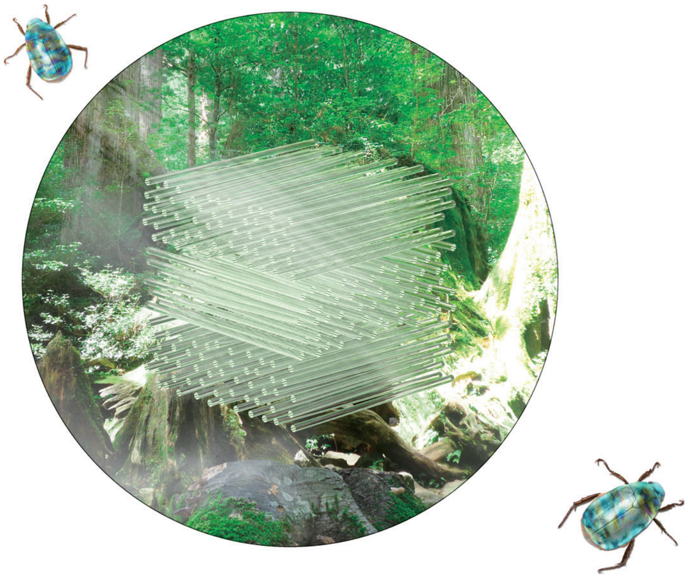
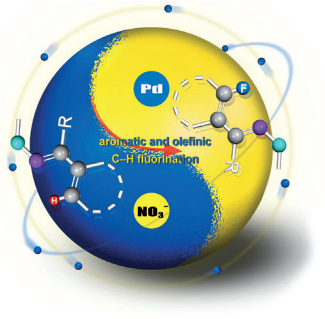
Aerogels ...

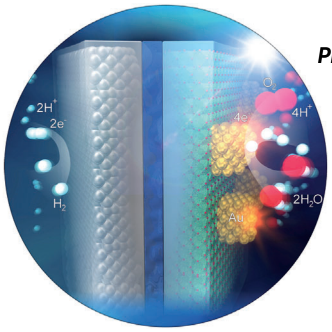


… with 3D-ordered nanofiber skeletons of liquid-crystalline nanocellulose are described by T. Saito et al. in their Communication on page 10394 ff. The nanocellulose is composed of mechanically strong, surface-carboxylated cellulose nanofibers dispersed in a nematic order, which were prepared from abundant wood biomass through a water-based process. These aerogels display good insulation properties, optical transparency, and mechanical toughness.

Fluorination

In their Communication on page 10329 ff., D.-Q. Xu, Z.-Y. Xu, and co-workers describe the fluorination of aromatic and olefinic C(sp^2)–H bonds in the presence of a catalytic amount of inexpensive and nontoxic nitrate.



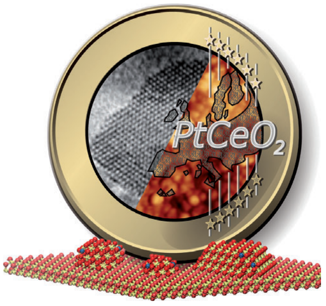


Photochemistry

H. Misawa and co-workers report in their Communication on page 10350 ff. how a plasmon-induced water splitting system operates under irradiation by visible light using both sides of the same strontium titanate substrate.

Platinum-Based Catalysts

V. Matolín, J. Libuda, K. M. Neyman, and co-workers show in their Communication on page 10525 ff. that Pt-CeO_2 materials with the highest possible noble-metal dispersion can be prepared as catalysts.



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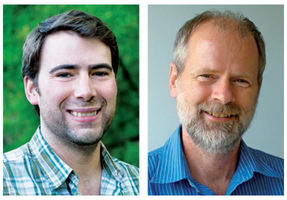
Editorial



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Author Profile

News


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M. C. Willis


E. K. Brechin


D. W. Bruce


H. Braunschweig


A. D. Smith


I. Paterson


T. J. Donohoe


F. Wudl

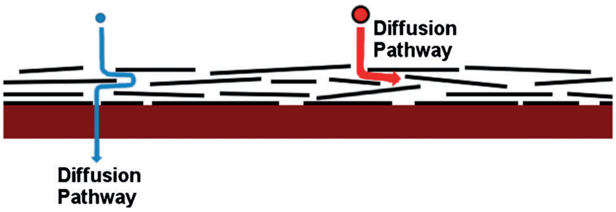

P. A. Gale


B. Binks

Books

Highlights

Membranes



Depending on size: Graphene oxide can be deposited into thin layers having defects and inter-layer structures with dimensions that are appropriate for separating molecules based on size differences and enable rapid transport through these structures. The picture illustrates the pathway of two differently sized molecules through the graphene oxide layers.

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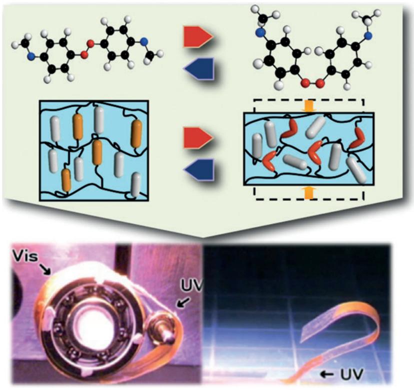
Minireviews

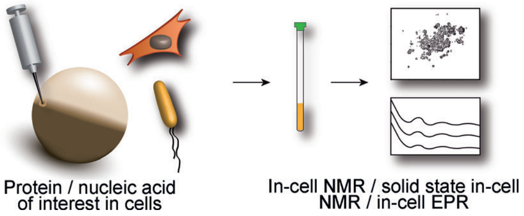
Photomechanics

The macroscopic deformation of photomobile polymer materials upon irradiation with light is a result of cooperative effects of crosslinked liquid-crystalline polymers. This review describes recent advances in the molecular design, fabrication methods, and composite structures of such materials for their application in various fields, such as soft robotics and microfluidics.



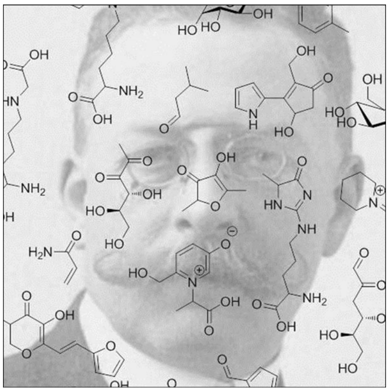
Reviews

Bioanalytical Methods



Magnets that attract cell biology: Magnetic resonance spectroscopy has been applied to cellular systems and tissues for a long time. The development of in-cell NMR and EPR spectroscopy now enables direct investigation of the conformation, dynamics, binding events, and posttranslational modifications of biological macromolecules in living cells. This Review summarizes the main techniques and applications to different cellular systems and macromolecules.

Glycation Reactions



Food for thought: The reaction of reducing carbohydrates with amino compounds described by Louis-Camille Maillard in 1912 is responsible for the aroma, taste, and appearance of thermally processed food. Corresponding reactions occur in the body and are important in diabetes and ageing processes. A historical overview of the most important findings is given in this Review.

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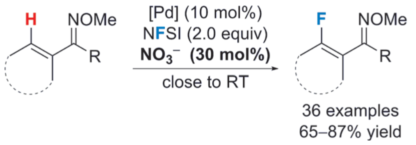
Communications

Fluorination

S.-J. Lou, D.-Q. Xu,*
Z.-Y. Xu* ______________ 10330 – 10335

Mild and Versatile Nitrate-Promoted C—H Bond Fluorination

Frontispiece



- mild reaction conditions (close to RT)
- promoted by inexpensive and non-toxic nitrates
- fluorination of aromatic and olefinic C(sp^2)–H bonds

Nitrate makes it possible: A novel and facile method for C—H bond fluorination entails remarkably mild reaction conditions (close to room temperature in most cases). Both aromatic and olefinic C(sp^2)—H bonds were selectively fluorinated in the presence of a catalytic amount of inexpensive and nontoxic nitrate as the promoter.

Platinum-Free Fuel Cell

A. Serov, M. Padilla, A. J. Roy,
P. Atanassov,* T. Sakamoto, K. Asazawa,
H. Tanaka ______________ 10336 – 10339

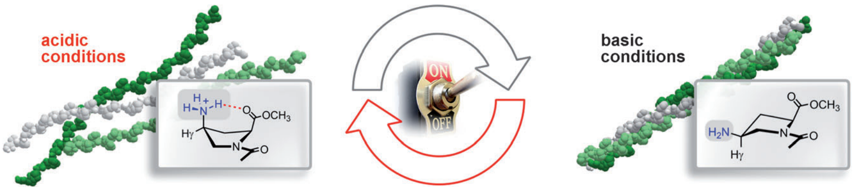
Anode Catalysts for Direct Hydrazine Fuel Cells: From Laboratory Test to an Electric Vehicle

Enjoy the ride: Highly active electrocatalysts for hydrazine hydrate fuel cells were developed, synthesized, and integrated into a vehicle prototype. The materials show the highest activity ever measured with a peak current density of 16000 A g^{-1} and a power density of 450 mW cm^{-2} under operation in air.

Collagen

C. Siebler, R. S. Erdmann,
H. Wennemers* ______________ 10340 – 10344

Switchable Proline Derivatives: Tuning the Conformational Stability of the Collagen Triple Helix by pH Changes

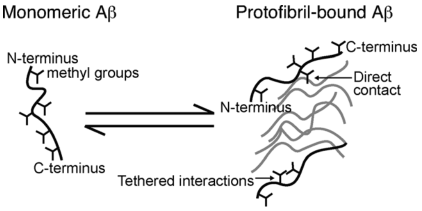


Small proton, big impact: (4*S*)-Aminoproline is introduced as a pH-sensitive probe for tuning the conformational properties of peptides and proteins. The pH-triggered flip of the ring puckering and the formation/release of a transannular H bond were used to switch the formation of collagen triple helices on and off reversibly.

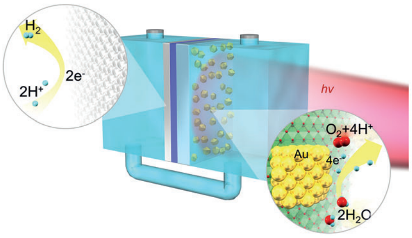
Protein Interactions

N. L. Fawzi,* D. S. Libich, J. Ying,
V. Tugarinov,
G. M. Clore* ______________ 10345 – 10349

Characterizing Methyl-Bearing Side Chain Contacts and Dynamics Mediating Amyloid β Protofibril Interactions Using ^{13}C$_{\text{methyl}}$-DEST and Lifetime Line Broadening



Amyloid β assemblies: Amyloid β plays a key role in the etiology of Alzheimer's disease. Solution NMR ^{13}C$_{\text{methyl}}$ lifetime line broadening and dark-state exchange saturation transfer spectroscopy (DEST) is used to probe the transient interactions of methyl groups of monomeric amyloid β exchanging on the surface of very large (2–80 MDa) protofibril assemblies.



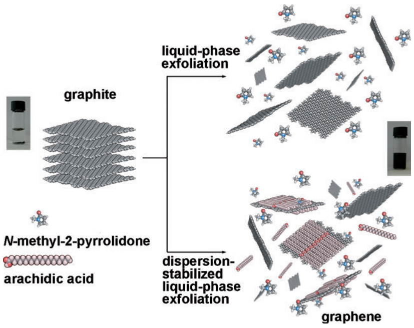
Photochemistry: A plasmon-induced water splitting system that operates under irradiation by visible light using both sides of the same $SrTiO_3$ substrate is reported (see picture). The hydrogen-evolution action spectrum closely corresponds to the plasmon resonance spectrum, indicating that the plasmon-induced charge separation at the Au/$SrTiO_3$ interface promotes water oxidation and the reduction of protons.

Water Splitting

Y. Zhong, K. Ueno, Y. Mori, X. Shi, T. Oshikiri, K. Murakoshi, H. Inoue, H. Misawa* ______ **10350 – 10354**

Plasmon-Assisted Water Splitting Using Two Sides of the Same $SrTiO_3$ Single-Crystal Substrate: Conversion of Visible Light to Chemical Energy

Inside Back Cover



Graphene dispersions: A simple method is reported for producing homogenous dispersions of unfunctionalized and non-oxidized graphene nanosheets in 1-methyl-2-pyrrolidinone (see picture). Simple molecular modules are used, which act as dispersion-stabilizing compounds during a liquid-phase exfoliation process, leading to an increase in the concentration of graphene dispersions.

Supramolecular Chemistry

A. Ciesielski, S. Haar, M. El Gemayel, H. Yang, J. Clough, G. Melinte, M. Gobbi, E. Orgiu, M. V. Nardi, G. Ligorio, V. Palermo, N. Koch, O. Ersen, C. Casiraghi, P. Samorì* _ **10355 – 10361**

Harnessing the Liquid-Phase Exfoliation of Graphene Using Aliphatic Compounds: A Supramolecular Approach

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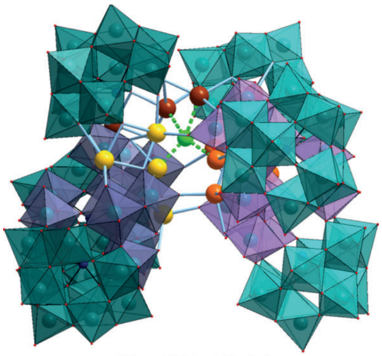

$\{Ag_{18}Cl(Te_3W_{38})_2\}$

Cluster-in-cluster: Polyoxometalate clusters $[H_{(10+m)}Ag_{18}Cl(Te_3W_{38}O_{134})_2]_n$ with $n=1$ and $m=0$, $n=2$ and $m=3$, and $n=\infty$ and $m=5$ were isolated after 4, 10, and 14 days from the same reaction mixture. The proposed mechanism for the formation of the clusters was confirmed by ESI-MS studies and control experiments, which demonstrate the crucial role that TeO_3^{2-}, Cl^-, and Ag^+ play in the self-assembly of these compounds.

Polyoxometalates

C. Zhan, J. M. Cameron, J. Gao, J. W. Purcell, D.-L. Long,* L. Cronin* ______ **10362 – 10366**

Time-Resolved Assembly of Cluster-in-Cluster $\{Ag_{12}\}$-in-$\{W_{76}\}$ Polyoxometalates under Supramolecular Control

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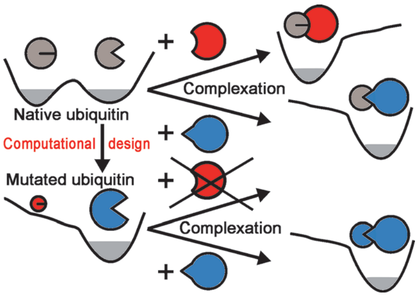


Since protein dynamics is inextricably linked to protein function, protein functionality can be altered by manipulating protein dynamics. The specificity of protein–protein binding can be altered solely by a designed change in conformational preference, while leaving the binding interface untouched. This mechanism, which nature utilizes to control binding specificity, provides a novel route to designing protein function.

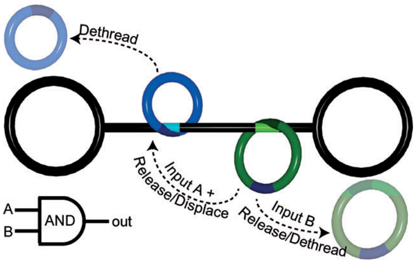
Protein Design

S. Michielssens, J. H. Peters, D. Ban, S. Pratihar, D. Seeliger, M. Sharma, K. Giller, T. M. Sabo, S. Becker, D. Lee, C. Griesinger, B. L. de Groot* ______ **10367 – 10371**

A Designed Conformational Shift To Control Protein Binding Specificity

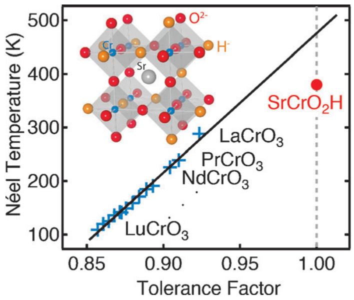
DNA Rotaxane Shuttles

Shuttling on a DNA track: A cascade macrocycle-displacement and -dethreading reaction triggered by light and toehold release oligodeoxynucleotides is used to assemble a logic AND gate on a double-stranded DNA [3]rotaxane. Such structures may find applications in nanoengineering, DNA computing, and even nanomedicine.

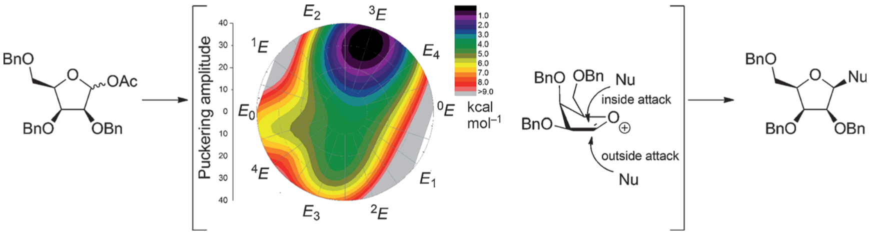


Chromium Oxyhydride

Performing better under pressure: A high-pressure, high-temperature route gives the first chromium oxyhydride, $SrCrO_2H$. It has a perovskite structure and the highest antiferromagnetic ordering temperature (T_N) among chromium oxides, which is remarkable given non-bonding nature of its Cr-H-Cr interaction. The high T_N arises from decreased octahedral tilting that enhances the Cr-O-Cr antiferromagnetic coupling and reduces the competition between nearest and next-nearest neighbor interactions.



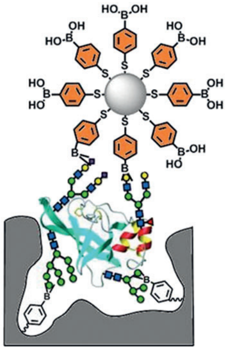
Carbohydrates



Mapping the landscape: The energy landscape of the complete conformational space of the oxocarbenium ions of the four pentofuranosides, ribose, arabinose, xylose, and lyxose, have been mapped. The free energy surfaces (FESs) provide a very detailed picture of the stability of the oxocarbenium ion conformers and the influence of the ring substituents on these. The FES maps can be used to account for the stereochemistry in condensations of furanosyl acetate donors.

Glycoprotein Assay

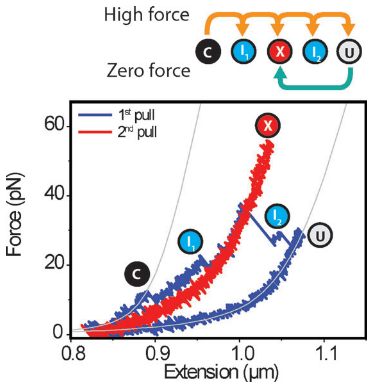
A specific and sensitive approach has been developed to detect trace levels of glycoproteins in complex samples. A target glycoprotein is specifically captured by a boronate-affinity molecular-imprinted polymer array and then labeled with boronate-affinity silver nanoparticles. The surface-enhanced Raman scattering of the resulting complex (see picture) is then measured.



Protein Folding

A. Mashaghi, S. Mashaghi,
S. J. Tans* ______ 10390 – 10393

Misfolding of Luciferase at the Single-Molecule Level



Use the force: When stretched from its ends, a single molecule of luciferase unfolds in a multistep process and visits multiple conformational intermediates (I) on the way to the fully unfolded state (U). When allowed to relax, the chain can refold to a misfolded state (X), which has a long lifetime and high mechanical stability, and suppresses formation of the fully folded state (C).

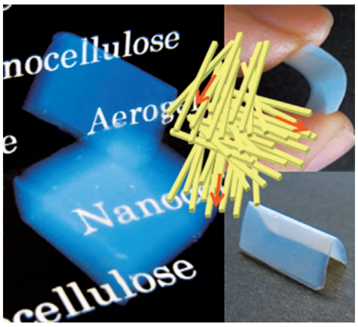
Ordered Aerogels

Y. Kobayashi, T. Saito,*
A. Isogai ______ 10394 – 10397

Aerogels with 3D Ordered Nanofiber Skeletons of Liquid-Crystalline Nanocellulose Derivatives as Tough and Transparent Insulators

Front Cover

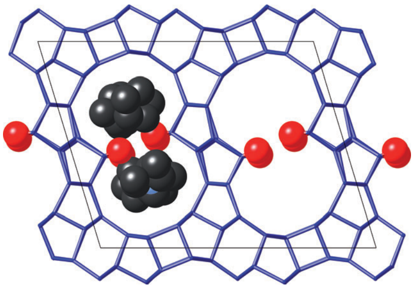
A structurally new type of aerogel was prepared from a multi-domain nematic liquid-crystalline dispersion of mechanically strong, surface-carboxylated cellulose nanofibers through acid-induced gelation and supercritical drying. This aerogel displays good insulation properties, optical transparency, and mechanical toughness.



Zeolite Structures

S. Smeets, D. Xie,* C. Baerlocher,
L. B. McCusker,* W. Wan, X. Zou,
S. I. Zones ______ 10398 – 10402

High-Silica Zeolite SSZ-61 with Dumbbell-Shaped Extra-Large-Pore Channels

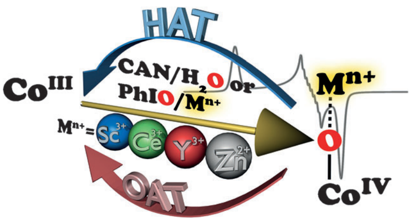


Molecular sieves: By combining several structure analysis techniques, the complex structure of the first high-silica zeolite with 18-ring channels (SSZ-61; see picture) could be derived. The material is stable to calcination, and the unusual dumbbell shape of the pore with terminal O atoms pointing into the channel offers the tantalizing possibility of inserting catalytically active centers between them.

Cobalt-Oxo Complexes

S. Hong, F. F. Pfaff, E. Kwon, Y. Wang,
M.-S. Seo, E. Bill, K. Ray,*
W. Nam* ______ 10403 – 10407

Spectroscopic Capture and Reactivity of a Low-Spin Cobalt(IV)-Oxo Complex Stabilized by Binding Redox-Inactive Metal Ions



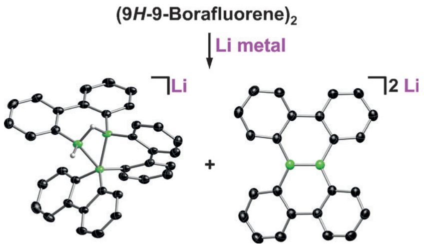
What is the metal's role? Cobalt(IV)-oxo complexes binding redox-inactive metal ions, such as Sc^{3+}, Ce^{3+}, Y^{3+}, and Zn^{2+}, are investigated in oxygenation reactions. Theory predicts that the binding of metal ions to the cobalt-oxo core increases the electrophilicity of the oxygen atom. This result supports the role of redox-inactive metal ions in facilitating the formation of high-valent metal-oxo cores as a necessary step for oxygen evolution in chemistry and biology. CAN = cerium ammonium nitrate.

Boron–Carbon Clusters

A. Hübner, M. Bolte, H.-W. Lerner,
M. Wagner* ______________ **10408 – 10411**

Extensive Structural Rearrangements upon Reduction of 9*H*-9-Borafluorene

What a difference an electron can make: Extensive rearrangements of the 9*H*-9-borafluorene scaffold occur upon injection of electrons into the system using Li metal. Two major reduction products are a $[B_3H_8]^-$ cluster analogue and a graphene flake with a central B=B bond (see picture; C black, H white, B green).

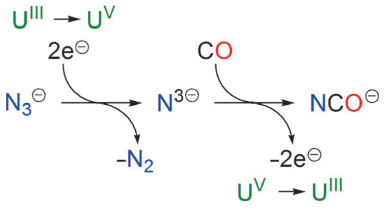


Metal Nitrides

P. A. Cleaves, D. M. King, C. E. Kefalidis,
L. Maron,* F. Tuna, E. J. L. McInnes,
J. McMaster, W. Lewis, A. J. Blake,
S. T. Liddle* ______________ **10412 – 10415**

Two-Electron Reductive Carbonylation of Terminal Uranium(V) and Uranium(VI) Nitrides to Cyanate by Carbon Monoxide

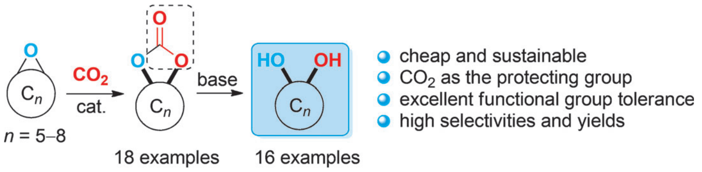
Exploiting U: A reductive f-block carbonylation of terminal uranium(V) and uranium(VI) nitrides affords cyanates, which can be retained at uranium or expelled. This method effects denitrification and the closure of a remarkably simple synthetic cycle for the conversion of azide to nitride to cyanate, exploiting a two-electron $U^{III/V}$ redox couple.



Temporary Protecting Groups

V. Laserna, G. Fiorani, C. J. Whiteoak,*
E. Martin, E. Escudero-Adán,
A. W. Kleij* ______________ **10416 – 10419**

Carbon Dioxide as a Protecting Group: Highly Efficient and Selective Catalytic Access to Cyclic *cis*-Diol Scaffolds

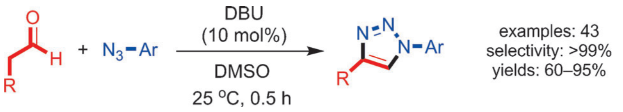


Protective Carbon: Aminotriphenolate complexes of Fe^{III} and Al^{III} are highly efficient and selective catalysts for the conversion of functional (multi)cyclic oxiranes into the corresponding *cis* carbonates. Basic hydrolysis of the latter provides a series of useful cyclic *cis*-diol scaffolds in high yield. In this process, CO_2 acts as both a temporary protecting group and an oxygen donor.

1,2,3-Triazoles

D. B. Ramachary,* A. B. Shashank,
S. Karthik ______________ **10420 – 10424**

An Organocatalytic Azide–Aldehyde [3+2] Cycloaddition: High-Yielding Regioselective Synthesis of 1,4-Disubstituted 1,2,3-Triazoles



Metal-free click: A variety of commercially available aldehydes was used in the metal-free organo-click reaction with aryl azides to obtain 1,4-disubstituted 1,2,3-triazoles. The method constitutes an alternative to previously known metal-catalyzed azide–alkyne cycloaddition reactions (AAC), such as CuAAC, RuAAC, and IrAAC. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; DMSO = dimethyl sulfoxide.

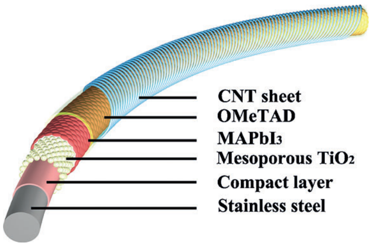
Solar Cells

L. Qiu, J. Deng, X. Lu, Z. Yang,
H. Peng* ______________ **10425 – 10428**

Integrating Perovskite Solar Cells into a Flexible Fiber

Inside Cover

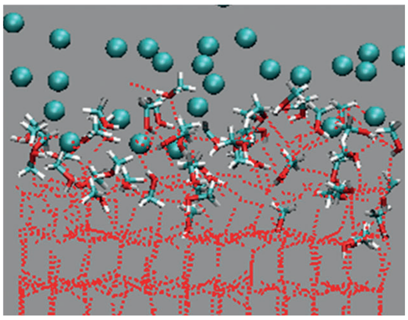
Wearable perovskite solar cells with a fiber structure are synthesized by continuously winding an aligned carbon nanotube (CNT) sheet onto a stainless-steel wire; photoactive materials are incorporated in between them through a solution process. The fiber-shaped perovskite solar cell exhibits an energy conversion efficiency of 3.3% and may be woven into electronic textiles.



Hydrates

G. McLaurin, K. Shin, S. Alavi,
J. A. Ripmeester* ______ **10429 – 10433**

Antifreezes Act as Catalysts for Methane Hydrate Formation from Ice

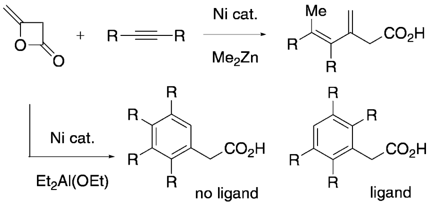


Catalytic methane hydrate formation: When powdered frozen water/methanol or water/ammonia solutions are exposed to methane gas at pressures of 30–125 bar and a temperature of 253 K (see picture), hydrate forms at greatly accelerated rates as compared to powdered ice without antifreeze added. The process gave near-complete conversion of ice to hydrate as shown by powder X-ray diffraction and Raman spectroscopy.

Synthetic Methods

T. Mori, Y. Akioka, H. Kawahara,
R. Ninokata, G. Onodera,
M. Kimura* ______ **10434 – 10438**

Efficient and Selective Formation of Unsaturated Carboxylic and Phenylacetic Acids from Diketene

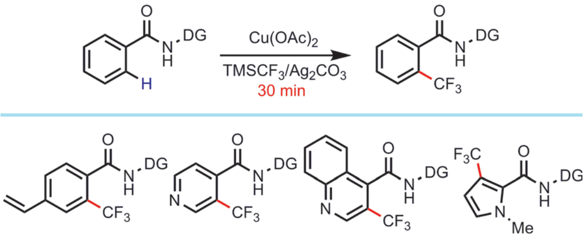


Have it three ways: A nickel catalyst promotes the multicomponent coupling reaction of diketene, an alkyne, and Me_2Zn to provide 3-methylene-4-hexenoic acids in excellent yields. Under similar conditions, the combination of the nickel catalyst and $Et_2Al(OEt)$ promotes a cycloaddition reaction involving dimerization of an alkyne to furnish phenylacetic acids. In the presence of PPh_3, a formal [2+2+1+1] cycloaddition reaction proceeds to afford regioisomeric phenylacetic acids.

C–H Activation

M. Shang, S.-Z. Sun, H.-L. Wang,
B. N. Laforteza, H.-X. Dai,*
J.-Q. Yu* ______ **10439 – 10442**

Exceedingly Fast Copper(II)-Promoted *ortho* C–H Trifluoromethylation of Arenes using $TMSCF_3$

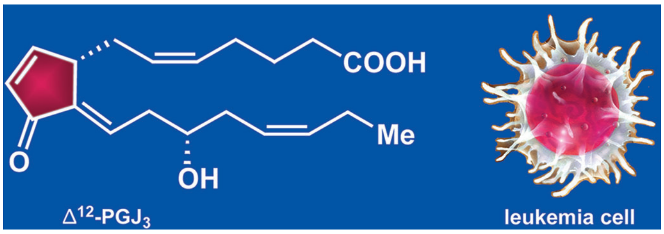


CF_3 installation: The direct *ortho*-trifluoromethylation of arenes including heteroarenes with $TMSCF_3$ has been accomplished by a copper(II)-promoted C–H activation reaction. Mechanistic investigations are consistent with the involvement of C–H activation rather than a simple electrophilic aromatic substitution as the key step. DG = directing group, TMS = trimethylsilyl.

Total Synthesis

K. C. Nicolaou,* P. Heretsch,
A. ElMarrouni, C. R. H. Hale,
K. K. Pulukuri, A. K. Kudva, V. Narayan,
K. S. Prabhu ______ **10443 – 10447**

Total Synthesis of Δ^{12}-Prostaglandin J_3, a Highly Potent and Selective Antileukemic Agent

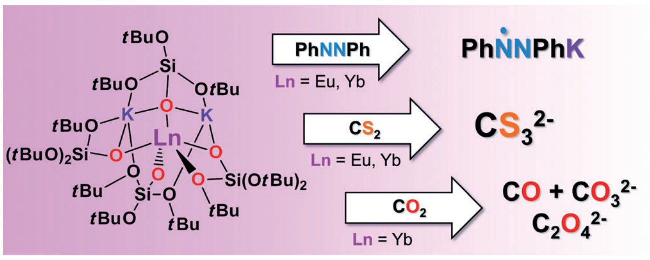


Leukemia ablator: The naturally occurring and highly potent and selective antileukemic agent Δ^{12}-prostaglandin J_3 (Δ^{12}-PGJ_3) has been assembled through a catalytic, asymmetric, and convergent strategy. The total synthesis renders this precious but rare substance readily available for thorough biological investigations and opens the way for analogue design, synthesis, and biological evaluation.

Small-Molecule Activation

J. Andrez, J. Pécaut, P.-A. Bayle,
M. Mazzanti* ________ 10448 – 10452

Tuning Lanthanide Reactivity Towards Small Molecules with Electron-Rich Siloxide Ligands

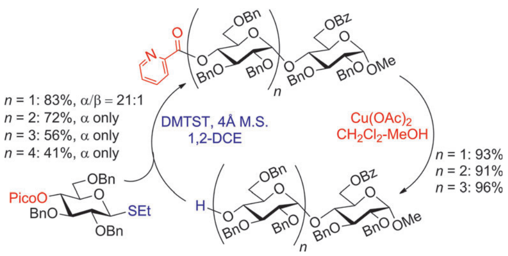


Yb and Eu can do it! The sterically demanding and electron-rich coordination environment of $\mathrm{Eu^{II}}$ and $\mathrm{Yb^{II}}$ in homoleptic siloxide complexes leads to the reduction of azobenzene, carbon disulfide, and carbon dioxide, and the ready release of the reduction products.

Glycosylation

J. P. Yasomanee,
A. V. Demchenko* ________ 10453 – 10456

Hydrogen Bond Mediated Aglycone Delivery: Synthesis of Linear and Branched α-Glucans



Special delivery: *O*-Picoloyl groups at remote positions can mediate the course of glycosylation reactions by providing high facial selectivity for the hydrogen bond mediated attack of the glycosyl acceptor. A new practical method for the stereoselective synthesis of oligosaccharides containing multiple 1,2-*cis* glucose residues is presented. 1,2-DCE = 1,2-dichloroethane, DMTST = dimethyl(methylthio)sulfonium triflate, M.S. = molecular sieves.

DOI: 10.1002/anie.201483914

Flashback: 50 Years Ago . . .

Hubert Schmidbaur et al. published three back-to-back Communications. The first two were on gallium chemistry, namely the reaction of organosilanes with gallium trihalides to form organogallium dihalides, and the use of gallium trichloride in the cleavage of siloxanes; and the third Communication was on alkali metal double silanolates $M^1\{M^2[OSi(CH_3)_3]_2\}$ (M^1 = Na or K, M^2 = Li or Na). Schmidbaur was previously Chairman of the Editorial Board of *Angewandte Chemie*, and published an Essay on coordination chemistry at carbon in the 125th Jubilee Issue (*Angew. Chem. Int. Ed.* **2013**, *52*, 176); a Review on argentophilic interactions is in press in this journal.

Rudolf Criegee and Fritz Zanker reported on the synthesis of dimethyl “Dewar tetramethylphthalate”, which is a crystalline derivative of Dewar benzene that can be prepared in decagram quantities and is more stable than related unsubstituted species. Criegee was an influential figure in German organic chemistry and both the Criegee intermediate and the Criegee rearrangement bear his name.

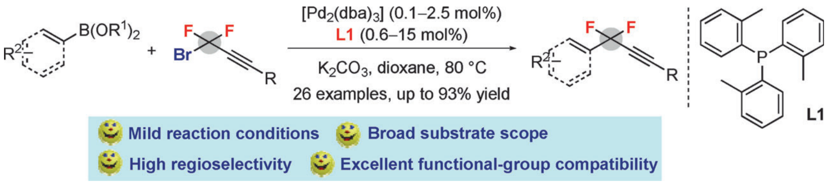
Herbert Roesky et al. published a Communication on the preparation of difluorodiazine (N_2F_2) by the treatment of sodium azide with elemental fluorine. The reaction proceeds through the dimerization of a biradical intermediate. Roesky is one of the authors who have published most manuscripts in *Angewandte Chemie* since 1946 (for a more complete list, see *Angew. Chem. Int. Ed.* **2013**, *52*, 2714). His most recent contribution is a Communication on cumulene structures.

Read more in Issue 10/1964.

Difluoroalkylation

Y.-B. Yu, G.-Z. He,
X. Zhang* ———— **10457 – 10461**

Synthesis of α,α-Difluoromethylene Alkynes by Palladium-Catalyzed *gem*-Difluoropropargylation of Aryl and Alkenyl Boron Reagents

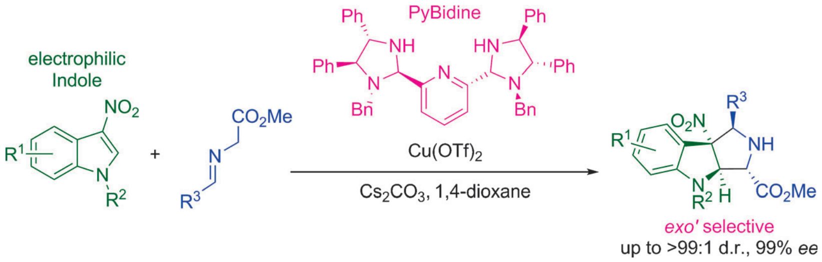


***gem*-Difluoropropargylation**: A palladium-catalyzed *gem*-difluoropropargylation of aryl and alkenyl boronic acids and boronates with *gem*-difluoropropargyl bromides has been developed (see Scheme). This cross-coupling process represents an attractive approach for the synthesis of complex fluorinated molecules, in particular for drug discovery and development.

Asymmetric Catalysis

A. Awata, T. Arai* ———— **10462 – 10465**

PyBidine/Copper Catalyst: Asymmetric *exo*′-Selective [3+2] Cycloaddition using Imino Ester and Electrophilic Indole

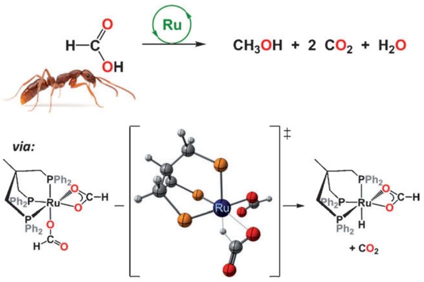


Under attack: An electrophilic indole undergo nucleophilic attack at C2 and electrophilic functionalization at C3. The PyBidine/Cu catalyst promoted highly enantio- and *exo*′-selective [3+2] cycloaddition using imino esters and 3-nitroindoles. This reaction can provide diverse chiral pyrroloindoline compounds.

Methanol Formation

S. Savourey, G. Lefèvre, J.-C. Berthet,
P. Thuéry, C. Genre,
T. Cantat* ———— **10466 – 10470**

Efficient Disproportionation of Formic Acid to Methanol Using Molecular Ruthenium Catalysts

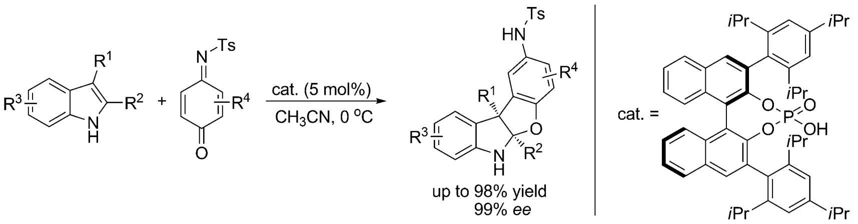


The search for selectivity: Methanol is efficiently produced in >50% yield by the disproportionation of formic acid using molecular ruthenium catalysts. Mechanistic experimental and DFT investigations have unveiled different pathways involving transient ruthenium hydride species.

Asymmetric Catalysis

L. Liao, C. Shu, M. Zhang, Y. Liao, X. Hu,
Y. Zhang, Z. Wu, W. Yuan,
X. Zhang* ———— **10471 – 10475**

Highly Enantioselective [3+2] Coupling of Indoles with Quinone Monoimines Promoted by a Chiral Phosphoric Acid

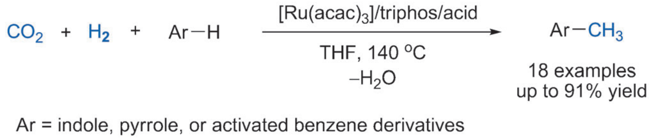


Benzofuroindolines: The title reaction has been realized. A wide variety of benzofuroindolines have been prepared with moderate to good yields in moderate to excellent enantioselectivities. Ts = 4-toluenesulfonyl.

Heterocycles

Y. Li, T. Yan, K. Junge,
M. Beller* ______________ 10476 – 10480

Catalytic Methylation of C–H Bonds Using CO_2 and H_2

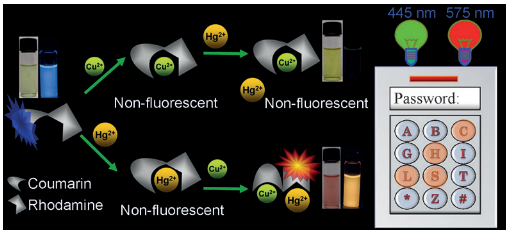


Capturing: Carbon dioxide in the presence of H_2 is shown to be an efficient methylating reagent for carbon nucleophiles such as 2-substituted indoles, pyrroles, and electron-rich arenes. Experimental data support the formal capture of formaldehyde. acac = acetylacetonate, triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane.

Molecular Devices

X.-J. Jiang, D. K. P. Ng* __ 10481 – 10484

Sequential Logic Operations with a Molecular Keypad Lock with Four Inputs and Dual Fluorescence Outputs



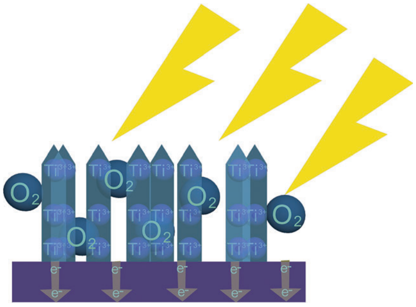
A coumarin–rhodamine conjugate serves as a ratiometric and highly selective fluorescent sensor for Hg^{2+} ions. Its metal-responsive spectral properties were utilized to construct an advanced molecular keypad lock with a high security level.

Photoanodes

C. Mao, F. Zuo, Y. Hou, X. Bu,*
P. Feng* ______________ 10485 – 10489

In Situ Preparation of a Ti^{3+} Self-Doped TiO_2 Film with Enhanced Activity as Photoanode by N_2H_4 Reduction

Ti time: A new method enables the fabrication of highly stable Ti^{3+}-modified TiO_2 photoanodes for H_2O oxidation. With Ti foil as the substrate and the Ti^{3+}/Ti^{4+} source, blue Ti^{3+}/TiO_2 crystals were grown by a one-step hydrothermal reaction. The Ti^{3+} concentration was increased by N_2H_4 reduction, leading to a greater activity. This method is also effective in improving other photoanodes.



Hypervalent Compounds

M. M. Konnick,* B. G. Hashiguchi,
D. Devarajan, N. C. Boaz, T. B. Gunnoe,
J. T. Groves, N. Gunsalus, D. H. Ess,*
R. A. Periana* __________ 10490 – 10494

Selective CH Functionalization of Methane, Ethane, and Propane by a Perfluoroarene Iodine(III) Complex

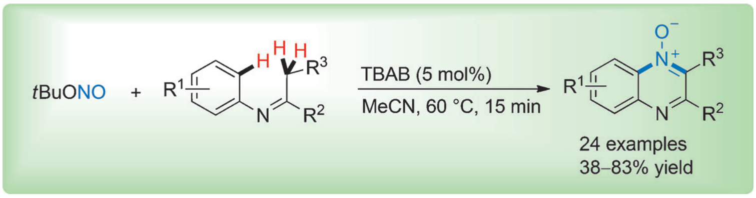
$$\text{R–H} \xrightarrow{C_6F_5I^{III}(TFA)_2} [C_6F_5I^{III}R][TFA] \xrightarrow{(-\,C_6F_5I^{I})} \text{R–TFA}$$

Gas up: Direct partial oxidation of methane, ethane, and propane to their respective trifluoroacetate (TFA) esters is achieved by a homogeneous hypervalent iodine(III) complex in non-superacidic solvent (HTFA). The reaction is highly selective, and for ethane, greater than 0.5 M Et–TFA can be achieved. Preliminary kinetic analysis and density functional calculations support a nonradical electrophilic CH activation and iodine alkyl functionalization mechanism.

C—N Bond Formation

F. Chen, X. Huang, X. Li, T. Shen, M. Zou, N. Jiao* ______ 10495 – 10499

Dehydrogenative N-Incorporation: A Direct Approach to Quinoxaline *N*-Oxides under Mild Conditions

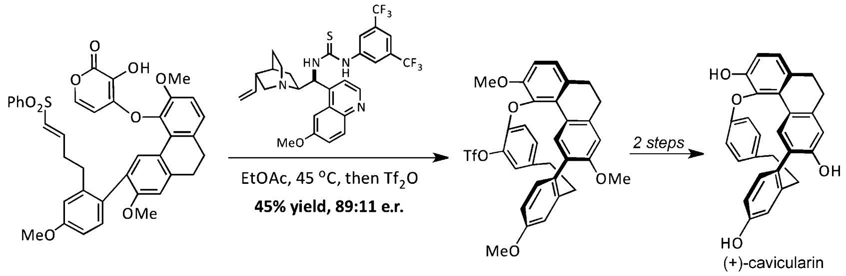


The dehydrogenative incorporation of a nitrogen atom for the synthesis of quinoxaline *N*-oxides through the functionalization of one C(sp^2)—H bond and two C(sp^3)—H bonds in imines proceeds under transition-metal-free conditions. Simple and readily available *tert*-butyl nitrite (TBN) was employed as the NO source. TBAB = tetrabutylammonium bromide.

Asymmetric Synthesis

P. Zhao, C. M. Beaudry* _ 10500 – 10503

Enantioselective and Regioselective Pyrone Diels–Alder Reactions of Vinyl Sulfones: Total Synthesis of (+)-Cavicularin

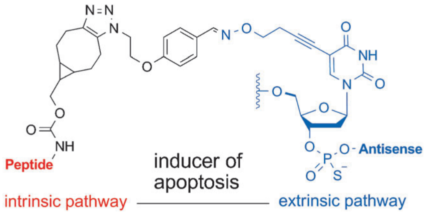


The total synthesis of (+)-cavicularin features an enantio- and regioselective Diels–Alder reaction of a pyrone with a vinyl sulfone. The substrate for this transformation is prepared by a regioselective one-pot three-component Suzuki reaction of a non-symmetric dibromoarene.

Bioconjugation

F. Abendroth, O. Seitz* __ 10504 – 10509

Double-Clicking Peptides onto Phosphorothioate Oligonucleotides: Combining Two Proapoptotic Agents in One Molecule

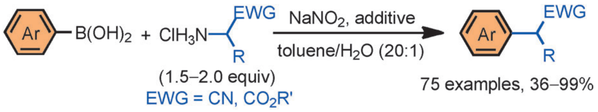


A stone for two birds is accessed through a combination of oxime ligation and strain-promoted [2+3] cycloaddition. This method was used to conjugate phosphorothioate antisense oligonucleotides (PSAOs) with peptide-based drugs. The activity of a PSAO sequence targeted against mRNA from c-Flip can be enhanced by conjugation with a peptide mimetic designed to inhibit the X-linked inhibitor of apoptosis protein (XIAP).

Synthetic Methods

G. Wu, Y. Deng, C. Wu, Y. Zhang, J. Wang* ______ 10510 – 10514

Synthesis of α-Aryl Esters and Nitriles: Deaminative Coupling of α-Aminoesters and α-Aminoacetonitriles with Arylboronic Acids

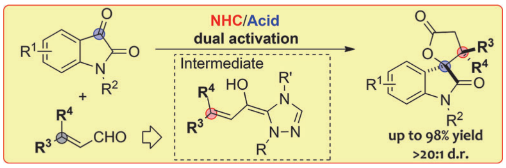


Touch base: A transition-metal-free protocol for the synthesis of α-aryl esters and nitriles by deaminative coupling is presented. Strong bases and transition-metal catalysts are not needed. The new synthetic method uses readily available starting materials and demonstrates wide substrate scope.

NHC Organocatalysis

J.-L. Li, B. Sahoo, C.-G. Daniliuc,
F. Glorius* ________ **10515 – 10519**

Conjugate Umpolung of β,β-Disubstituted Enals by Dual Catalysis with an N-Heterocyclic Carbene and a Brønsted Acid: Facile Construction of Contiguous Quaternary Stereocenters

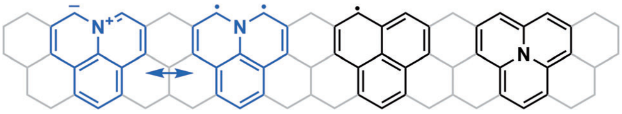


Hey neighbor! A previously unreported conjugate umpolung of β,β-disubstituted enals through NHC catalysis has been discovered, allowing the formation of products containing contiguous quaternary centers. Densely substituted spirocyclic oxindoles were readily prepared using a dual activation strategy.

Zigzag Ribbons

R. Berger, A. Giannakopoulos, P. Ravat,
M. Wagner, D. Beljonne,* X. Feng,*
K. Müllen* ________ **10520 – 10524**

Synthesis of Nitrogen-Doped ZigZag-Edge Peripheries: Dibenzo-9*a*-azaphenalene as Repeating Unit

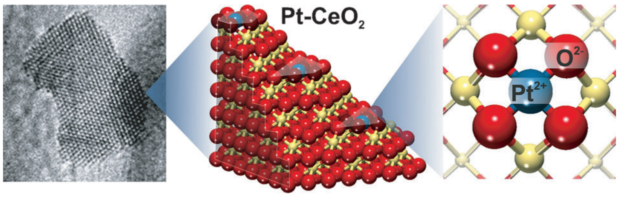


Having the edge: The unprecedented dibenzo-9*a*-azaphenalene has been used as a core motif in a bottom-up approach toward stable and monodisperse segments of graphenes with a nitrogen-doped zigzag edges. The goal of the approach is the synthesis of larger nitrogen-doped zigzag nanographenes and graphene nanoribbons.

Heterogeneous Catalysis

A. Bruix, Y. Lykhach, I. Matolínová,
A. Neitzel, T. Skála, N. Tsud, M. Vorokhta,
V. Stetsovych, K. Ševčíková, J. Mysliveček,
R. Fiala, M. Václavů, K. C. Prince,
S. Bruyère, V. Potin, F. Illas, V. Matolín,*
J. Libuda,*
K. M. Neyman* ________ **10525 – 10530**

Maximum Noble-Metal Efficiency in Catalytic Materials: Atomically Dispersed Surface Platinum



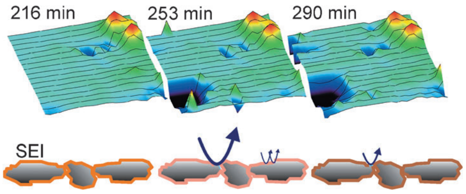
Platinum stuck in my pocket: Pt-CeO_2 materials with highest possible noble-metal dispersion can be prepared by stabilizing surface Pt^{2+} species in {100} "nanopockets" of nanostructured CeO_2 (see picture). Such materials can dramatically decrease the amount of noble metal required for catalysts.

Back Cover

Lithium-Ion Batteries

H. Bülter, F. Peters, J. Schwenzel,
G. Wittstock* ________ **10531 – 10535**

Spatiotemporal Changes of the Solid Electrolyte Interphase in Lithium-Ion Batteries Detected by Scanning Electrochemical Microscopy

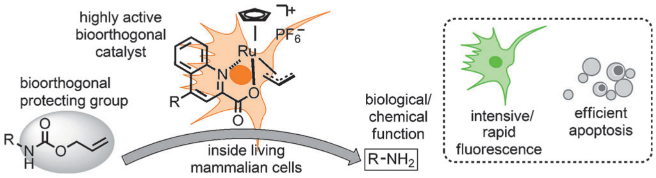


Actively passivating: Lithium-ion batteries only operate safely if a passivating solid electrolyte interphase (SEI) prevents chemical reactions between strongly reducing lithiated graphite and electrolyte components. Spontaneous local fluctuations of the passivating properties of the SEI are detected by scanning electrochemical microscopy. The direct monitoring of the spatiotemporal dynamics of this critical SEI property offers potential for their optimization.

Bioorthogonal Catalysis

T. Völker, F. Dempwolff, P. L. Graumann, E. Meggers* ———— 10536 – 10540

Progress towards Bioorthogonal Catalysis with Organometallic Compounds

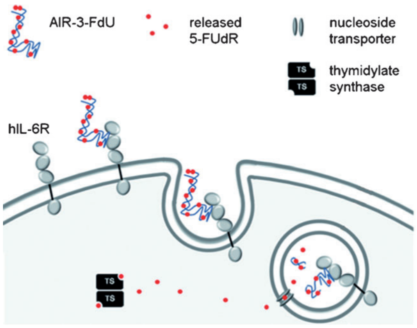


Organometallic ruthenium complexes have been developed for bioorthogonal catalysis under biologically relevant conditions as well as inside living mammalian cells. The catalysts activate allyl carbamate protected amines with unprecedented high catalytic activity. A fluorescence probe and a caged anticancer drug were efficiently activated within the cellular cytoplasm.

Drug Delivery

S. Kruspe, U. Hahn* ———— 10541 – 10544

An Aptamer Intrinsically Comprising 5-Fluoro-2′-deoxyuridine for Targeted Chemotherapy



A trojan chemotherapeutic: An aptamer intrinsically comprising multiple units of the nucleoside analogue 5-fluoro-2′-deoxyuridine can exert a direct cytostatic effect on certain cells. The aptamer, which can be synthesized in a single enzymatic step, binds to a cell surface receptor that is conveyed into the lysosome. Upon lysosomal degradation of the aptamer by intracellular nucleases, the active drug is released within the targeted cells exclusively.

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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