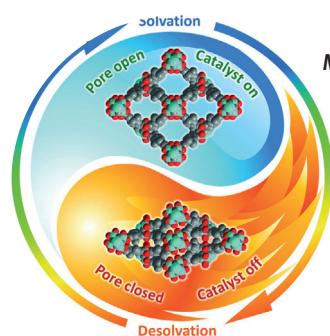
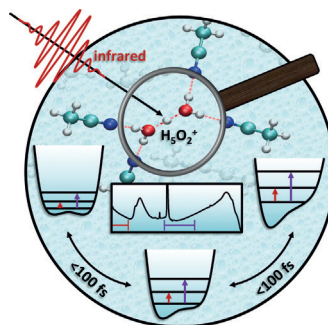


... is expected to be a general phenomenon in exothermic chemical reactions at the gas/solid and solid/liquid interface. In their Communication on page 10859 ff., J. Y. Park and co-workers demonstrate the detection of hot electrons as a chemicurrent generated at the solid/liquid interface during the decomposition of hydrogen peroxide catalyzed on Schottky nanodiodes, and show that the chemicurrent yield can reach values of up to 1/10 electrons per O_2 molecule.

Femtochemistry

In their Communication on page 10600 ff., E. T. J. Nibbering, T. Elsaesser, and co-workers analyze the Zundel cation by ultrafast pump-probe infrared spectroscopy.

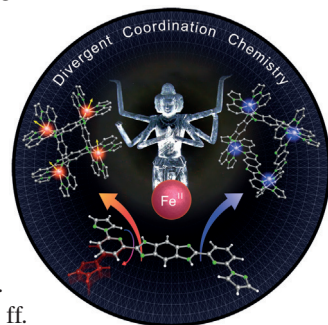


MOF Catalysts

Switchable catalysts are prepared by W. Lu, M. B. Hall, H.-C. Zhou, and co-workers in their Communication on page 10776 ff. They show that the catalytic properties of the metal-organic frameworks (MOFs) are controlled by reversible pore opening and closing.

Divergent Coordination Chemistry

The coordination of Fe^{II} ions by a homoditopic ligand yields two tauto-isomeric complexes with different magnetic properties. This tautomerism-driven emergence of complexity is explained by M. Ruben et al. in their Communication on page 10881 ff.



How to contact us:

Editorial Office:

E-mail: angewandte@wiley-vch.de

Fax: (+49) 62 01-606-331

Telephone: (+49) 62 01-606-315

Reprints, E-Prints, Posters, Calendars:

Carmen Leitner

E-mail: chem-reprints@wiley-vch.de

Fax: (+49) 62 01-606-331

Telephone: (+49) 62 01-606-327

Copyright Permission:

Bettina Loycke

E-mail: rights-and-licences@wiley-vch.de

Fax: (+49) 62 01-606-332

Telephone: (+49) 62 01-606-280

Online Open:

Margitta Schmitt

E-mail: angewandte@wiley-vch.de

Fax: (+49) 62 01-606-331

Telephone: (+49) 62 01-606-315

Subscriptions:

www.wileycustomerhelp.com

Fax: (+49) 62 01-606-184

Telephone: 0800 1800536 (Germany only)
+44(0) 1865476721 (all other countries)

Advertising:

Marion Schulz

E-mail: mschulz@wiley-vch.de

Fax: (+49) 62 01-606-550

Telephone: (+49) 62 01-606-565

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

Get the **Angewandte App**
International Edition



Enjoy Easy Browsing and a New Reading Experience on Your Smartphone or Tablet

- Keep up to date with the latest articles in Early View.
- Download new weekly issues automatically when they are published.
- Read new or favorite articles anytime, anywhere.



Service

Spotlight on Angewandte's Sister Journals

10550 – 10553

Author Profile



*"My favorite author (fiction) is Shiono Nanami.
My favorite pieces of music are The Phantom of the Opera
and Mozart's Requiem. ..."*
This and more about Young-Tae Chang can be found on
page 10554.

Young-Tae Chang _____ 10554

News



T. Magauer



O. García Mancheño



D. Trauner



J. P. Richmond

ORCHEM Prize: T. Magauer
and O. García Mancheño _____ 10555

Emil Fischer Medal:
D. Trauner _____ 10555

Gmelin–Beilstein Memorial Medal:
J. P. Richmond _____ 10555

Highlights

C–H Arylation

S. De Sarkar* — 10558 – 10560

Remote C–H Functionalization by
a Palladium-Catalyzed Transannular
Approach



Transannular C–H activation

Now within reach: In the remote C–H arylation of alicyclic amines the key step is the transannular coordination of the palladium catalyst (see picture, DG = direct-

ing group). This strategy is convenient for the late-stage functionalization of complex bioactive molecules in order to probe structure–activity relationships.

Minireviews

Beryllium

D. Naglav, M. R. Buchner, G. Bendt, F. Kraus,* S. Schulz* — 10562 – 10576



Off the Beaten Track—A Hitchhiker's
Guide to Beryllium Chemistry

Be prepared: This Minireview presents an introduction to beryllium chemistry. Its toxicity, and that of its compounds, is put into perspective, and safe handling practices are presented. Observations demonstrating the unique chemistry of beryllium and its industrial use are shown and future challenges identified. The picture shows Be metal under Ar in a glass ampule. Picture: A. Heddergott.

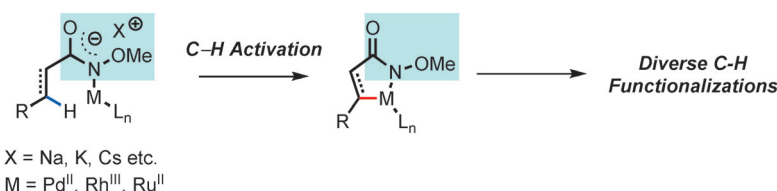


Reviews

Directing Groups

R.-Y. Zhu, M. E. Farmer, Y.-Q. Chen, J.-Q. Yu* — 10578 – 10599

A Simple and Versatile Amide Directing
Group for C–H Functionalizations



Clear directions: The simple *N*-methoxy amide moiety is a versatile directing group for a wide range of C–H functionalization reactions using Pd, Rh, and Ru catalysis. Whereas it was initially used for Pd-

catalyzed C–H activation, it has also been employed in Rh^{III}-catalyzed variants and in combination with cheaper ruthenium catalysts.

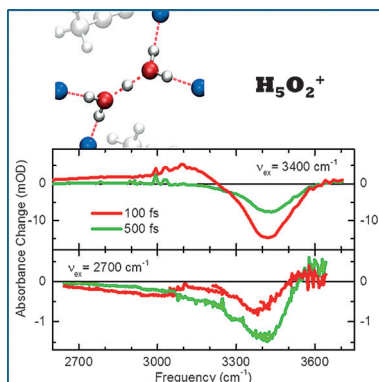
For the USA and Canada:

ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 101161, 69451 Weinheim, Germany. US mailing agent: SPP, PO Box 437, Emigsville, PA 17318. Periodicals postage

paid at Emigsville, PA. US POSTMASTER: send address changes to *Angewandte Chemie*, John Wiley & Sons Inc., C/O The Sheridan Press, PO Box 465, Hanover, PA 17331. Annual subscription price for institutions: US\$ 16.862/14.051 (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.

The Zundel continuum: Transient infrared pump-probe spectra of the Zundel cation H_5O_2^+ dissect OH stretching and bending vibrations from the underlying broadband absorption. The Zundel continuum originates from an ultrafast frequency modulation of the H^+ transfer vibration and its combination and overtones by fluctuating electrical interactions with the solvent and stochastic thermal excitations of low-frequency modes.



Communications

Femtochemistry



F. Dahms, R. Costard, E. Pines,
B. P. Fingerhut, E. T. J. Nibbering,*
T. Elsaesser* ————— 10600–10605

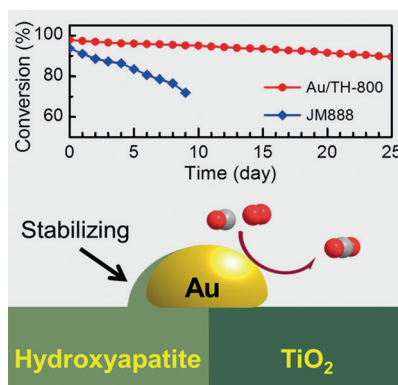
The Hydrated Excess Proton in the Zundel Cation H_5O_2^+ : The Role of Ultrafast Solvent Fluctuations



Frontispiece



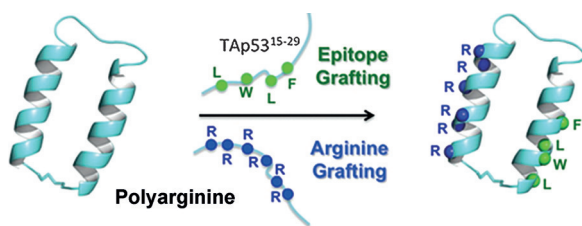
Partially covered and supported: An ultrastable gold nanocatalyst was prepared by tuning the strong metal–support interaction between Au nanoparticles (NPs) and a titanium dioxide–hydroxyapatite (HAP) support (see picture). The Au NPs are located at the interfaces of TiO_2 /HAP support, forming anchored and partially covered active Au NPs.



Metal–Support Interaction

H. Tang, F. Liu, J. Wei, B. Qiao,* K. Zhao,
Y. Su, C. Jin, L. Li, J. Liu, J. Wang,*
T. Zhang ————— 10606–10611

Ultrastable Hydroxyapatite/Titanium-Dioxide-Supported Gold Nanocatalyst with Strong Metal–Support Interaction for Carbon Monoxide Oxidation



Hard graft: A cyclized helix-loop-helix peptide (cyan) was used as a scaffold to generate cell-permeable PPI inhibitors through bifunctional grafting: epitope grafting for binding activity, and arginine grafting for cell permeability. To inhibit

p53–HDM2 interactions, the p53 epitope was grafted onto the C-terminal helix and six Arg residues were grafted onto the other helix. The resulting peptide showed cell membrane permeability and inhibitory activity for the intracellular PPI.

Therapeutic Peptides

D. Fujiwara, H. Kitada, M. Oguri,
T. Nishihara, M. Michigami, K. Shiraishi,
E. Yuba, I. Nakase, H. Im, S. Cho,
J. Y. Joung, S. Kodama, K. Kono, S. Ham,*
I. Fujii* ————— 10612–10615

A Cyclized Helix-Loop-Helix Peptide as a Molecular Scaffold for the Design of Inhibitors of Intracellular Protein–Protein Interactions by Epitope and Arginine Grafting



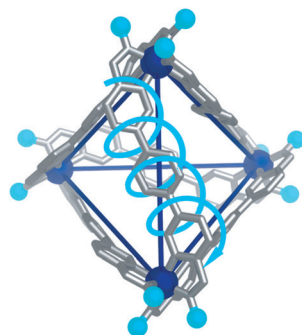
Diastereoselectivity



A. M. Castilla, M. A. Miller,
J. R. Nitschke,*
M. M. J. Smulders* — 10616–10620



Quantification of Stereochemical
Communication in Metal–Organic
Assemblies



Powerful coupling: The derivation and application of a statistical mechanical model to describe stereochemical communication across a range of metal–organic assemblies in terms of intra-vertex and inter-vertex coupling energies is reported. The effect of various structural parameters is thus quantified, allowing for subtle stereochemical outcomes to be predicted.

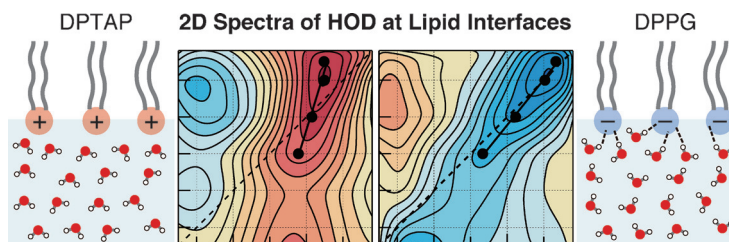
Liquid Interfaces



P. C. Singh, K. Inoue, S. Nihonyanagi,
S. Yamaguchi, T. Tahara* — 10621–10625



Femtosecond Hydrogen Bond Dynamics
of Bulk-like and Bound Water at Positively
and Negatively Charged Lipid Interfaces
Revealed by 2D HD-VSFG Spectroscopy



Femtosecond hydrogen bond fluctuation at lipid membranes: Interface specific, phase- and time-resolved 2D HD-VSFG spectroscopy, combined with the isotopic dilution technique, has shown that femtosecond water dynamics at lipid

interfaces are essentially different, reflecting the chemical structure of the lipid. The observed distinct hydrogen bond fluctuation and dynamics of interfacial water may have a significant influence on cell membrane processes.

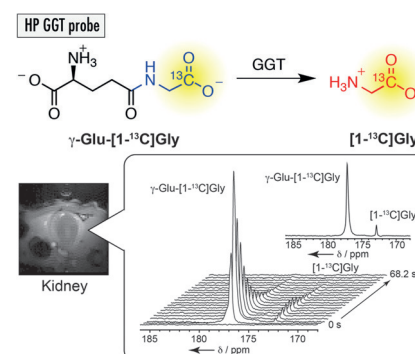
Biosensors

T. Nishihara, H. A. I. Yoshihara,
H. Nonaka, Y. Takakusagi, F. Hyodo,
K. Ichikawa, E. Can, J. A. M. Bastiaansen,
Y. Takado, A. Comment,*
S. Sando* — 10626–10629



Direct Monitoring of γ -Glutamyl
Transpeptidase Activity In Vivo Using
a Hyperpolarized ^{13}C -Labeled Molecular
Probe

See enzymatic reactions in vivo: γ -Glu-[^{13}C]Gly was designed as a hyperpolarized NMR probe for monitoring of GGT activity. The properties of this probe, for example, a large chemical shift change and sufficient hyperpolarization lifetime, are suitable for hyperpolarized ^{13}C metabolic analysis. The designed probe allowed for the first time the real-time analysis of in vivo GGT activity.

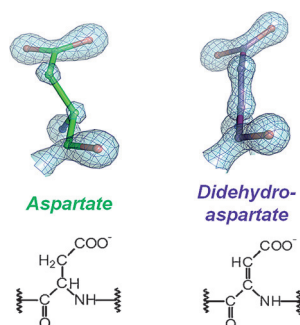


Protein Structures

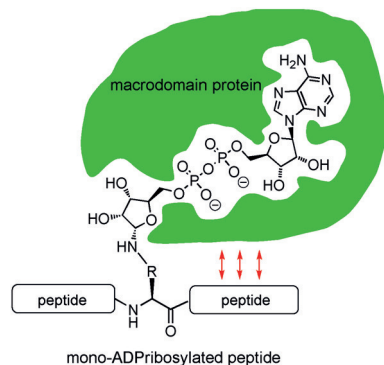
T. Wagner, J. Kahnt, U. Ermler,
S. Shima* — 10630–10633



Didehydroaspartate Modification in
Methyl-Coenzyme M Reductase
Catalyzing Methane Formation



2H less: Methyl-coenzyme M reductase catalyzes the reversible reduction of methyl-coenzyme M to methane. Near the active site, it contains the following modified amino acid residues: a thioglycine and four methylated amino acid residues. The presence of a novel post-translationally modified amino acid, didehydroaspartate, adjacent to the thioglycine is revealed by mass spectrometry and high resolution X-ray crystallography.

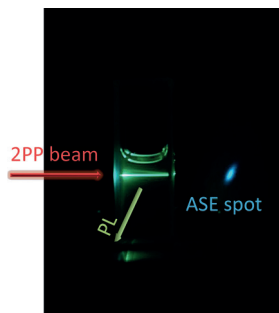


Ties that bind: The synthesis of a number of mono-ADP-ribosylated peptides is described. Binding studies of these peptides with different macrodomains showed that the peptide fragment surrounding the ADPr modification influences the binding properties.

Posttranslational Modifications

H. A. V. Kistemaker, A. P. Nardoza,
H. S. Overkleeft, G. A. van der Marel,
A. G. Ladurner,*
D. V. Filippov* ————— **10634–10638**

Synthesis and Macrodomain Binding of
Mono-ADP-Ribosylated Peptides

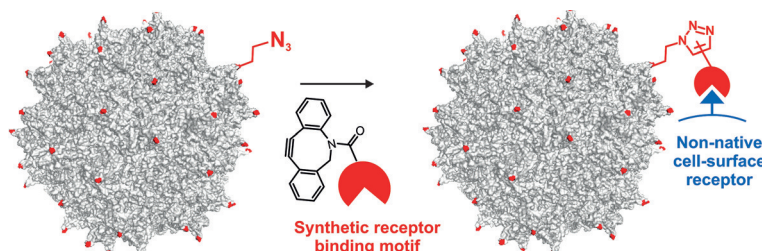


Highly extended π -conjugated ladder-type oligo(*p*-phenylene)s containing up to 10 phenyl rings with or without diphenyl-amino endcaps were synthesized and investigated for their multiphoton absorption properties for blue amplified spontaneous emission (ASE)/lasing. Extremely large two-photon absorption (2PA) cross-sections and highly efficient 2PA ASE/lasing with ultralow threshold were achieved from two-photon pumping (2PP). PL = photoluminescence.

Multiphoton Absorption

L. Guo, K. F. Li, X. Zhang, K. W. Cheah,*
M. S. Wong* ————— **10639–10644**

Highly Efficient Multiphoton-Pumped
Frequency-Upconversion Stimulated Blue
Emission with Ultralow Threshold from
Highly Extended Ladder-Type
Oligo(*p*-phenylene)s



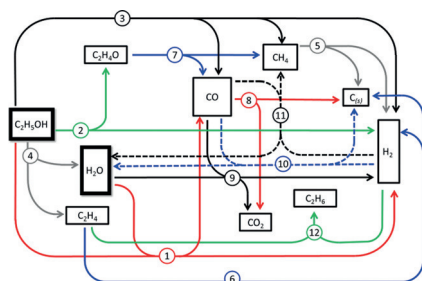
An adeno-associated virus (AAV) production platform is reported that enables efficient incorporation of unnatural amino acids into specific sites of the virus capsid. This work provides a general

chemical approach to introduce various receptor binding agents onto the AAV capsid with exquisite site selectivity to generate optimized vectors with engineered infectivity.

Chemical Conjugation

R. E. Kelemen, R. Mukherjee, X. Cao,
S. B. Erickson, Y. Zheng,
A. Chatterjee* ————— **10645–10649**

A Precise Chemical Strategy To Alter the
Receptor Specificity of the Adeno-
Associated Virus



The tracking of atoms from reactants to products during Rh/Pt catalytic ethanol steam reforming using $H_3^{12}C^{13}CH_2^{16}OH$ and $H_2^{18}O$ provided new insight into the overall reaction mechanism. All combinations of isotope- and non-isotope-labeled atoms were detected in the products, thus there are multiple pathways involved in H_2 , CO , CO_2 , CH_4 , C_2H_4 , and C_2H_6 product formation.

Reaction Mechanisms

S. Crowley,
M. J. Castaldi* ————— **10650–10655**

Mechanistic Insights into Catalytic
Ethanol Steam Reforming Using Isotope-
Labeled Reactants



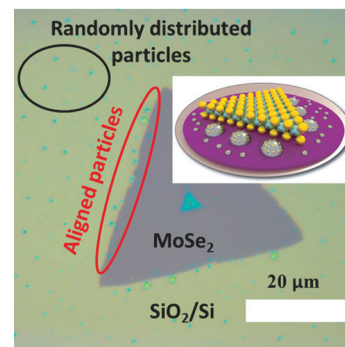
Chemical Vapor Deposition

B. Li, Y. Gong, Z. Hu, G. Brunetto, Y. Yang, G. Ye, Z. Zhang, S. Lei, Z. Jin, E. Bianco, X. Zhang, W. Wang, J. Lou, D. S. Galvão, M. Tang, B. I. Yakobson, R. Vajtai,* P. M. Ajayan* — 10656 – 10661



Solid–Vapor Reaction Growth of Transition-Metal Dichalcogenide Monolayers

The critical role of metastable nanoparticles that are deposited on the substrate during the growth of MoSe₂ monolayers in chemical vapor deposition was elucidated. A three-step growth mechanism was proposed to explain their formation and the conversion of these non-stoichiometric nanoparticles into stoichiometric two-dimensional materials.



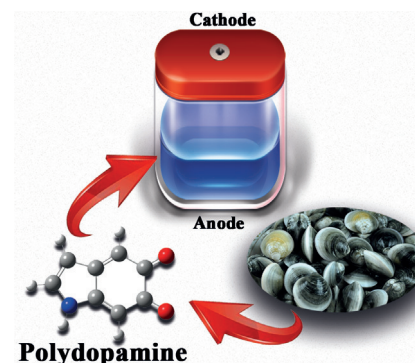
Electrode Materials

T. Sun, Z. J. Li, H. G. Wang, D. Bao, F. L. Meng, X. B. Zhang* — 10662 – 10666



A Biodegradable Polydopamine-Derived Electrode Material for High-Capacity and Long-Life Lithium-Ion and Sodium-Ion Batteries

Mussel power: A polydopamine-derived material can act as both electrode and binder material for lithium-ion and sodium-ion batteries, and exhibits superior electrochemical performances including high capacity and stable cyclability. The material is synthesized by the oxidative polymerization of dopamine, which is both naturally occurring and biodegradable.

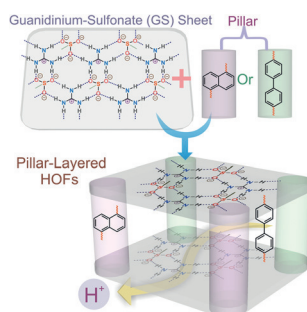


Proton Conduction

A. Karmakar, R. Illathvalappil, B. Anothumakkool, A. Sen, P. Samanta, A. V. Desai, S. Kurungot, S. K. Ghosh* — 10667 – 10671



Hydrogen-Bonded Organic Frameworks (HOFs): A New Class of Porous Crystalline Proton-Conducting Materials



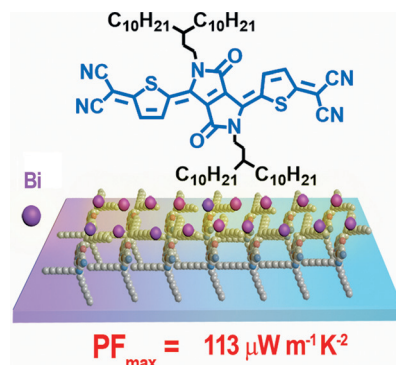
H⁺ conduction: Two porous hydrogen-bonded organic frameworks (HOFs) based on arene sulfonates and guanidinium ions exhibit ultra-high proton conductivity (σ), $0.75 \times 10^{-2} \text{ S cm}^{-1}$ and $1.8 \times 10^{-2} \text{ S cm}^{-1}$, under humidified conditions. They also have very low activation energies and higher proton conductivity at ambient conditions compared to other porous crystalline materials, such as MOFs and COFs.

Organic Thermoelectric Materials

D. Huang, C. Wang, Y. Zou, X. Shen, Y. Zang, H. Shen, X. Gao, Y. Yi, W. Xu, C.-a. Di,* D. Zhu* — 10672 – 10675

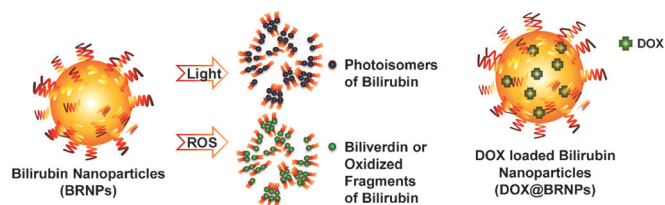


Bismuth Interfacial Doping of Organic Small Molecules for High Performance n-type Thermoelectric Materials



Interfacial doping for organic thermoelectrics: Bismuth interfacial doping of thiophene-diketopyrrolopyrrole-based quinoidal molecules results in a maximum power factor (PF_{max}) of $113 \mu\text{W m}^{-1} \text{ K}^{-2}$. Heavy metal doping of organic semiconductors can open up a new strategy for exploring high performance organic thermoelectric materials.

$$PF_{\text{max}} = 113 \mu\text{W m}^{-1} \text{ K}^{-2}$$



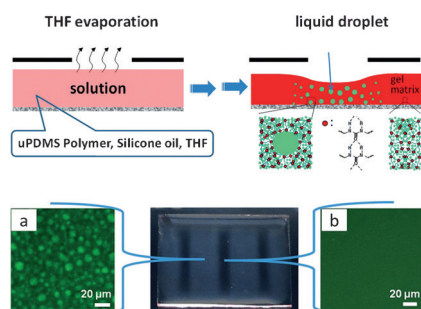
Aye, there's the rub: Nanoparticles made of bilirubin, which is an endogenous bioactive bile pigment, show reactive oxygen species (ROS)- and light-responsive particle disruption. Therefore, as well

as exerting potent anticancer activity in its own right, bilirubin can be used for the controlled delivery and release of other anticancer drugs, such as doxorubicin (Dox).

Drug Delivery

Y. Lee, S. Lee, D. Y. Lee, B. Yu, W. Miao, S. Jon* — 10676 – 10680

Multistimuli-Responsive Bilirubin Nanoparticles for Anticancer Therapy

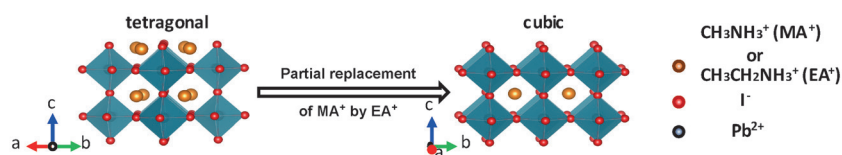


Evaporative lithography can be used to control the localization of liquid droplets in a silicone-based polymer matrix. When the solution is placed under a mask, selective solvent evaporation leads to a redistribution of the liquid and polymer components, which results in a patterned film with droplet-containing and droplet-free domains.

Dynamic Materials

H. Zhao, J. Xu, G. Jing, L. O. Prieto-López, X. Deng,* J. Cui* — 10681 – 10685

Controlling the Localization of Liquid Droplets in Polymer Matrices by Evaporative Lithography



Despite its large ionic radius, ethylammonium can partially replace methylammonium in the widely studied 3D hybrid perovskites CH₃NH₃PbI₃. This par-

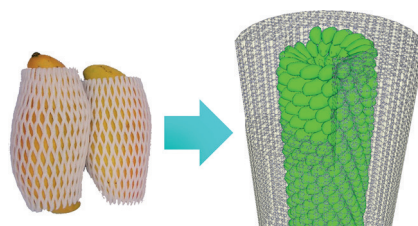
tial replacement results in higher crystal symmetry, improved material stability, and markedly enhanced photocarrier lifetime of the alloy perovskites.

Hybrid Composites

W. Peng, X. Miao, V. Adinolfi, E. Alarousu, O. El Tall, A. H. Emwas, C. Zhao, G. Walters, J. Liu, O. Ouellette, J. Pan, B. Murali, E. H. Sargent, O. F. Mohammed, O. M. Bakr* — 10686 – 10690

Engineering of CH₃NH₃PbI₃ Perovskite Crystals by Alloying Large Organic Cations for Enhanced Thermal Stability and Transport Properties

It's a wrap: Sleeve netting provides a cost-effective solution to keep fresh fruits safe and sound. A metal–organic framework (MOF) is used to construct a molecular protective netting on the surface of the rod-like tobacco mosaic virus. The shell thickness was discovered to play a crucial role in the stability of the core–shell composite. More interestingly, the embedded virus particle can be chemically modified using a standard bioconjugation reaction, showing mass transportation within the MOF shell.



Metal–Organic Frameworks

S. Li, M. Dharmarwardana, R. P. Welch, Y. Ren, C. M. Thompson, R. A. Smaldone, J. J. Gassensmith* — 10691 – 10696

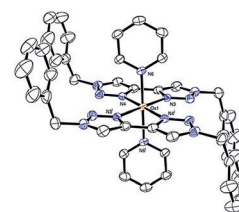
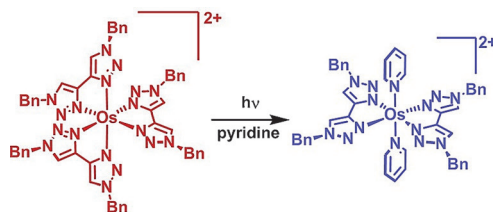
Template-Directed Synthesis of Porous and Protective Core–Shell Bionanoparticles

Photochemistry

P. A. Scattergood, D. A. W. Ross,
C. R. Rice, P. I. P. Elliott* 10697 – 10701



Labilizing the Photoinert: Extraordinarily Facile Photochemical Ligand Ejection in an $[\text{Os}(\text{N}^{\wedge}\text{N})_3]^{2+}$ Complex



Defying convention: The extraordinary ligand ejection photochemistry of the complex $[\text{Os}(\text{btz})_3]^{2+}$ in donor solvents is reported along with observation and

characterization of both *cis* and *trans* isomers of the ligand-loss intermediate $[\text{Os}(\kappa^2\text{-btz})_2(\kappa^1\text{-btz})(\text{NCMe})]^{2+}$ (btz = 1,1'-dibenzyl-4,4'-bi-1,2,3-triazolyl).

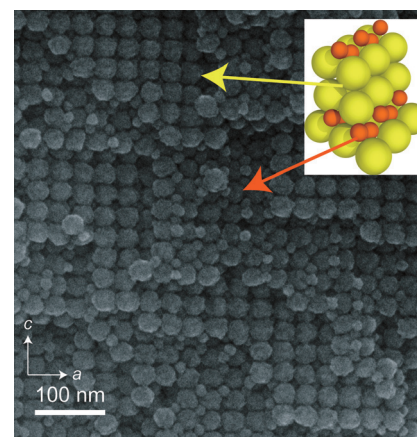
Mesoporous Materials

Y. Kuroda,* Y. Shimbo, Y. Sakamoto,
H. Wada, K. Kuroda* 10702 – 10706



A Mesoporous Superlattice Consisting of Alternately Stacking Interstitial Nanospace within Binary Silica Colloidal Crystals

Pores for thought: The assembly of silica nanospheres of different sizes into a binary colloidal crystal has resulted in a superlattice of nanospace. The CrB-type binary silica colloidal crystals contain interstitial mesopores of different sizes that are spatially separated along the stacking direction. An oriented thin film of the binary nanoparticle mesoporous superlattice has been fabricated on a silicon substrate by dip coating.

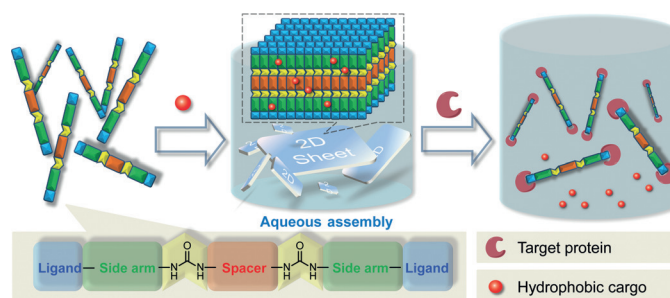


Organic 2D Materials

W. Bai, Z. Jiang, A. E. Ribbe,
S. Thayumanavan* 10707 – 10711

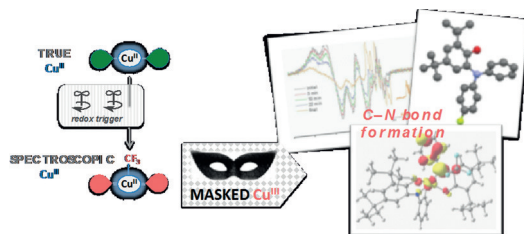


Smart Organic Two-Dimensional Materials Based on a Rational Combination of Non-covalent Interactions



Special assemblies of small organic molecules form nano/microscale supramolecular 2D materials in aqueous media. These assemblies can be pro-

grammed to disassemble in response to a protein and release their non-covalently bound guest molecules.



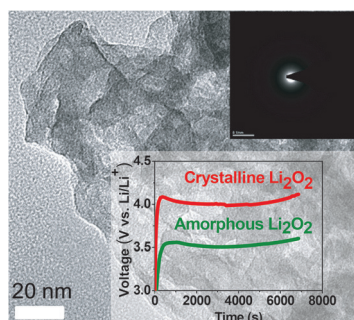
Cu^{III} in hiding: A stable copper(II) complex bearing fully oxidized iminobenzoquinone redox ligands reacts as a copper(III) species and performs high-yielding C–N bond formation. Mechanistic

studies suggest that this behavior could stem from a mechanism akin to reductive elimination occurring at the metal center but facilitated by the ligand.

Ligand Effects

J. Jacquet, P. Chaumont, G. Gontard, M. Orio, H. Vezin, S. Blanchard, M. Desage-El Murr,*
L. Fensterbank* — 10712–10716

C–N Bond Formation from a Masked High-Valent Copper Complex Stabilized by Redox Non-Innocent Ligands

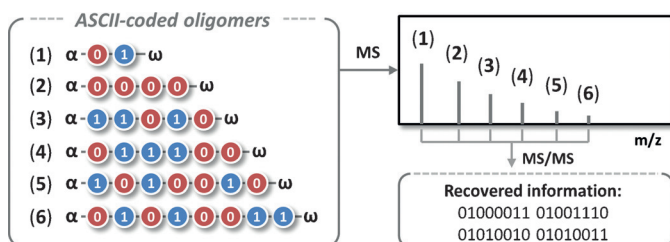


Better off amorphous: Amorphous Li₂O₂ has been synthesized by a rapid reaction of TMAO₂ and LiClO₄ in solution, and its amorphous nature has been confirmed by a range of techniques. Compared with its crystalline siblings, amorphous Li₂O₂ demonstrates increased charge-transport capabilities and enhanced oxidation kinetics, manifesting itself a desirable discharge phase for high-performance Li–O₂ batteries.

Li–O₂ Batteries

Y. Zhang, Q. Cui, X. Zhang, W. C. McKee, Y. Xu, S. Ling, H. Li, G. Zhong, Y. Yang, Z. Peng* — 10717–10721

Amorphous Li₂O₂: Chemical Synthesis and Electrochemical Properties



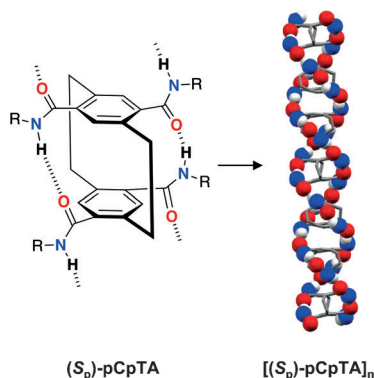
Mass-produced encryption: Mixtures of monodisperse sequence-coded oligomers of different length were studied by tandem mass spectrometry. These “intentionally

polydisperse” mixtures allow storage of a substantial amount of molecular information that can be rapidly deciphered.

Polymer Barcodes

C. Laure, D. Karamessini, O. Milenkovic, L. Charles,* J.-F. Lutz* — 10722–10725

Coding in 2D: Using Intentional Dispersity to Enhance the Information Capacity of Sequence-Coded Polymer Barcodes



Laced up: [2.2]Paracyclophane (pCp) derivatives are capable of programmed self-assembly into extended cofacial π -stacks in solution and in the solid state. The one-dimensional arrangements are homochiral and helically laced-up by a combination of transannular (intra-molecular) and intermolecular hydrogen bonds. pCpTA = pCp-4,7,12,15-tetra-carboxamide.

Cyclophanes

D. E. Fagnani, M. J. Meese, Jr., K. A. Abboud, R. K. Castellano* — 10726–10731

Homochiral [2.2]Paracyclophane Self-Assembly Promoted by Transannular Hydrogen Bonding

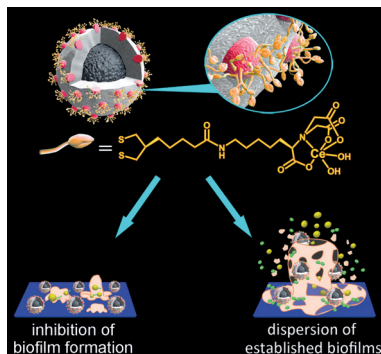


Biofilms

Z. Chen, H. Ji, C. Liu, W. Bing, Z. Wang,
X. Qu* ————— 10732 – 10736



A Multinuclear Metal Complex Based
DNase-Mimetic Artificial Enzyme: Matrix
Cleavage for Combating Bacterial Biofilms



An artificial enzyme for DNA cleavage was obtained by confining protected gold nanoparticles with multiple Ce^{IV} centers on colloidal magnetic $\text{Fe}_3\text{O}_4/\text{SiO}_2$ core/shell particles. This system efficiently inhibited the formation of biofilms, dispersed preformed films, and enabled the eradication of biofilms when used in combination with common antibiotics.

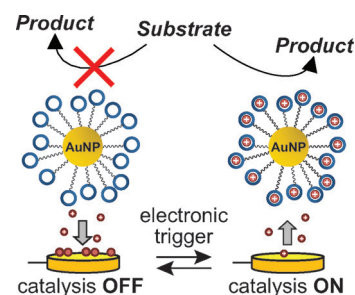
Supramolecular Catalysis

F. della Sala, J. L.-Y. Chen, S. Ranallo,
D. Badocco, P. Pastore, F. Ricci,*
L. J. Prins* ————— 10737 – 10740



Reversible Electrochemical Modulation of
a Catalytic Nanosystem

Hop on, hop off: Metal ions are reversibly released from an electrode to regulate the activity of a gold nanoparticle catalyst (see picture). The system catalyzes the cleavage of 2-hydroxypropyl-*p*-nitrophenyl phosphate and the formation of *p*-nitrophenolate can be monitored by UV/Vis spectroscopy.



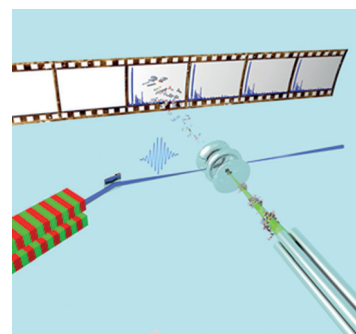
Protein Ionization

T. Schlathölter,* G. Reitsma, D. Egorov,
O. Gonzalez-Magaña, S. Bari,
L. Boschman, E. Bodewits, K. Schnorr,
G. Schmid, C. D. Schröter,
R. Moshhammer,
R. Hoekstra ————— 10741 – 10745



Multiple Ionization of Free Ubiquitin
Molecular Ions in Extreme Ultraviolet
Free-Electron Laser Pulses

Multiple ionization: Exposure of gas-phase ubiquitin ions to intense femto-second pulses from an extreme ultraviolet free-electron laser leads to almost simultaneous removal of many electrons. Before the deposited excitation energy equilibrates, localized fragmentation processes at the ionization sites predominantly lead to formation of immonium ions.



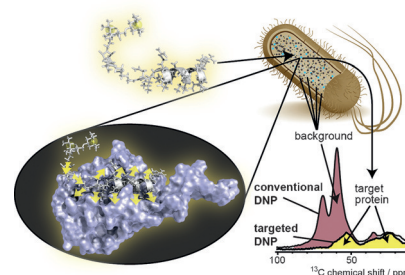
NMR Spectroscopy

T. Viennet, A. Viegas, A. Kuepper, S. Arens,
V. Gelev, O. Petrov, T. N. Grossmann,
H. Heise, M. Etzkorn* — 10746 – 10750



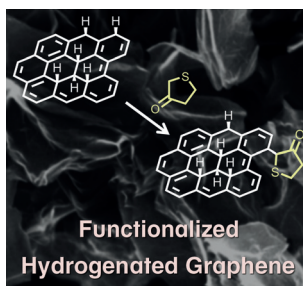
Selective Protein Hyperpolarization in Cell
Lysates Using Targeted Dynamic Nuclear
Polarization

Directing polarization: By using a biradical-labeled ligand, dynamic nuclear polarization (DNP) can be efficiently and very specifically directed to a target protein. This behavior makes it possible to filter out the signal of the target protein from a large background (see picture), enabling a selective solid-state NMR characterization in increasingly native environments such as found in crude cell lysates.



Inside Cover

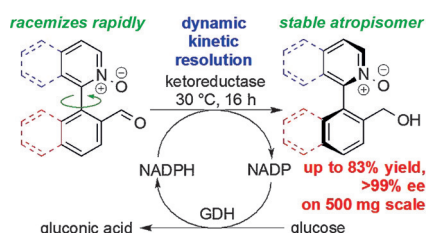
Hydrogenated graphene was functionalized through a dehydrogenative cross-coupling reaction between an allylic C–H bond on the graphene material and an α -C–H bond of tetrahydrothiophen-3-one. The functionalized hydrogenated graphene material benefits from improved dispersion stability in water.



Graphene

C. K. Chua, Z. Sofer,
M. Pumera* 10751–10754

Functionalization of Hydrogenated Graphene: Transition-Metal-Catalyzed Cross-Coupling Reactions of Allylic C–H Bonds

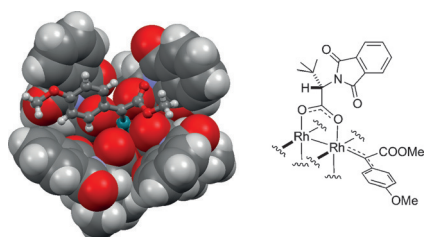


Speedy resolution: Enzymatic reduction of rapidly racemizing biaryl aldehydes yields, by highly selective dynamic kinetic resolution (DKR), single enantiomers of atropisomeric biaryls in high yield and with high *ee* values. This first atropselective enzymatic DKR gives products that contain a pyridine N-oxide and primary alcohol groups and function as catalysts of asymmetric aldehyde allylation.

Atropisomerism

S. Staniland, R. W. Adams,
J. J. W. McDouall, I. Maffucci, A. Contini,
D. M. Grainger, N. J. Turner,*
J. Clayden* 10755–10759

Biocatalytic Dynamic Kinetic Resolution for the Synthesis of Atropisomeric Biaryl N-Oxide Lewis Base Catalysts

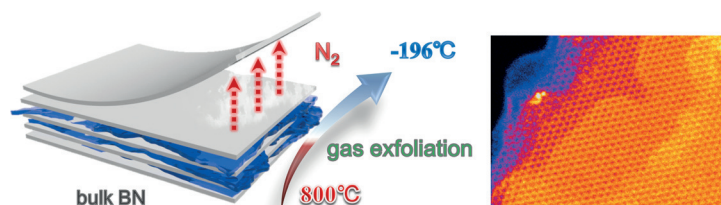


Avec des “Si” on refait le monde: The Si-face of a chiral push/pull dirhodium carbene has been shown to be open to attack by an incoming partner (e.g. styrene) when $[\text{Rh}_2\{(\text{S})\text{-PTTL}\}_4]$ (PTTL = *N*-phthaloyl-*tert*-leucinate) is used as a precatalyst. The shape of the chiral binding site is primarily defined by the conformational preferences of the chiral ancillary ligands and reinforced by a network of weak interligand interactions.

Reactive Intermediates

C. Werlé, R. Goddard, P. Philipps, C. Farès,
A. Fürstner* 10760–10765

Stabilization of a Chiral Dirhodium Carbene by Encapsulation and a Discussion of the Stereochemical Implications



Layered structures: A novel and efficient thermal-expansion-triggered gas exfoliation of boron nitride into few-layered nanosheets was successfully developed

(see picture). This method can also be used to produce other layered materials in high yields.

Two-Dimensional Nanomaterials

W. S. Zhu,* X. Gao, Q. Li, H. P. Li,
Y. H. Chao, M. J. Li, S. M. Mahurin,
H. M. Li, H. Y. Zhu,*
S. Dai* 10766–10770

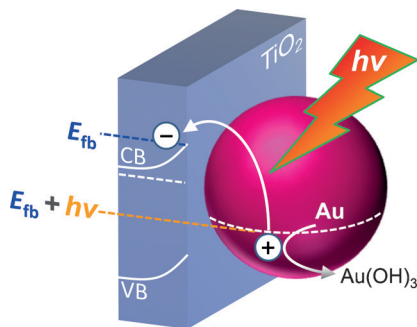
Controlled Gas Exfoliation of Boron Nitride into Few-Layered Nanosheets



Plasmonic Nanostructures

H. Nishi, T. Tatsuma* — 10771 – 10775

Oxidation Ability of Plasmon-Induced Charge Separation Evaluated on the Basis of Surface Hydroxylation of Gold Nanoparticles

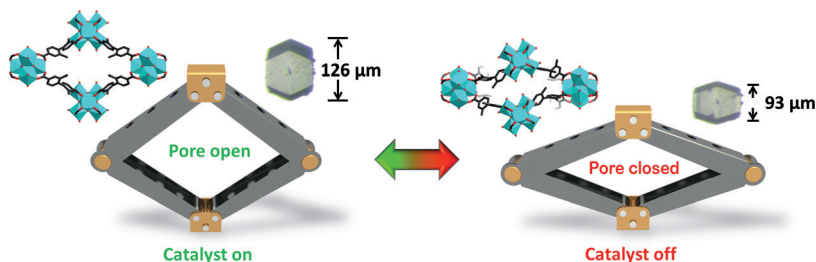


Plasmonic photooxidation ability: The anodic photopotential of plasmon-induced charge separation was evaluated on the basis of surface hydroxylation of gold nanoparticles deposited on TiO₂. It was found that the potential is determined by the flat band potential of TiO₂ (E_{fb}), which depends on the electrolyte pH, and irradiated photon energy ($h\nu$).

Metal–Organic Frameworks

S. Yuan, L. Zou, H. Li, Y.-P. Chen, J. Qin, Q. Zhang, W. Lu,* M. B. Hall,* H.-C. Zhou* — 10776 – 10780

Flexible Zirconium Metal–Organic Frameworks as Bioinspired Switchable Catalysts



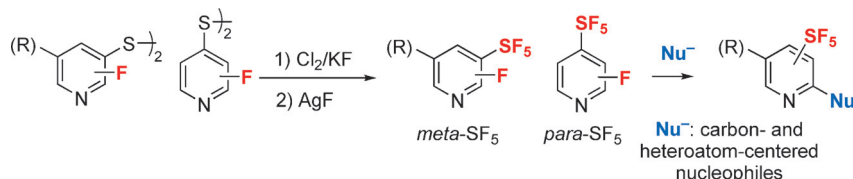
An open and shut case: The inherent cavities and dynamic behavior of flexible MOFs, bear a close resemblance to regulatory enzymes. Switchable activation

and deactivation of their catalytic properties occurs on pore opening and closing by solvation/solvent removal.

Halogenation

M. Kosobokov, B. Cui, A. Balia, K. Matsuzaki, E. Tokunaga, N. Saito, N. Shibata* — 10781 – 10785

Importance of a Fluorine Substituent for the Preparation of *meta*- and *para*-Pentafluoro- λ^6 -sulfanyl-Substituted Pyridines



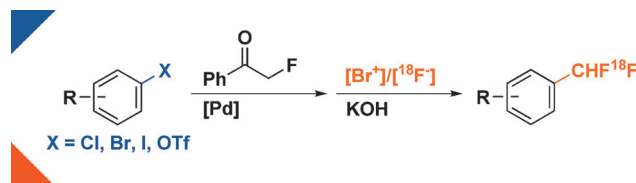
It had to be you... A general route for the synthesis of *m*- and *p*-SF₅-substituted pyridines is disclosed. The fundamental synthetic sequence is the same as those reported for *ortho*-SF₅-substituted pyridines and SF₅-substituted arenes. In this

case, however, at least one fluorine atom on the pyridine ring is essential for the success of the transformation. The fluorine substituent can later be substituted by a C, N, O, or S nucleophile (see scheme).

¹⁸F-Fluorination

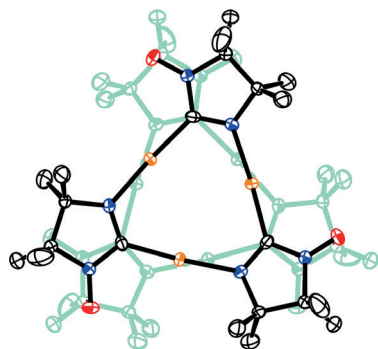
H. Shi, A. Braun, L. Wang, S. H. Liang,* N. Vasdev,* T. Ritter* — 10786 – 10790

Synthesis of ¹⁸F-Difluoromethylarenes from Aryl (Pseudo) Halides



PET peeve resolved: A general method for the synthesis of [¹⁸F]CHF₂-arenes from [¹⁸F]fluoride enables labeling of a variety of arenes and heteroarenes with radiochemical yields (not decay-corrected) from 10 to 60%. The ¹⁸F-fluorination precursors

are readily prepared from aryl chlorides, bromides, iodides, and triflates. Seven ¹⁸F-difluoromethylarene drug analogues and radiopharmaceuticals were synthesized to show the potential of the method.



Triangulation: An open-shell iminonitroxide/gold(I) trimer complex was prepared. The intramolecular exchange interaction between the iminonitroxide moieties was found to be positive ($J_{\text{intra}}/k_B \approx +29$ K). This quartet iminonitroxide/gold complex produced an intercalated silver(I) complex with a ferromagnetic interaction ($J_{\text{intra}}/k_B \approx +25$ K) for the trimer unit.

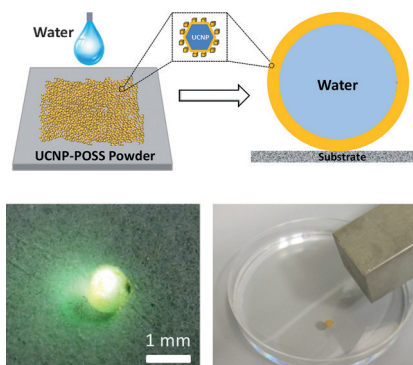
Magnetic Properties

S. Suzuki, T. Wada, R. Tanimoto, M. Kozaki, D. Shiomi, K. Sugisaki, K. Sato, T. Takui, Y. Miyake, Y. Hosokoshi, K. Okada* — 10791 – 10794

Cyclic Triradicals Composed of Iminonitroxide–Gold(I) with Intramolecular Ferromagnetic Interactions



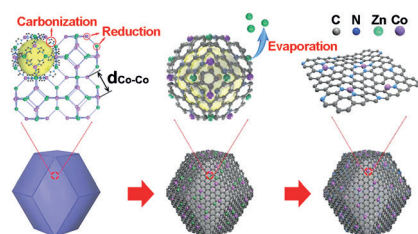
All rolled into one: Liquid marbles based on magnetic upconversion nanoparticles (UCNPs) exhibit excellent magnetic and mechanical properties and were used for the conversion of low-energy near-infrared photons into high-energy UV/Vis photons. They might find application in photodynamic therapy as well as for magnetically controlled drug delivery and release and multifunctional actuation.



Photodynamic Therapy

D. Wang, L. Zhu, J.-F. Chen,* L. Dai* — 10795 – 10799

Liquid Marbles Based on Magnetic Upconversion Nanoparticles as Magnetically and Optically Responsive Miniature Reactors for Photocatalysis and Photodynamic Therapy

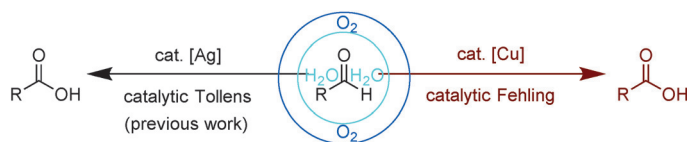


Singles Club: A general strategy enabling the practical and controlled synthesis of supported metal single-atom catalysts with atomic dispersion, high metal loading, and excellent molecular accessibility has been developed and applied to a series of metal single atoms supported on N-doped carbon.

Single-Atom Catalysis

P. Yin, T. Yao, Y. Wu,* L. Zheng, Y. Lin, W. Liu, H. Ju, J. Zhu, X. Hong, Z. Deng, G. Zhou, S. Wei, Y. Li* — 10800 – 10805

Single Cobalt Atoms with Precise N-Coordination as Superior Oxygen Reduction Reaction Catalysts



Without 'Fehl': The first example of homogeneous copper-catalyzed aerobic oxidation of aldehydes is reported. This method utilizes atmospheric oxygen as the sole oxidant, proceeds under

extremely mild aqueous conditions, and covers a wide range of various functionalized aldehydes. Chromatography is generally not necessary for product purification.

Oxidation

M. Liu, C.-J. Li* — 10806 – 10810

Catalytic Fehling's Reaction: An Efficient Aerobic Oxidation of Aldehyde Catalyzed by Copper in Water



Sulfoxidation

Q. Wang, X. Y. Tang,*
M. Shi* 10811–10815



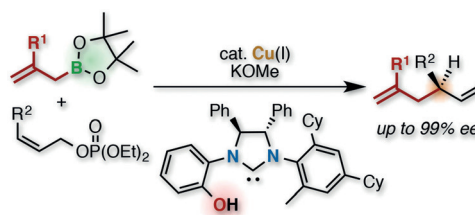
Metal-Free Cross-Coupling of Arylboronic Acids and Derivatives with DAST-Type Reagents for Direct Access to Diverse Aromatic Sulfinamides and Sulfonamides

Mighty mild: A wide range of arylboronic acids and their derivatives underwent efficient cross-coupling under mild and metal-free conditions with reagents based on the electrophilic fluorination reagent diethylaminosulfur trifluoride (DAST).

This simple and convenient method directly afforded sulfinamides, which could be further converted into sulfonamides through a straightforward oxidation step (see scheme).

Asymmetric Catalysis

Y. Yasuda, H. Ohmiya,*
M. Sawamura* 10816–10820



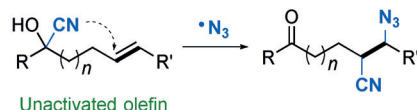
Copper-Catalyzed Enantioselective Allyl–Allyl Coupling between Allylic Boronates and Phosphates with a Phenol/N-Heterocyclic Carbene Chiral Ligand

Novel NHC: Copper-catalyzed enantioselective allyl–allyl couplings between allyl boronates and either Z-acyclic or cyclic allylic phosphates are accomplished by using a new chiral NHC ligand bearing

a phenolic hydroxy group. This reaction occurs with exceptional $\text{S}_{\text{N}}2'$ -type regioselectivities to deliver chiral 1,5-dienes with a tertiary stereogenic center at the allylic/homoallylic position.

Synthetic Methods

Z. Wu, R. Ren, C. Zhu* 10821–10824

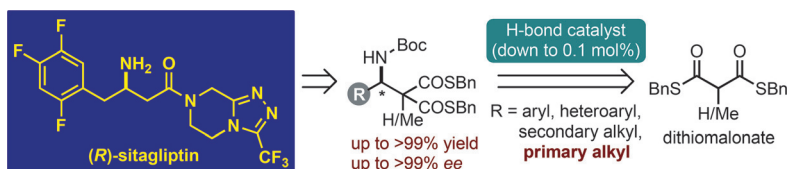


Combination of a Cyano Migration Strategy and Alkene Difunctionalization: The Elusive Selective Azidocyanation of Unactivated Olefins

Expanding the scope: An efficient and metal-free approach for the elusive azidocyanation of unactivated alkenes is proposed. The strategy of intramolecular distal cyano migration is combined with alkene difunctionalization for the first time. A variety of useful azido-substituted alkyl nitriles are readily prepared in good yields and with exquisite regio- and stereoselectivities.

Asymmetric Catalysis

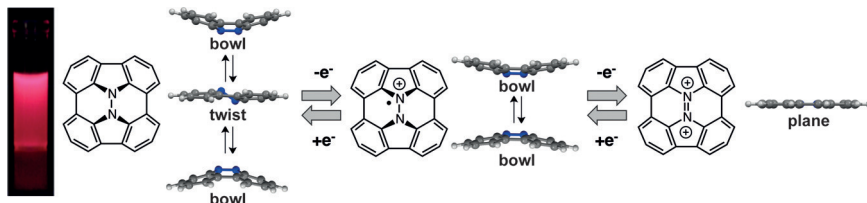
H. Y. Bae, M. J. Kim, J. H. Sim,
C. E. Song* 10825–10829



Direct Catalytic Asymmetric Mannich Reaction with Dithiomalonates as Excellent Mannich Donors: Organocatalytic Synthesis of (R)-Sitagliptin

The third pillar: The intrinsic limitation of asymmetric Mannich reactions—their failure with imine substrates containing a primary alkyl substituent—was solved by employing dithiomalonates as Mannich donors and a chiral squaramide

organocatalyst. This protocol was used to develop a concise organocatalytic, coupling-reagent-free synthesis of the anti-diabetic drug (–)-(R)-sitagliptin (see scheme).



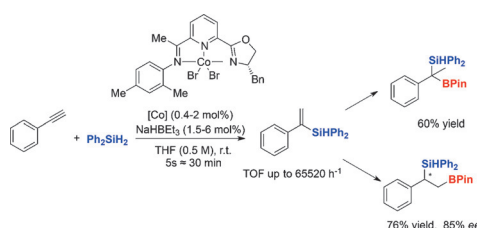
Behavior to bowl you over: A red-fluorescent heterobuckybowl—a heteroatom-containing partial bowl structure of fullerene—was synthesized that had bowl and twist structures in the neutral state, a shallow bowl structure in the monocat-

ion state, and a planar structure in the dication state. A reversible transformation from the curved bowl/twist shape to the planar shape was found to occur upon two-electron oxidation (see picture).

Heterobuckybowls

S. Higashibayashi,* P. Pandit, R. Haruki, S. Adachi, R. Kumai — 10830–10834

Redox-Dependent Transformation of a Hydrazinobuckybowl between Curved and Planar Geometries



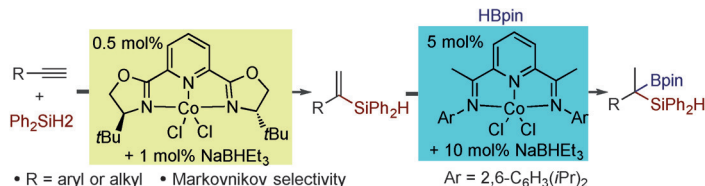
Cobalt catalysis: A highly chemo-, regio- and stereoselective cobalt-catalyzed hydrosilylation reaction of alkynes with silanes was developed (see picture; HBPIn = pinacol borane; TOF = turnover

frequency). The reaction tolerates various functionalized groups, which may lead to further applications and late-stage derivatizations.

Hydrosilylation of Alkynes

J. Guo, Z. Lu* — 10835–10838

Highly Chemo-, Regio-, and Stereoselective Cobalt-Catalyzed Markovnikov Hydrosilylation of Alkynes



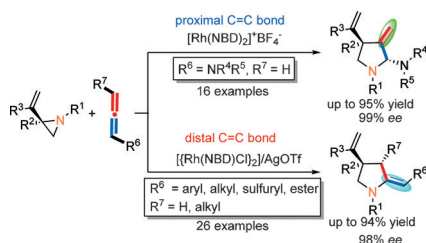
Terminal alkynes can be converted into α -vinylsilanes in a cobalt-catalyzed Markovnikov alkyne hydrosilylation reaction with Ph_2SiH_2 . The reaction products were

further transformed into novel geminal borosilanes in a cobalt-catalyzed hydroboration process, also with Markovnikov selectivity.

Vinylsilanes

Z. Zuo, J. Yang, Z. Huang* — 10839–10843

Cobalt-Catalyzed Alkyne Hydrosilylation and Sequential Vinylsilane Hydroboration with Markovnikov Selectivity



Adding together rapidly: A regiodivergent synthesis of enantioenriched functionalized pyrrolidines, such as 2-methylene- and 3-methylene-pyrrolidines, has been developed through a regioselective [3+2] cycloaddition of vinyl aziridines with allenes and N-alleneamines, respectively. The reaction demonstrates general substrate scope, mild conditions, atom-economy, and proceeds with complete chirality transfer.

Heterocycles

T.-Y. Lin, C.-Z. Zhu, P. Zhang, Y. Wang, H.-H. Wu, J.-J. Feng,* J. Zhang* — 10844–10848

Regiodivergent Intermolecular [3+2] Cycloadditions of Vinyl Aziridines and Allenes: Stereospecific Synthesis of Chiral Pyrrolidines



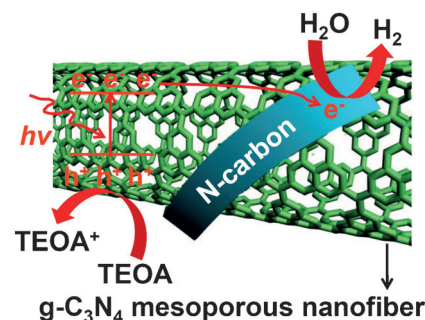
**Photocatalysis**

Q. Han, B. Wang, J. Gao,
L. Qu* _____ **10849 – 10853**



Graphitic Carbon Nitride/Nitrogen-Rich Carbon Nanofibers: Highly Efficient Photocatalytic Hydrogen Evolution without Cocatalysts

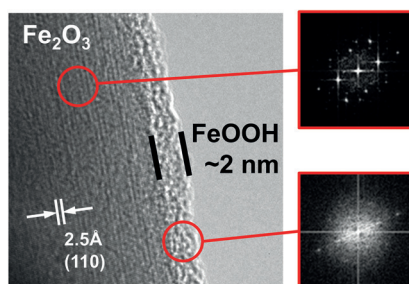
High in fiber: An interconnected framework of mesoporous graphitic- C_3N_4 nanofibers with in situ incorporated N-rich carbon possesses a highly efficient photocatalytic activity for hydrogen evolution under visible light irradiation without cocatalysts. The activity is much higher than that of most previously reported g- C_3N_4 photocatalysts, even in the presence of Pt-based cocatalysts.

**Solar Water Splitting**

J. Y. Kim, D. H. Youn, K. Kang,
J. S. Lee* _____ **10854 – 10858**



Highly Conformal Deposition of an Ultrathin FeOOH Layer on a Hematite Nanostructure for Efficient Solar Water Splitting



Skinny malinks: An ultrathin (ca. 2 nm) amorphous FeOOH overlayer was deposited conformally on a hematite nanostructure by a simple solution-based precipitation method, to generate an oxygen evolution cocatalyst for efficient solar water splitting. With an FeOOH overlayer, the water oxidation performance of hematite increased as a result of improved water oxidation kinetics and passivation of the surface states.

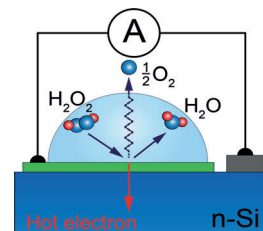
Hot Electrons

I. I. Nedrygailov, C. Lee, S. Y. Moon,
H. Lee, J. Y. Park* _____ **10859 – 10862**



Hot Electrons at Solid–Liquid Interfaces: A Large Chemoelectric Effect during the Catalytic Decomposition of Hydrogen Peroxide

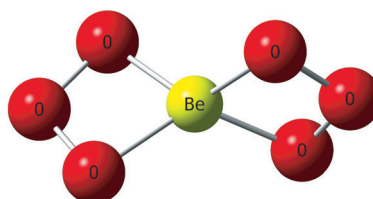
Some like it hot: The detection of hot electrons as a chemicurrent generated at the solid–liquid interface during catalytic decomposition of hydrogen peroxide is possible using metal/n-Si Schottky nanodiodes. The dependence of the detected current on the metal-film thickness confirms the chemical nature of the hot electrons.

**Front Cover****Beryllium Compounds**

Q. Zhang, P. Jerabek, M. Chen, M. Zhou,*
G. Frenking* _____ **10863 – 10867**



The Oxygen-Rich Beryllium Oxides BeO_4 and BeO_6



Give Be an O: The oxygen-rich beryllium oxide species BeO_4 with the structures OBeOOO , $\text{OBe}(\text{O}_3)$, and the bis(ozonide) complex $\text{Be}(\text{O}_3)_2$ were synthesized and structurally characterized by matrix isolation infrared spectroscopy and quantum chemical calculations.

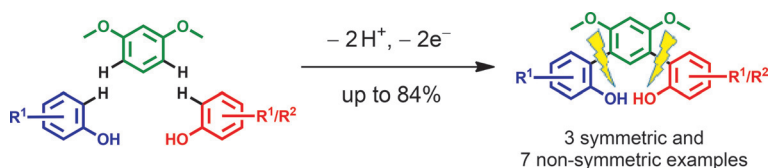
Chemical twins: The subnitridometalates $\text{Ba}_{23}\text{Na}_{11}(\text{MN}_4)_4$ ($\text{M} = \text{V}, \text{Nb}, \text{or Ta}$) can be described as “chemical twins” with separated ionic and metallic motifs. The chemistry of the subnitrides was thus extended through the incorporation of complex nitridometalate anions into a metallic matrix of barium and sodium atoms.



Subnitridometalates

M. Wörsching, F. Tambornino, S. Datz, C. Hoch* 10868 – 10871

Chemical Twinning of Salt and Metal in the Subnitridometalates $\text{Ba}_{23}\text{Na}_{11}(\text{MN}_4)_4$ with $\text{M} = \text{V}, \text{Nb}, \text{Ta}$



Two selective couplings enable the generation of *meta*-terphenyl-2,2''-diols in a metal- and reagent-free manner in an electrosynthetic process. The reactions

are scalable and very simple to perform and provide access to precursors for pincer ligands.

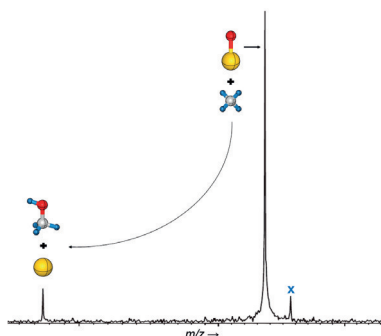
Electrosynthesis

S. Lips, A. Wiebe, B. Elsler, D. Schollmeyer, K. M. Dyballa, R. Franke, S. R. Waldvogel* 10872 – 10876

Synthesis of *meta*-Terphenyl-2,2''-diols by Anodic C–C Cross-Coupling Reactions



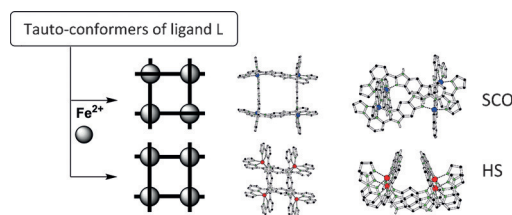
Give me an O: Mass spectrometry studies and quantum chemical calculations show that the selective oxidation of methane to methanol promoted by $[\text{AuO}]^+$ proceeds by oxygen-atom transfer. The signal labeled with “x” is due to reactions with background contaminants.



Gas-Phase Reactions

S. Zhou, J. Li, M. Schlagen, H. Schwarz* 10877 – 10880

The Unique Gas-Phase Chemistry of the $[\text{AuO}]^+/\text{CH}_4$ Couple: Selective Oxygen-Atom Transfer to, Rather than Hydrogen-Atom Abstraction from, Methane



The coordination of Fe^{II} metal ions by a homoditopic ligand **L** with two tridentate chelates leads to the tautomerism-driven emergence of complexity. The two tautoisomeric $\text{Fe}^{\text{II}}_4\text{L}_4$ tetramers that were thus

formed exhibit different magnetic properties. One complex undergoes spin cross-over (SCO), whereas the other one is blocked in the Fe^{II} high spin (HS) state.

Iron(II) Complexes

B. Schäfer, J.-F. Greisch, I. Faus, T. Bodenstein, I. Šalitroš, O. Fuhr, K. Fink, V. Schünemann, M. M. Kappes, M. Ruben* 10881 – 10885

Divergent Coordination Chemistry: Parallel Synthesis of $[2 \times 2]$ Iron(II) Grid-Complex Tauto-Conformers



Back Cover



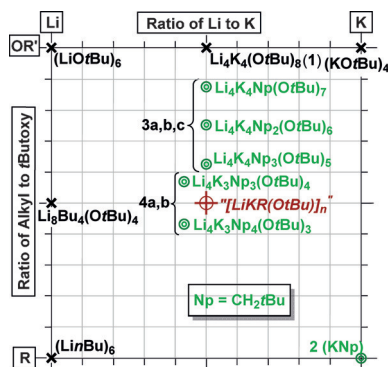


Superbases

P. Benrath, M. Kaiser, T. Limbach,
M. Mondeshki, J. Klett* 10886–10889



Combining Neopentyllithium with
Potassium *tert*-Butoxide: Formation of an
Alkane-Soluble Lochmann–Schlosser
Superbase



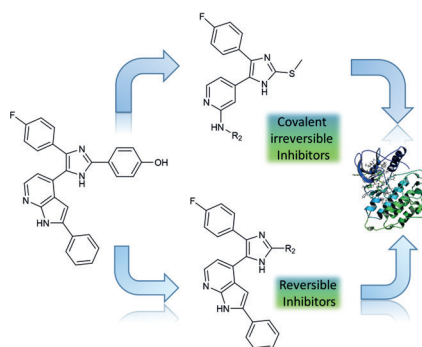
Bases à la carte: A reaction of neopentyl-lithium (LiCH_2tBu) with potassium *tert*-butoxide (KOtBu) forms alkane-soluble mixed alkyl/alkoxy aggregates containing both lithium and potassium ions. These neopentyl analogues of the Lochmann–Schlosser superbase are products with varying compositions $\text{Li}_x\text{K}_y\text{Np}_z(\text{OtBu})_{x+y-z}$ (see Scheme), the outcome of a complicated equilibrium based on the concentration and solubilities of its components.

Kinase Inhibitors

M. Günther, M. Juchum, G. Kelter,
H. Fiebig, S. Laufer* 10890–10894



Lung Cancer: EGFR Inhibitors with Low
Nanomolar Activity against a Therapy-
Resistant L858R/T790M/C797S Mutant



From reversible to irreversible and back: A new class of trisubstituted imidazoles (see scheme) was designed to overcome drug resistance caused by the EGFR mutation T790M in non-small-cell lung cancer, predominantly through non-covalent interactions. In contrast to third-generation irreversible EGFR inhibitors, these imidazoles are up to 350-fold less vulnerable to Cys 797 mutation and show high cellular activity in the low double-digit nanomolar range.

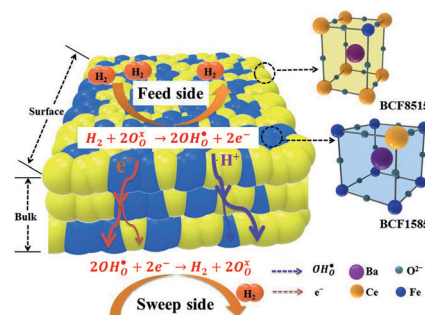
Ceramic Membranes

S. Cheng, Y. Wang, L. Zhuang, J. Xue,
Y. Wei,* A. Feldhoff, J. Caro,*
H. Wang* 10895–10898



A Dual-Phase Ceramic Membrane with
Extremely High H_2 Permeation Flux
Prepared by Autoseparation of a Ceramic
Precursor

A dual-phase ceramic membrane consisting of 50 mol % $\text{BaCe}_{0.85}\text{Fe}_{0.15}\text{O}_{3-\delta}$ and 50 mol % $\text{BaCe}_{0.15}\text{Fe}_{0.85}\text{O}_{3-\delta}$ is formed automatically by demixing of $\text{BaCe}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ through calcination. The first perovskite phase acts as the main proton conductor and the other as the main electron conductor. The composite ceramic shows an extremely high H_2 permeation flux. This concept can also be used for the synthesis of other ceramics.



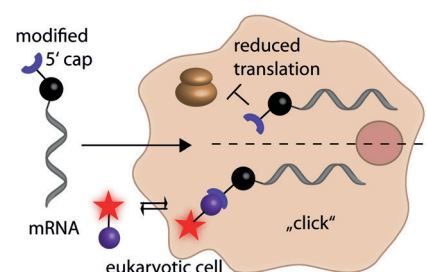
RNA Labeling

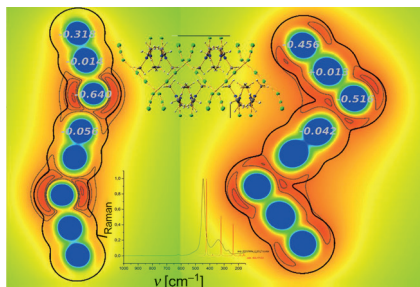
J. M. Holstein, L. Anhäuser,
A. Rentmeister* 10899–10903



Modifying the 5'-Cap for Click Reactions of
Eukaryotic mRNA and To Tune Translation
Efficiency in Living Cells

A feather in your cap: A straightforward approach is presented for the efficient production of a range of *N*7-modified 5'-caps on mRNAs based on the highly promiscuous methyltransferase Ecm1. These can be used to tune translation of the respective mRNAs both in vitro and in cells. Appropriate modifications allow subsequent bioorthogonal reactions, as demonstrated by intracellular live-cell labeling of a target mRNA.





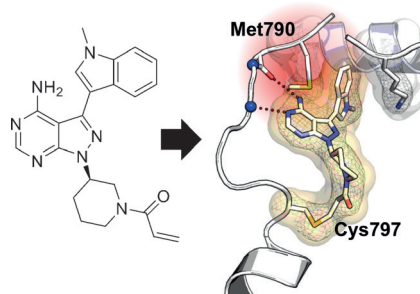
Being discrete: The new polychloride salt $[\text{CCl}(\text{NMe}_2)_2]^+_2[\text{Cl}_8]^{2-}$ (tetramethylchloroamidinium octachloride) was crystallized from an ionic liquid and fully characterized. It is the first dianion of a polychloride to be reported. Detailed quantum-chemical calculations show the salt is made up of discrete $[\text{Cl}_8]^{2-}$ anions which do not show any tendency to build up networks through halogen bonding.

Polychlorides

R. Brückner, P. Pröhm, A. Wiesner, S. Steinhauer, C. Müller, S. Riedel* — 10904–10908

Structural Proof for the First Dianion of a Polychloride: Investigation of $[\text{Cl}_8]^{2-}$

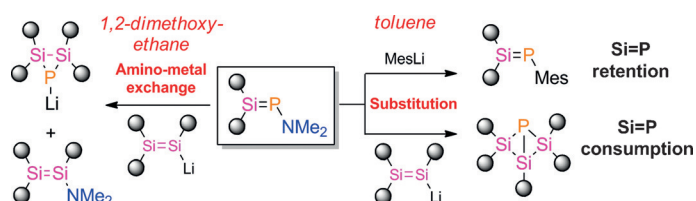
Methods against mutants: Targeting acquired drug resistance represents the major challenge in the treatment of EGFR-driven non-small-cell lung cancer. Complex crystal structures of new covalent inhibitors and detailed kinetic studies provide insight into the key features required for targeting EGFR mutations, including EGFR-L858R/T790M/C797S.



Enzyme Inhibitors

J. Engel, C. Becker, J. Lategahn, M. Keul, J. Ketzer, T. Mühlenberg, L. Kolipara, C. Schultz-Fademrecht, R. P. Zahedi, S. Bauer, D. Rauh* — 10909–10912

Insight into the Inhibition of Drug-Resistant Mutants of the Receptor Tyrosine Kinase EGFR



The NMe_2 group as a leaving group on the $\text{P}=\text{Si}$ bond: An electrophilic phosphasilene reacts with MesLi under substitution and retention of the double bond. With $\text{Tip}_2\text{Si}=\text{Si}(\text{Tip})\text{Li}$ ($\text{Tip} = 2,4,6\text{-}i\text{Pr}_3\text{C}_6\text{H}_2$) the

$\text{Si}=\text{P}$ bond is consumed after initial substitution to yield a trisilaphospha-[1.1.0]bicyclobutane. In contrast, in the donor solvent dme, an amino-metal exchange occurs.

Main-Group Chemistry

P. Willmes, L. Junk, V. Huch, C. B. Yildiz,* D. Scheschkewitz* — 10913–10917

Diverse Reactivity of an Electrophilic Phosphasilene towards Anionic Nucleophiles: Substitution or Metal-Amino Exchange



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.

Angewandte Corrigendum

Water-Assisted Nitrile Oxide
Cycloadditions: Synthesis of Isoxazoles
and Stereoselective Syntheses of
Isoxazolines and 1,2,4-Oxadiazoles

C. Kesornpun, T. Aree,
C. Mahidol, S. Ruchirawat,
P. Kittakoop* — 3997–4001

Angew. Chem. Int. Ed. **2016**, 55

DOI: 10.1002/anie.201511730

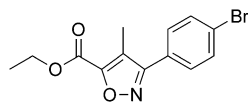
In this Communication, the following mistakes need to be corrected:

Page 3997: The sentence “Therefore, the synthesis of isoxazolines and isoxazoles is carried out in solvents containing bases as catalysts” should be corrected as “Therefore, the synthesis of isoxazolines and isoxazoles is carried out in solvents containing bases.” The minor regioisomer of individual isoxazolines shown in Scheme 2 and Figure 2S (Supporting Information) and isoxazoles displayed in Scheme 5 and Figure 5S might be present in the crude products; details of regioisomers of some compounds were previously reported by Huisgen and co-workers.^[1]

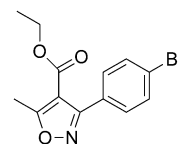
Page 3999: The claim that “the preparation of the novel hybrid isoxazoline-oxadiazoles presented here has never been reported” is wrong. The hybrid isoxazoline-oxadiazole was previously reported by Bettinetti and Gamba in 1970.^[2] However, the spectroscopic and crystallographic determination of the stereochemistry of this compound class has been successfully established in the current work.

Page 3999: “... converted into (bis)**6bo** during crystallization, and it has a plane of symmetry (*meso* form)”. The optical rotation of (bis)**6bo** that was incorrectly measured to a close-to-zero value led to the wrong conclusion that (bis)**6bo** has *meso* form. The correct optical rotation of (bis)**6bo** is -289.0 ($c=0.42$ in DMSO). Moreover, after examining X-ray crystallographic data, it was found that (bis)**6bo** has a pseudo-twofold axis through the bridge oxygen atom; therefore it is a chiral molecule.

Page 4000: In Scheme 5, the structure of **8dh** needs to be revised as shown below.



Previously proposed structure of **8dh**



The correct structure of **8dh**

The authors sincerely apologize for these errors. They are grateful to Prof. Manfred Christl, University of Würzburg, for helpful comments.

- [1] a) K. Bast, M. Christl, R. Huisgen, W. Mack, R. Sustmann, *Chem. Ber.* **1973**, 106, 3258–3274; b) K. Bast, M. Christl, R. Huisgen, W. Mack, *Chem. Ber.* **1972**, 105, 2825–2840; c) M. Christl, R. Huisgen, *Chem. Ber.* **1973**, 106, 3345–3367; d) M. Christl, R. Huisgen, R. Sustmann, *Chem. Ber.* **1973**, 106, 3275–3290.
[2] G. F. Bettinetti, A. Gamba, *Gazz. Chim. Ital.* **1970**, 100, 1144–1159.

Angewandte Corrigendum

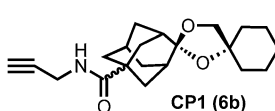
A Click Chemistry-Based Proteomic
Approach Reveals that 1,2,4-Trioxolane
and Artemisinin Antimalarials Share
a Common Protein Alkylation Profile

H. M. Ismail, V. E. Barton, M. Panchana,
S. Charoensutthivarakul, G. A. Biagini,
S. A. Ward, P. M. O'Neill* — 6401–6405

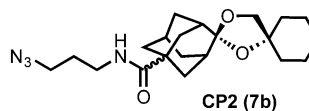
Angew. Chem. Int. Ed. **2016**, 55

DOI: 10.1002/anie.201512062

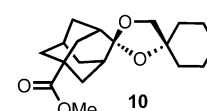
In this Communication there was an error in the structures of negative controls CP1 (**6b**) and CP2 (**7b**) (Figures 2 and 3) and intermediate **10** (Scheme 2). The correct structures are given below.



CP1 (**6b**)



CP2 (**7b**)



10

These errors have no bearing on the conclusions reached in the manuscript. The authors apologize for these errors.

Angewandte Corrigendum

In Figure 2c of this Communication, the label on the horizontal axis was wrongly given as “t/h” instead of “t/min”. The correct version of Figure 2c is given below. The authors apologize for this mistake.

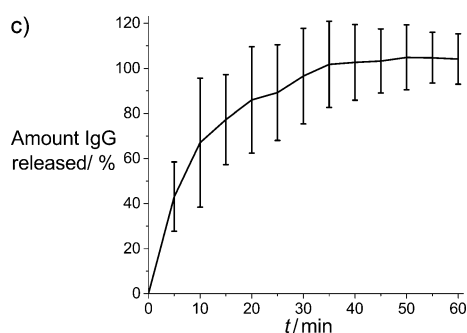


Figure 2. [...] c) Release of fluorescence-labeled IgG antibodies from hydrogel beads (10 mg mL^{-1}).

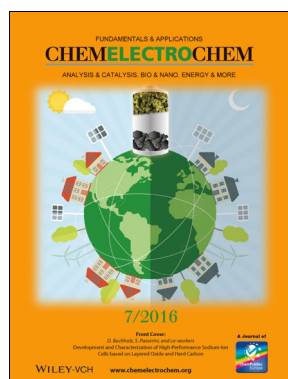
Noncovalent Hydrogel Beads as
Microcarriers for Cell Culture

R. Wieduwild, S. Krishnan, K. Chwalek,
A. Boden, M. Nowak, D. Drechsel,
C. Werner,* Y. Zhang* — 3962–3966

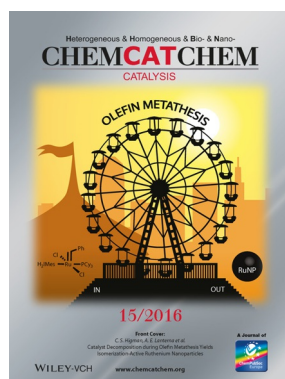
Angew. Chem. Int. Ed. **2015**, *54*

DOI: 10.1002/anie.201411400

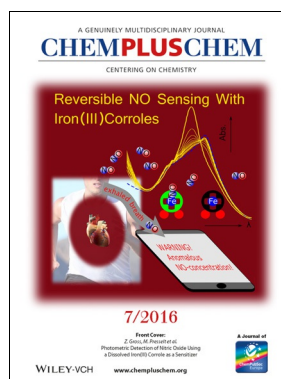
Check out these journals:



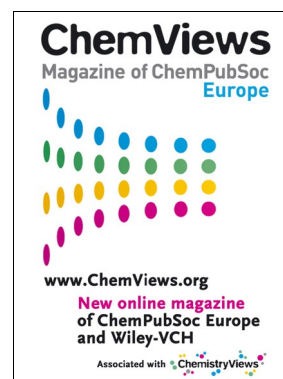
www.chemelectrochem.org



www.chemcatcher.org



www.chempluschem.org



www.chemviews.org