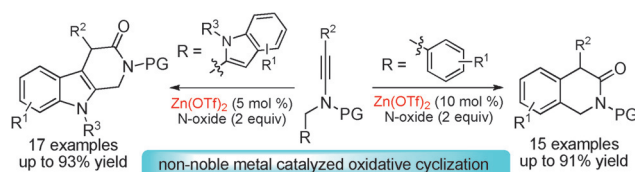
binap complex catalyzes the enantioselective [2+2+2] cycloaddition of terminal alkynes, acetylenedicarboxylates, and cyclopropylideneacetamides to produce spiro-cyclohexadienes.

Heterocycles

L. Li, B. Zhou, Y.-H. Wang, C. Shu,
Y.-F. Pan, X. Lu,* L.-W. Ye* — 8245–8249



Zinc-Catalyzed Alkyne Oxidation/C–H
Functionalization: Highly Site-Selective
Synthesis of Versatile Isoquinolones and
 β -Carbolines



Swap gold for zinc: The title reaction was achieved by a zinc(II)-catalyzed alkyne oxidation/C–H functionalization sequence. In contrast to the well-established gold-catalyzed intermolecular

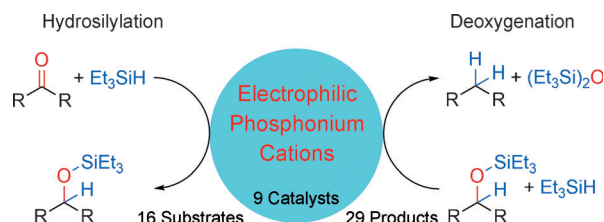
alkyne oxidation, the over-oxidation can be suppressed in this system and the reaction most likely proceeds by a Friedel–Crafts-type pathway. Tf = trifluoromethanesulfonyl, PG = protecting group.

Synthetic Methods

M. Mehta, M. H. Holthausen, I. Mallov,
M. Pérez, Z.-W. Qu, S. Grimme,*
D. W. Stephan* ————— 8250–8254

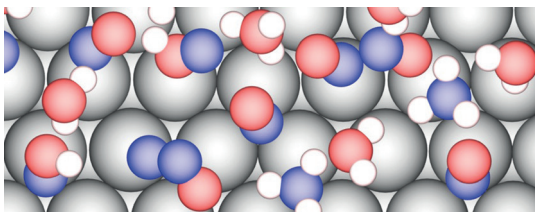


Catalytic Ketone Hydrodeoxygenation
Mediated by Highly Electrophilic
Phosphonium Cations



Taking out the O: The salts of the title cations were used in the catalytic stepwise hydrosilylation and deoxygenation of ketones. The dependency of the reaction

outcome on Lewis acidity was investigated. In addition, the mechanism of the reduction was probed experimentally as well as with DFT calculations.



Path finder: The mechanism of nitric oxide electroreduction to ammonia on Pt(111) is investigated using a combination of first principles calculations and electrokinetic rate theories. The results

demonstrate that ammonia is produced through a series of water-assisted protonation and bond dissociation steps at modest voltages.

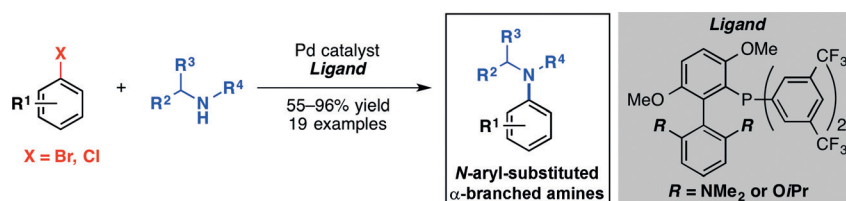
NO Electroreduction

A. Clayborne, H.-J. Chun, R. B. Rankin, J. Greeley* **8255–8258**

Elucidation of Pathways for NO Electroreduction on Pt(111) from First Principles



Inside Back Cover



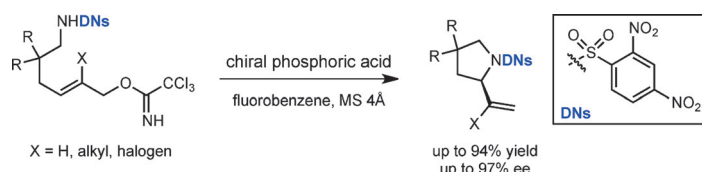
Coupled by design: The arylation of sterically demanding α -branched secondary amines was enabled through the design of new palladium catalyst systems. These catalysts help suppress the undesired β -

hydride elimination pathways and are effective for the cross-coupling of a wide array of hindered amine nucleophiles with aryl and heteroaryl electrophiles.

Cross-Coupling

N. H. Park, E. V. Vinogradova, D. S. Surry, S. L. Buchwald* **8259–8262**

Design of New Ligands for the Palladium-Catalyzed Arylation of α -Branched Secondary Amines



Leaving-group activation: A Brønsted acid catalyzed intramolecular enantioselective S_N2' reaction was developed utilizing trichloroacetimidate as a leaving group. The findings indicated that dual activation

of the substrates is operative. This metal-free allylic alkylation allows highly enantioselective access to 2-vinylpyrrolidines bearing various substituents.

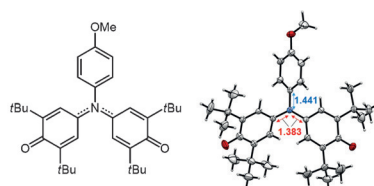
Organocatalysis

Y. Kuroda, S. Harada, A. Oonishi, Y. Yamaoka, K. Yamada,* K. Takasu* **8263–8266**

Organocatalytic Activation of the Leaving Group in the Intramolecular Asymmetric S_N2' Reaction



In a (closed) nut shell: A novel triphenylamine derivative having two phenoxy radicals appended to the amino nitrogen atom has been prepared. This molecule has an unexpected closed-shell electronic state, even at room temperature, in spite of its structural similarity to the galvinoxyl radical. The molecule features two C–N bonds with multiple-bond character and a remarkably low HOMO–LUMO gap.



Structure Elucidation

D. Sakamaki,* S. Yano, T. Kobashi, S. Seki,* T. Kurahashi, S. Matsubara, A. Ito,* K. Tanaka **8267–8270**

A Triphenylamine with Two Phenoxy Radicals Having Unusual Bonding Patterns and a Closed-Shell Electronic State

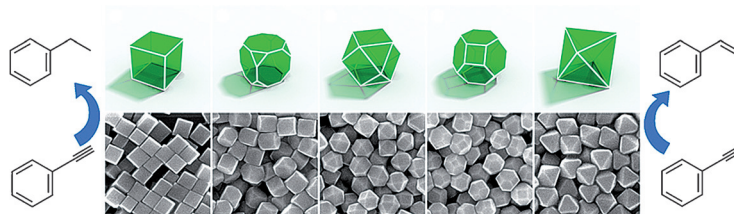


Hydrogenation Reactions

W. X. Niu, Y. J. Gao, W. Q. Zhang, N. Yan,*
X. M. Lu* 8271–8274



Pd–Pb Alloy Nanocrystals with Tailored Composition for Semihydrogenation: Taking Advantage of Catalyst Poisoning



Taking advantage of poisons: The poisoning effect of lead(II) ions can alter the shapes of Pd–Pb alloy nanocrystals. It

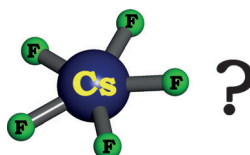
endows the alloy nanocrystals with superior selectivity for the semihydrogenation of alkynes.

Cesium Fluorides

A. Yu. Rogachev, M.-S. Miao, G. Merino,
R. Hoffmann* 8275–8278



Molecular CsF_5 and CsF_2^+



Breaking into cores: Formal core orbitals sometimes may take part in bonding. An instance is provided in theoretical studies of the bonding of CsF_5 (see picture) and CsF_2^+ . The results also suggest that these metastable high fluorides of cesium may be experimentally accessible.

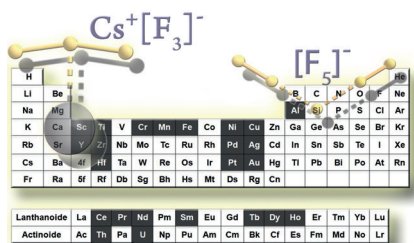


Polyfluoride Anions

T. Vent-Schmidt, F. Brosi, J. Metzger,
T. Schlöder, X. Wang, L. Andrews,
C. Müller, H. Beckers,
S. Riedel* 8279–8283



Fluorine-Rich Fluorides: New Insights into the Chemistry of Polyfluoride Anions



Give me F,F,F,F,F, five: The polyfluoride anions $[\text{F}_5]^-$ and $\text{Cs}^+[\text{F}_5]^-$ have been identified by matrix-isolation spectroscopy and quantum-chemical methods. The V-shaped $[\text{F}_5]^-$ ion gives rise to a band found in many IR laser ablation experiments that, up to now, could not be assigned.

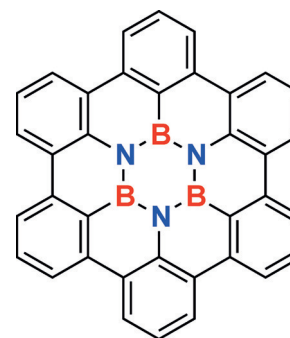
Heterocycles

M. Krieg, F. Reicherter, P. Haiss,
M. Ströbele, K. Eichele, M.-J. Treanor,
R. Schaub, H. F. Bettinger* 8284–8286



Construction of an Internally B_3N_3 -Doped Nanographene Molecule

A change of heart: The borazine derivative of hexa-*peri*-hexabenzocoronene was produced in a high-temperature reaction through multiple dehydrogenation of a borazine. The solid-state structure of this BN-doped HBC (BN-HBC) is isotypic with that of the parent HBC. Scanning tunneling microscopy shows that BN-HBC lies flat on $\text{Au}(111)$ in a two-dimensional pattern.

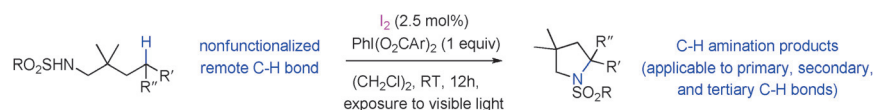


Synthetic Methods

C. Martínez, K. Muñiz* 8287–8291

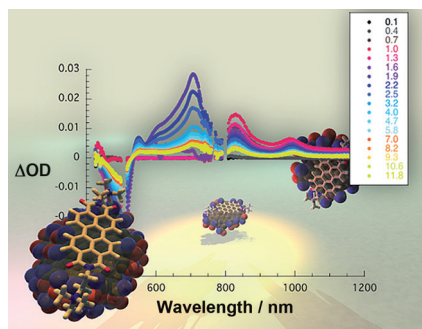


An Iodine-Catalyzed Hofmann–Löffler Reaction



Iodine does it! The first catalytic Hofmann–Löffler reaction proceeds with a combination of catalytic amounts of molecular iodine and a modified hypervalent iodine(III) reagent. The reaction

proceeds under mild catalytic conditions and the intramolecular C–H amination addresses primary, secondary, and tertiary C–H groups.



Long-term separation: Charge-transfer complexes formed by electron-donating carbon nanodots and electron-accepting perylenediimides are prepared. In ultra-fast pump-probe experiments (see picture) the charge-separated state with a lifetime of 210 ps was found.

Charge Transfer

V. Strauss, J. T. Margraf, K. Dirian, Z. Syrgiannis, M. Prato, C. Wessendorf, A. Hirsch, T. Clark, D. M. Guldi* — 8292–8297

Carbon Nanodots: Supramolecular Electron Donor–Acceptor Hybrids Featuring Perylenediimides



Supporting information is available on www.angewandte.org (see article for access details).



A video clip is available as Supporting Information on www.angewandte.org (see article for access details).



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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.

Angewandte Corrigendum

The *Journal of the American Chemical Society* article on which this Highlight is based has been retracted (Retraction on “Mechanical Reconfiguration of Stereoisomers” by K. M. Wiggins, T. W. Hudnall, Q. Shen, M. J. Kryger, J. S. Moore, C. W. Bielawski, *J. Am. Chem. Soc.* **2015**, *137*, 3428) based on an investigation conducted by the University of Texas at Austin, which concludes that the data and scientific conclusions of this study are unreliable.

Regardless of the results reported in the retracted publication, the use of force-sensitive functional groups (mechanophores) has become a useful concept of wide applicability. Pulsed sonication is frequently employed to test the mechanochemical response of polymeric materials. In addition, the Highlight provides some valid insights into the mechanisms of sonochemical activation.

Reconfiguration of Stereoisomers under Sonomechanical Activation

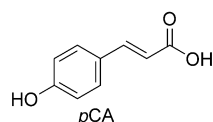
G. Cravotto,* P. Cintas* — 6028–6030

Angew. Chem. Int. Ed. **2010**, *49*

DOI: 10.1002/anie.201001360

Angewandte Corrigendum

Figure 1 of this Communication contains a wrong structure for *p*CA. The correct structure is shown below.



Controlling Radical Formation in the Photoactive Yellow Protein Chromophore

C. R. S. Mooney, M. A. Parkes, A. Iskra, H. H. Fielding* — 5646–5649

Angew. Chem. Int. Ed. **2015**, *54*

DOI: 10.1002/anie.201500549

Angewandte Corrigendum

Well-Defined Copper(I) Fluoroalkoxide
Complexes for Trifluoroethoxylation of
Aryl and Heteroaryl Bromides

R. Huang, Y. Huang, X. Lin, M. Rong,
Z. Weng* 5736–5739

Angew. Chem. Int. Ed. 2015, 54

DOI: 10.1002/anie.201501257

In this Communication, the structure of complex **1a** in Figure 1 contains an error. The correct structure contains two $[\text{CF}_3\text{CH}_2\text{O}]$ moieties, as indicated by a revised X-ray crystal structure. The distinct proton and carbon resonance signals appear in the ^1H and ^{13}C NMR spectra of compound, indicative of diamagnetic copper(I) species. Deducing from the charge balance, among two $[\text{CF}_3\text{CH}_2\text{O}]$ groups, one of them is protonated. The cocrystallized $\text{CF}_3\text{CH}_2\text{OH}$ can be removed by washing the complex with diethyl ether and drying under vacuum overnight. The reaction exploiting $[\text{Cu}(\text{phen})_2(\text{CF}_3\text{CH}_2\text{O})](\text{CF}_3\text{CH}_2\text{OH})$ as described in the original paper.

Furthermore, in the Experimental Section, “ $\text{CF}_3\text{CH}_2\text{OH}$ (0.60 g, 6.0 mmol)” should be “ $\text{CF}_3\text{CH}_2\text{OH}$ (1.20 g, 12.0 mmol)” and “ ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$) δ 9.10 (s, 4H), 8.64 (d, $J = 7.9$ Hz, 4H), 8.12 (s, 4H), 7.89 (s, 4H), 3.86 (s, 2H). ^{19}F NMR (376 MHz, $[\text{D}_6]\text{DMSO}$) δ –75.4 (s, 3F)” should be “ ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$) δ 11.0 (br, 1H), 9.10 (s, 4H), 8.64 (d, $J = 7.9$ Hz, 4H), 8.12 (s, 4H), 7.89 (s, 4H), 3.86 (br, 4H). ^{19}F NMR (376 MHz, $[\text{D}_6]\text{DMSO}$) δ –75.4 (s, 6F)”.

Similarly, **1c** contains about 0.5 molecule of $\text{CF}_2\text{HCF}_2\text{CH}_2\text{OH}$ as indicated by the ^{19}F NMR spectrum with *p*-(trifluoromethyl)toluene as an internal standard. For the synthesis of **1c**, “ $\text{HCF}_2\text{CF}_2\text{CH}_2\text{OH}$ (0.78 g, 6.0 mmol)” should be “ $\text{HCF}_2\text{CF}_2\text{CH}_2\text{OH}$ (1.56 g, 12.0 mmol)”.

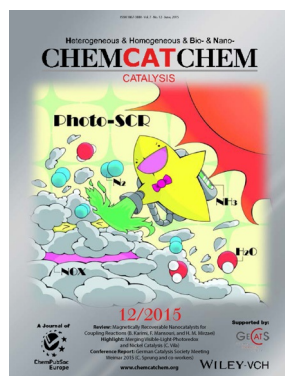
In the Supporting Information, on page S4, for the ^{13}C NMR data of **1b**, “155.1 (s), 155.0 (s), 154.9 (s)” should be “155.0 (m)”.

The authors would like to acknowledge Dr. Peter Mueller and Dr. Fang Wang at the Massachusetts Institute of Technology for pointing out these errors which do not affect the main conclusions of the work.

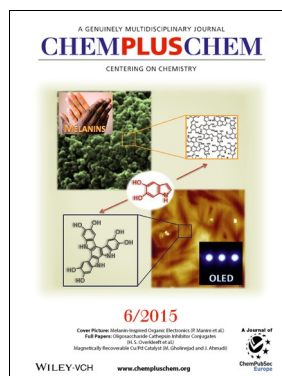
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