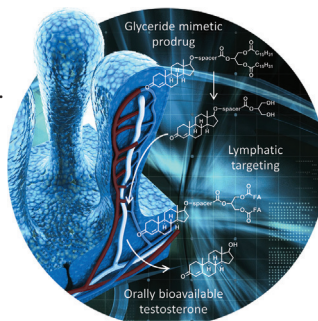




... of aggressive reagents in organic crystals facilitates their handling while their reactivity is restored upon release in a suitable solvent. In their Communication on page 13706 ff., C. Richert et al. show that noxious reagents, such as benzoyl chloride,  $\text{PCl}_3$ , and cyclohexyl isocyanide, can be encapsulated in tetrakis(dimethoxyphenyl)adamantane crystals. The cover picture depicts a forest, through which hazardous reagents may now be transported more safely, as well as the release of benzoyl chloride from the inclusion complex upon demand. Graphic credit: Matthäus Kalinowski and Alexander Schwenger.

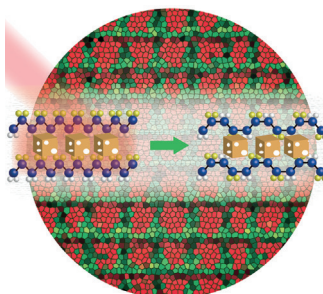
## Prodrugs

In their Communication on page 13700 ff., J. S. Simpson, C. H. J. Porter et al. report how the oral bioavailability of testosterone is significantly enhanced by generating glyceride-based prodrugs that promote drug release and direct the drugs to the lymphatic system.



## Adaptive Materials

A photoswitchable crosslinker was mixed with functionalized polysiloxane to yield a material with tunable self-healing properties, as described by S. Hecht and co-workers in their Communication on page 13882 ff.



## Phase Transitions

In their Communication on page 13828 ff., Y. Xia and co-workers report the induction of ferroelectric-to-paraelectric phase transitions by plasmonic heating using gold nanocages.

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GDCh

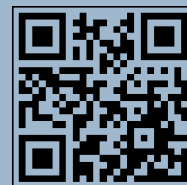
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## Editorial



**Preprints as well?** There is already the Accepted Article (published directly after refereeing and author revision), the Early-View/ASAP-Version (after refereeing, editing and proofing), and the final Version of Record. The problems with preprints are discussed in this Editorial along with the undeclared resubmission of previously rejected manuscripts: publication times, color costs, and *Angewandte* Symposia are further topics.

P. Göltz\* \_\_\_\_\_ 13621 – 13623

Preprints, Impact Factors, and Unethical Behavior, but also Lots of Good News

## Service

*Spotlight on Angewandte's* Sister Journals

13638 – 13641

## Author Profile



*"My favorite composer is Dmitri Shostakovich.*

*My favorite time of day is late evening. ..."*

This and more about Bernhard Rieger can be found on page 13642.

Bernhard Rieger \_\_\_\_\_ 13642

## News



P. J. Pérez



H. J. Bolink



S. Castellón



R. Martínez-Máñez



P. Melchiorre

Real Sociedad Española  
de Química Prizes 2016 \_\_\_\_\_ 13643



J. J. Novoa



R. D. Costa



M. Fañanás-Mastral

G. Mínguez  
Espallargas

S. Osuna

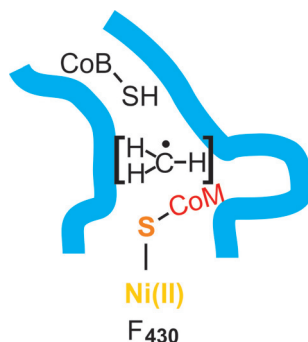
## Books

Basic X-ray Scattering Applied to Soft  
Matter

Wim H. de Jeu

reviewed by K. Huber \_\_\_\_\_ 13645

**Find your path:** Methyl-coenzyme M reductase (MCR, turquoise) reversibly catalyzes the reduction of methyl-coenzyme M (methyl-S-CoM) with coenzyme B (CoB-SH) to form methane and the heterodisulfide. Recently, spectroscopic methods were used to detect trapped intermediates in a stopped-flow system, and CoM-S-Ni<sup>II</sup> was identified after half a turnover of the MCR reaction ( $F_{430}$  = nickel porphinoid). This finding supports a methyl-radical catalytic mechanism.



## Highlights

## Enzyme Mechanisms

S. Shima\* \_\_\_\_\_ 13648 – 13649

The Biological Methane-Forming  
Reaction: Mechanism Confirmed Through  
Spectroscopic Characterization of a Key  
Intermediate

## For the USA and Canada:

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electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.



## Minireviews

## Synthetic Methods

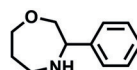


D. J. Foley, A. Nelson,\*  
S. P. Marsden\* ————— 13650 – 13657

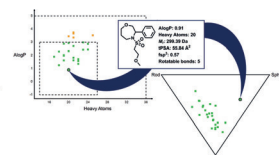


Evaluating New Chemistry to Drive  
Molecular Discovery: Fit for Purpose?

Scaffold



Decorate



Analyse

**The property ladder:** Careful control of molecular properties is closely linked to success in small-molecule-led discovery ventures. Computational tools to calculate molecular properties are now widely

available, many of them as freeware. These tools can be used to help guide the application of new synthetic methods and to evaluate alignment with future discovery needs.

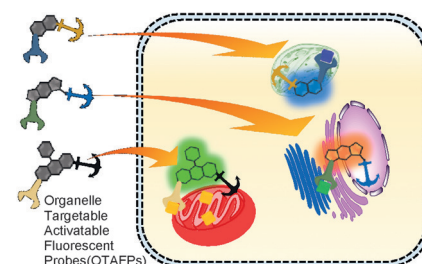
## Reviews

## Bioimaging

W. Xu, Z. Zeng, J.-H. Jiang,\* Y.-T. Chang,\*  
L. Yuan\* ————— 13658 – 13699

Discerning the Chemistry in Individual  
Organelles with Small-Molecule  
Fluorescent Probes

**See below the surface:** Fluorescent probes that target individual organelles and elucidate their functionalities are systematically summarized in this Review. The design strategy towards organelle targeting will shed light on basic studies of cell biology.



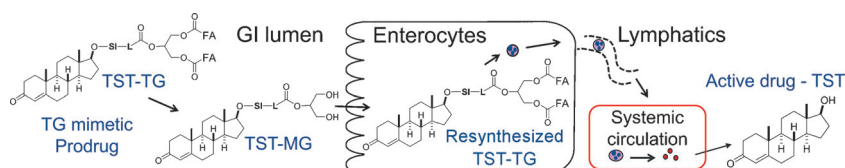
## Communications

## Prodrugs

L. Hu, T. Quach, S. Han, S. F. Lim,  
P. Yadav, D. Senyschyn, N. L. Trevaskis,  
J. S. Simpson,\*  
C. J. H. Porter\* ————— 13700 – 13705



Glyceride-Mimetic Prodrugs Incorporating  
Self-Immolative Spacers Promote Lymphatic  
Transport, Avoid First-Pass Metabolism, and  
Enhance Oral Bioavailability



**Bioavailable lymphotropic prodrugs:** The oral bioavailability of testosterone is significantly enhanced by the generation of glyceride-based prodrugs characterized by self-immolative triggers to promote drug

release. The prodrugs redirect drug absorption away from the portal blood and the liver, and instead promote drug delivery directly to the general circulation through the lymphatic system.

## Frontispiece

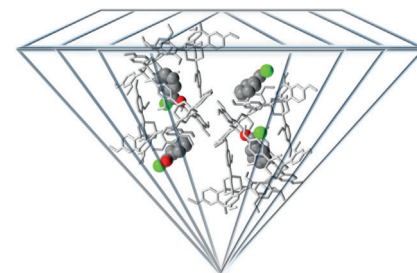
## Encapsulated Reagents

A. Schwenger, W. Frey,  
C. Richert\* ————— 13706 – 13709



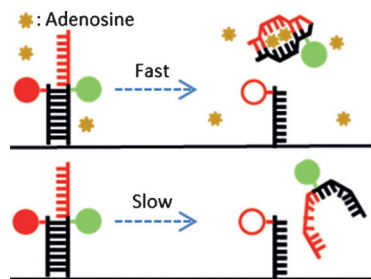
Reagents with a Crystalline Coat

**Toxic and malodorous** reagents, such as benzoyl chloride, acetyl chloride, cyclohexyl isocyanide, or phosphorus trichloride, are readily encapsulated in organic crystals of tetrakis(dimethoxyphenyl)adamantane. The crystalline formulation stabilizes the reagent, masks problematic properties, and unleashes the reagent in organic solvents.



## Front Cover



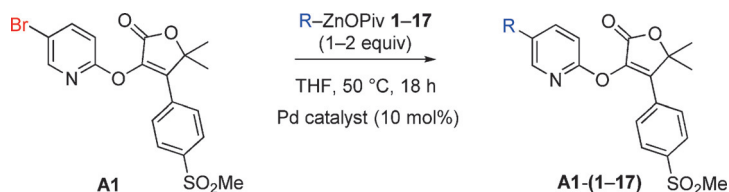


The kinetics of strand-displacement from an aptamer-complement complex by the aptamer ligand were investigated by using high-throughput single-molecule FRET. The ligands actively disrupt the DNA duplex in the presence of a DNA toehold, with kinetic details specific to the aptamer structure, thus suggesting that the DNA strand-displacement concept can be extended to functional DNA-ligand systems.

### Aptamers

J. H. Monserud, K. M. Macri,  
D. K. Schwartz\* 13710–13713

Toehold-Mediated Displacement of an Adenosine-Binding Aptamer from a DNA Duplex by its Ligand



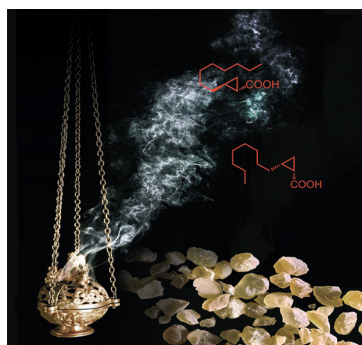
**A solid foundation for drug discovery:** The reactivity of a set of 17 organozinc pivalates with 18 polyfunctional, druglike electrophiles (informers) in Negishi cross-coupling reactions was evaluated by high-throughput experimentation (see

scheme). The high-fidelity scaleup of successful reactions in parallel gave sufficient material for biological testing, thus demonstrating the high value of these solid zinc reagents in a drug-discovery setting.

### Drug Discovery

T. J. Greshock,\* K. P. Moore,  
R. T. McClain, A. Bellomo, C. K. Chung,  
S. D. Dreher, P. S. Kutchukian, Z. Peng,  
I. W. Davies, P. Vachal, M. Ellwart,  
S. M. Manolikakes, P. Knochel,\*  
P. G. Nantermet 13714–13718

Synthesis of Complex Druglike Molecules by the Use of Highly Functionalized Bench-Stable Organozinc Reagents



**Millennia old odors:** (1*S*,2*R*)-(+)-*cis*- and (1*S*,2*S*)-(+)-*trans*-2-octylcyclopropyl-1-carboxylic acids were identified as new trace constituents of frankincense gum resin, one of the oldest aromatic resources known to man. Both molecules are highly potent and substantive odorants which have a crucial contribution to the very characteristic odor of frankincense.

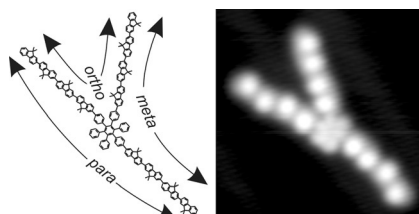
### Fragrances

C. Cerutti-Delasalle, M. Mehiri,  
C. Cagliero, P. Rubiolo, C. Bicchi,  
U. J. Meierhenrich,  
N. Baldovini\* 13719–13723

The (+)-*cis*- and (+)-*trans*-Olibanic Acids: Key Odorants of Frankincense



**The path matters!** Hexaphenylbenzene-based molecular nodes and polyfluorene wires are the constituents used for the on-surface synthesis of asymmetric node structures with a well-defined geometry, size, and composition (see structure). Measurements of electronic transport through individual molecular nodes when lifted from the surface by an STM tip revealed different transport behavior depending on the  $\pi$ -conjugation pathway.



### Molecular Electronics

C. Nacci, A. Viertel, S. Hecht,  
L. Grill\* 13724–13728

Covalent Assembly and Characterization of Nonsymmetrical Single-Molecule Nodes

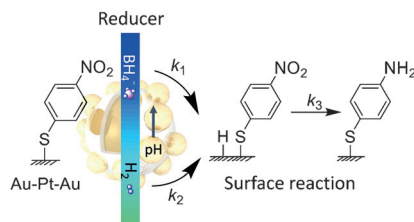


## Raman Spectroscopy

W. Xie,\* R. Grzeschik,  
S. Schlücker\* — 13729 – 13733



Metal Nanoparticle-Catalyzed Reduction  
Using Borohydride in Aqueous Media:  
A Kinetic Analysis of the Surface Reaction  
by Microfluidic SERS



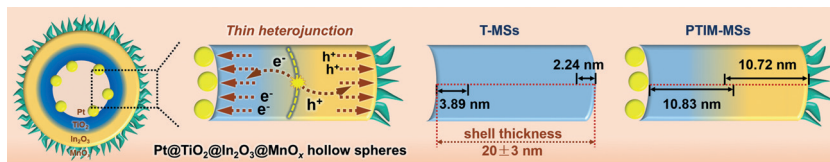
**Competing reducers:** The kinetics of a platinum-catalyzed surface reaction using sodium borohydride in aqueous media is studied by surface-enhanced Raman spectroscopy in a microfluidic reactor (see picture). The reduction by hydride occurs only at pH values higher than 13 (zero-order reaction), while at pH values lower than 13 the reduction proceeds through molecular hydrogen (first-order reaction).

## Water Oxidation

A. Li, X. Chang, Z. Huang, C. Li, Y. Wei,  
L. Zhang, T. Wang,  
J. Gong\* — 13734 – 13738



Thin Heterojunctions and Spatially  
Separated Cocatalysts To Simultaneously  
Reduce Bulk and Surface Recombination  
in Photocatalysts



**Mesoporous hollow spheres** with the composition Pt@TiO<sub>2</sub>@In<sub>2</sub>O<sub>3</sub>@MnO<sub>x</sub> can absorb both UV and visible light. Owing to the presence of thin heterojunctions and spatially separated cocata-

lysts, charge recombination is efficiently reduced in both the bulk phase and the surface/subsurface. These hollow spheres can be used as efficient photocatalysts for water and alcohol oxidation.

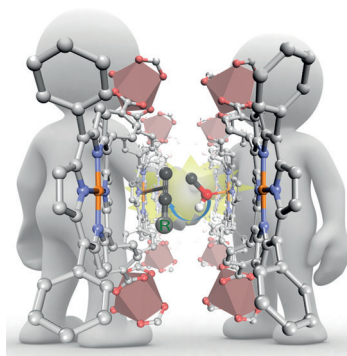
## Inside Cover

## Heterogeneous Catalysis

Z. Lin, Z.-M. Zhang, Y.-S. Chen,  
W. Lin\* — 13739 – 13743



Highly Efficient Cooperative Catalysis by  
Co<sup>III</sup>(Porphyrin) Pairs in Interpenetrating  
Metal–Organic Frameworks



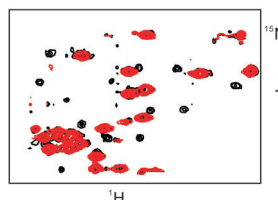
**Hand in hand:** Co<sup>III</sup>(porphyrin) pairs in an interpenetrating metal–organic frameworks work hand in hand to activate both substrates for highly efficient hydration of terminal alkynes. The twofold interpenetrating structure brings adjacent Co<sup>III</sup>(porphyrins) in the two networks parallel to each other, with a distance of about 8.8 Å, which is ideal for the simultaneous activation of both substrates of the reaction.

## Enzyme Catalysis

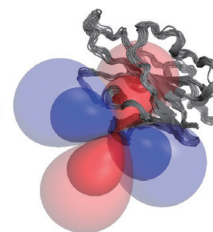
J.-L. Chen, X. Wang, F. Yang, C. Cao,  
G. Otting, X.-C. Su\* — 13744 – 13748



3D Structure Determination of an  
Unstable Transient Enzyme Intermediate  
by Paramagnetic NMR Spectroscopy



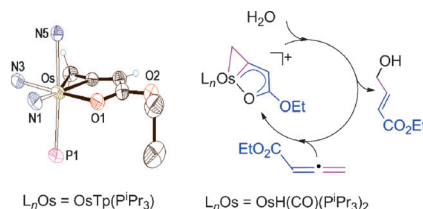
1) Paramagnetic labeling  
2) PCSs



**Now you see it:** 3D structures of low-abundance transient enzyme intermediates can be determined from pseudocontact shifts (PCSs) measured by NMR spectroscopy. The method is demon-

strated with the unstable thioester intermediate formed between *Staphylococcus aureus* sortase A and the peptide substrate.

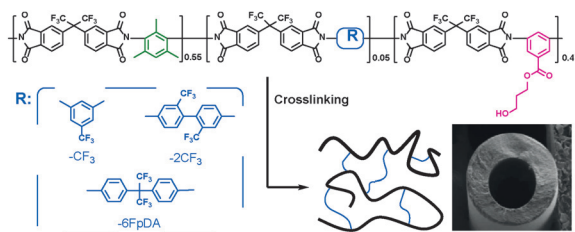
**At the cr-Os-sroads:** The unsaturated three-membered ring of osmacyclopropenefuran bicycles was found to show significant  $\sigma$ -aromaticity. Such compounds can play a key role in the hydration of functionalized allenes, depending on the  $L_nOs$  unit (see scheme).



### Metallaheterobicycles

M. Batuecas, R. Castro-Rodrigo, M. A. Esteruelas,\* C. García-Yebra, A. M. López, E. Oñate — **13749–13753**

Aromatic Osmacyclopropenefuran Bicycles and Their Relevance for the Metal-Mediated Hydration of Functionalized Allenes



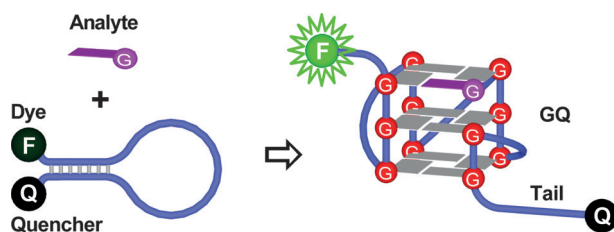
**High-performance membranes:** Nano-scale-stabilized asymmetric hollow fiber membranes derived from synthesized rigid polyimides with bulky  $CF_3$  groups

showed greatly improved carbon dioxide and methane separation performance compared to conventional materials for aggressive natural gas feeds.

### Carbon Dioxide Capture

G. Liu,\* N. Li,\* S. J. Miller, D. Kim, S. Yi, Y. Labreche, W. J. Koros\* — **13754–13758**

Molecularly Designed Stabilized Asymmetric Hollow Fiber Membranes for Aggressive Natural Gas Separation



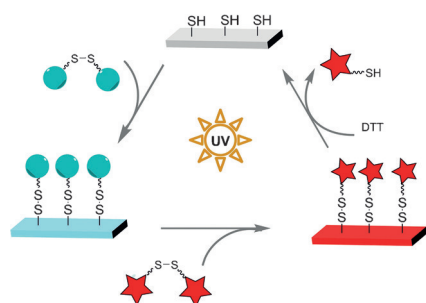
**Structured approach:** A guanine-vacancy-bearing G-quadruplex (GVBQ) interacts with guanine and derivatives by a structural complementation to form a more stable and intact G-quadruplex. The

structural conversion is used to sense guanine derivatives and analogues with exceptional specificity through dedicated hydrogen bonds between the probe and analyte in a G-quadruplex (GQ) structure.

### Sensors

X.-m. Li, K.-w. Zheng,\* Y.-h. Hao, Z. Tan\* — **13759–13764**

Exceptionally Selective and Tunable Sensing of Guanine Derivatives and Analogues by Structural Complementation in a G-Quadruplex



**Shine a light on thiols:** UV-induced disulfide formation (UV-DF) and disulfide reduction (UV-DR) reactions are demonstrated to be effective for reversible surface modification, patterning, and attachment and detachment of functional groups. This photodynamic thiol-disulfide exchange process will be useful for the design of novel dynamic and responsive functional interfaces and micropatterns.

### Surface Chemistry

L. Li, W. Feng, A. Welle, P. A. Levkin\* — **13765–13769**

UV-Induced Disulfide Formation and Reduction for Dynamic Photopatterning





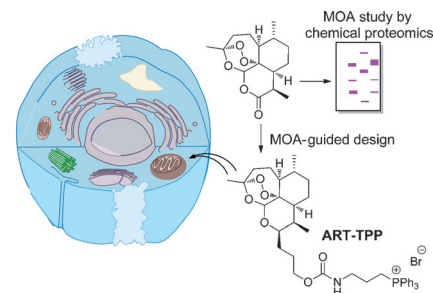
## Drug Delivery

C. Zhang, J. Wang,\* J. Zhang, Y. M. Lee, G. Feng, T. K. Lim, H. M. Shen, Q. Lin,\* B. Liu\* — 13770–13774



Mechanism-Guided Design and Synthesis of a Mitochondria-Targeting Artemisinin Analogue with Enhanced Anticancer Activity

A mechanism of action (MOA) study by chemical proteomics indicates that free heme plays a decisive role in the activation of artemisinin in cancer cells. Guided by this MOA, a mitochondria targeting analogue (ART-TPP; see picture) was developed that shows remarkable anti-cancer activities.

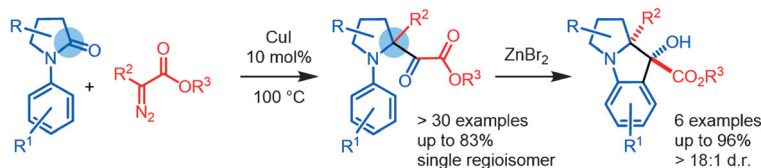


## Metal Carbenes

S. Gouedranche, C. Besnard, L. Egger, J. Lacour\* — 13775–13779



Synthesis of Pyrrolidines and Pyrrolizidines with  $\alpha$ -Pseudoquaternary Centers by Copper-Catalyzed Condensation of  $\alpha$ -Diazodicarbonyl Compounds and Aryl  $\gamma$ -Lactams



From  $C=O$  to  $CR_2$ : Functionalized pyrrolidines were readily prepared by condensation reactions of  $\gamma$ -lactams with acceptor-acceptor diazo reagents under copper catalysis. Preferential 1,2-acyl- or -phos-

phoryl migration led to the formation of single regioisomers. These products could be further transformed into tricyclic pyrrolizidines in the presence of a Lewis acid.



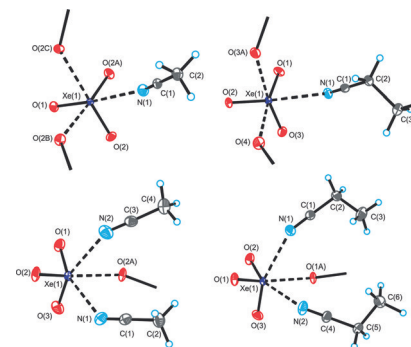
## Noble-Gas Chemistry

J. T. Goettel, K. Matsumoto, H. P. A. Mercier, G. J. Schrobilgen\* — 13780–13783



Syntheses and Structures of Xenon Trioxide Alkyl nitrile Adducts

Xenon trioxide forms stable 1:1 and 1:2 adducts with  $CH_3CN$  and  $CH_3CH_2CN$ , which were characterized by Raman spectroscopy and X-ray crystallography. Computational studies show that the  $Xe \cdots N$  interactions are essentially electrostatic. The amphoteric Lewis acid/base nature of  $XeO_3$  influences the geometries of these adducts in the solid state where the structural units interact through  $Xe=O \cdots Xe$  bridges.

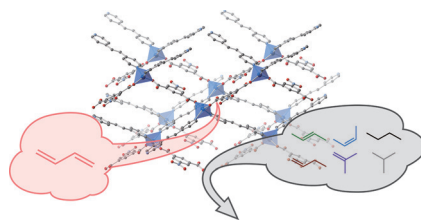


## Microporous Materials

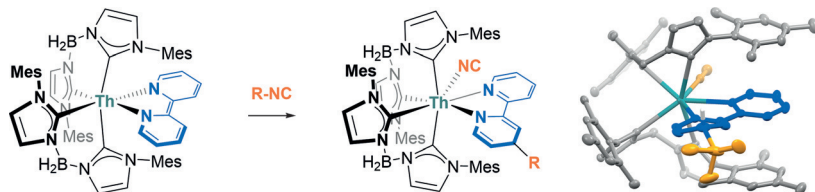
K. Kishida, Y. Okumura,\* Y. Watanabe, M. Mukoyoshi, S. Bracco, A. Comotti, P. Sozzani, S. Horike,\* S. Kitagawa\* — 13784–13788



Recognition of 1,3-Butadiene by a Porous Coordination Polymer



A selective gas guzzler: A hydrophobic and flexible triply interpenetrated porous coordination polymer (PCP) recognized 1,3-butadiene gas among six other  $C_4$  gases under ambient conditions (see picture). Specific  $C-H \cdots \pi$  interactions in the restricted voids is the key to the accommodation of 1,3-butadiene, as determined by solid-state NMR spectroscopy.



**Thor's hammer:** A bis(NHC)borate thorium-bpy complex (**1**) is described that reductively cleaves the R–NC bond in a series of organic isocyanides. In contrast to most actinide-mediated bond activations, the dealkylation event mediated by

**1** is remarkably general and yields very well-defined products. The production of the rearranged but-3-enyl product from the reaction of **1** and cyclopropylmethyl isocyanide supports the notion of a radical-based mechanism.

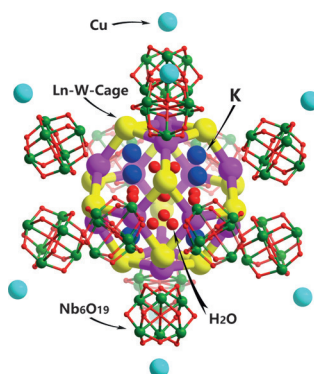
### Organometallic Chemistry

M. E. Garner, S. Hohloch, L. Maron,\*  
J. Arnold\* ————— **13789 – 13792**

Carbon–Nitrogen Bond Cleavage by  
a Thorium–NHC–bpy Complex



**Giant heterometallic polyoxoniobates:** A family of polyoxometalate-based frameworks has been made by integrating s, 3d, 4d, 5d, and 4f metals. Multi-component self-assembly offers the first series of niobium–tungsten–lanthanide heterometallic polyoxometalates, which are the largest multi-metal polyoxoniobates and contain rare nanosized hollow sodalite-type tungsten–lanthanide–oxide cages.



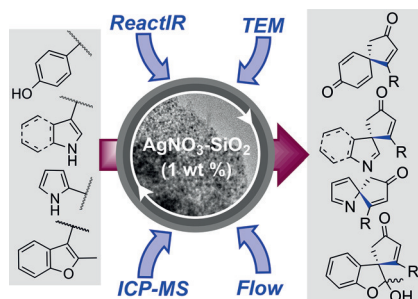
### Giant Inorganic Molecules

L. Jin, X.-X. Li, Y.-J. Qi, P.-P. Niu,  
S.-T. Zheng\* ————— **13793 – 13797**

Giant Hollow Heterometallic  
Polyoxoniobates with Sodalite-Type  
Lanthanide–Tungsten–Oxide Cages:  
Discrete Nanoclusters and Extended  
Frameworks



**Nanoparticle catalysis:** Silica-supported AgNO<sub>3</sub> catalyzes the dearomatizing spirocyclization of alkyne-tethered aromatics far more effectively than the analogous unsupported reagent. Mechanistic studies indicate that this is a consequence of silver nanoparticle formation on the silica surface combined with a synergistic effect caused by the silica support itself.



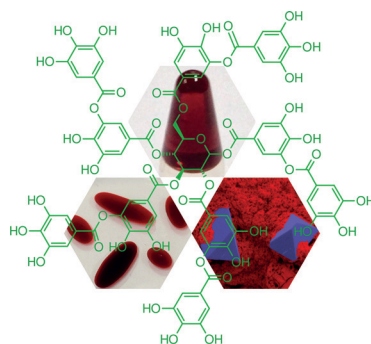
### Supported Catalysts

A. K. Clarke, M. J. James, P. O'Brien,  
R. J. K. Taylor,\*  
W. P. Unsworth\* ————— **13798 – 13802**

Silica-Supported Silver Nitrate as a Highly  
Active Dearomatizing Spirocyclization  
Catalyst: Synergistic Alkyne Activation by  
Silver Nanoparticles and Silica



**Ti-tannic gels:** The direct gelation of the natural polyphenol tannic acid, by coordination-driven supramolecular assembly with titanium(IV), is reported. These metallogels exhibit a range of properties, including transparency, injectability, moldability, self-healing, shape persistence, adhesiveness, and tunable mechanics.



### Gels

M. A. Rahim, M. Björnalm, T. Suma,  
M. Faria, Y. Ju, K. Kempe, M. Müllner,  
H. Ejima, A. D. Stickland,  
F. Caruso\* ————— **13803 – 13807**

Metal–Phenolic Supramolecular Gelation

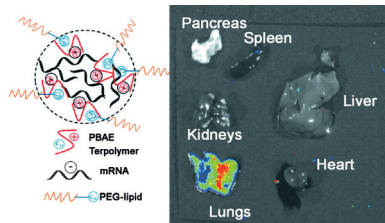


## Drug Delivery

J. C. Kaczmarek, A. K. Patel,  
K. J. Kauffman, O. S. Fenton, M. J. Webber,  
M. W. Heartlein, F. DeRosa,  
D. G. Anderson\* — 13808 – 13812



Polymer–Lipid Nanoparticles for Systemic  
Delivery of mRNA to the Lungs



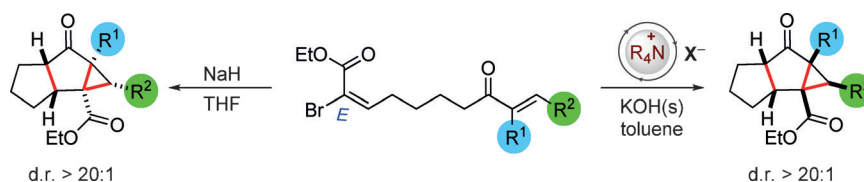
**mRNA-loaded nanoparticles** were synthesized using degradable poly( $\beta$ -amino ester) terpolymers formulated with a PEG-lipid. The PEG-lipid imparted serum stability to the nanoparticles, which resulted in successful mRNA delivery to the lungs after systemic nanoparticle administration in mice.

## Cycloaddition

E. Kiss, C. D. Campbell, R. W. Driver,  
J. D. Jolliffe, R. Lang, T. Sergeieva,  
S. Okovytyy, R. S. Paton,\*  
M. D. Smith\* — 13813 – 13817



A Counterion-Directed Approach to the  
Diels–Alder Paradigm: Cascade Synthesis  
of Tricyclic Fused Cyclopropanes



**Role play:** An approach to the intramolecular Diels–Alder reaction has led to a cascade synthesis of complex carbocycles composed of three fused rings and up to five stereocenters with complete stereocontrol. Computational analysis

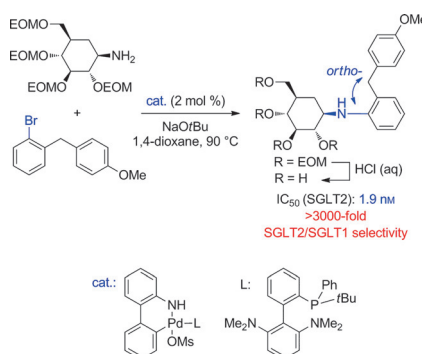
reveals that the reaction proceeds by a Michael/Michael/epimerization/cyclopropanation cascade in which size and coordination of the achiral counterion plays a key role in the stereochemical outcome of the reaction.

## Drug Discovery

W.-L. Ng, K.-M. Lau, C. B.-S. Lau,  
T. K. M. Shing\* — 13818 – 13821



Palladium-Catalyzed Arylation of  
Carbasugars Enables the Discovery of  
Potent and Selective SGLT2 Inhibitors



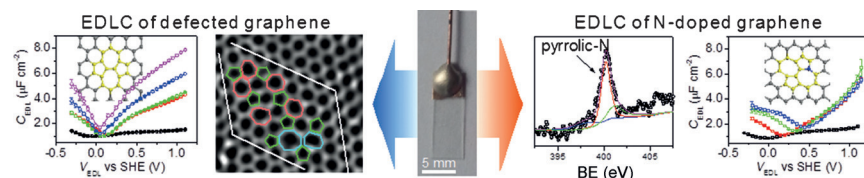
**Sweet therapeutics:** A chemo- and diastereospecific palladium-catalyzed arylation enables a facile synthetic route towards some carbohydrate-based SGLT2 inhibitors. It leads to the discovery of two highly selective and potent SGLT2 inhibitors, thereby paving the way towards the development of carbasugar SGLT2 inhibitors as potential antidiabetic/antitumor agents. EOM = ethoxymethyl.

## Electrochemistry

J. F. Chen, Y. L. Han, X. H. Kong,  
X. Z. Deng, H. J. Park, Y. L. Guo, S. Jin,  
Z. K. Qi, Z. Lee, Z. H. Qiao,\* R. S. Ruoff,\*  
H. X. Ji\* — 13822 – 13827



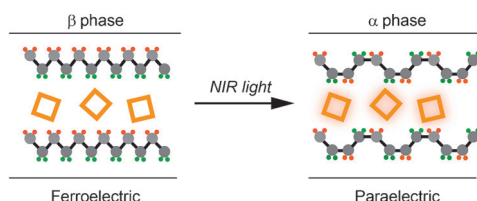
The Origin of Improved Electrical Double-  
Layer Capacitance by Inclusion of  
Topological Defects and Dopants in  
Graphene for Supercapacitors



**Dopants, defects, and double layers:** Electrochemical measurements and ab initio calculations on single-layer CVD-grown graphene show that topological defects improve the density of states and N-dopants can tune the Fermi level of

graphene, both of which influence the quantum capacitance connected in series with the Helmholtz capacitance and therefore modify the electrical double-layer (EDL) capacitance.





**$\beta$  to  $\alpha$ :** A very small amount of Au nanocages was incorporated into a polymer thin film to achieve a plasmon-assisted phase transition to pattern the freestanding ferroelectric thin film into

arrayed domains within a few seconds. The patterned array of ferroelectric domains could serve as discrete pixels for infrared sensing or imaging.

## Phase Transitions

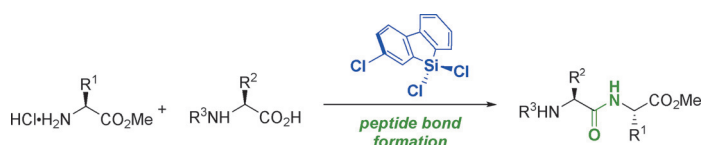


J. Li, M. Yang, X. Sun, X. Yang, J. Xue, C. Zhu, H. Liu, Y. Xia\* — **13828–13832**

Micropatterning of the Ferroelectric Phase in a Poly(vinylidene difluoride) Film by Plasmonic Heating with Gold Nanocages



Back Cover



**A chemical ligation mechanism** was proposed for amide bond formation with 9-silafluorenyl dichlorides as new coupling reagents. This approach enabled the

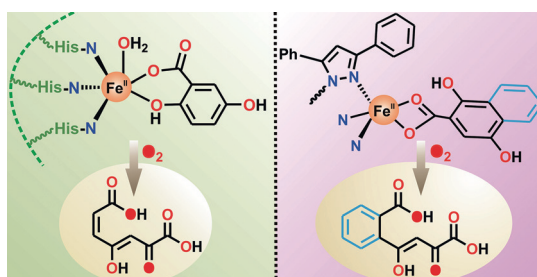
synthesis of peptides in a simple and unprecedented manner without preactivation of either the carboxylic acid or amine termini of the amino acids.

## Peptide Synthesis



S. J. Aspin, S. Taillemaud, P. Cyr, A. B. Charette\* — **13833–13837**

9-Silafluorenyl Dichlorides as Chemically Lignating Coupling Agents and Their Application in Peptide Synthesis



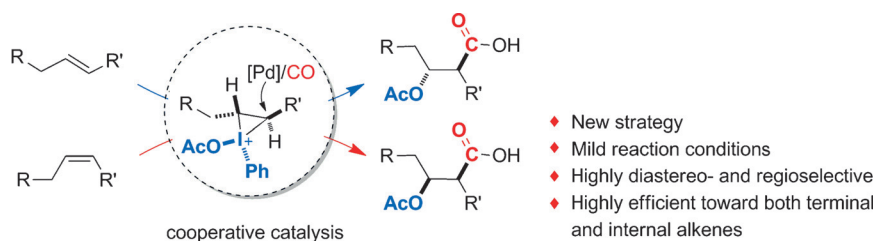
**Breaking rings:** An iron(II) complex of a facial  $N_3$  ligand carries out the  $O_2$ -dependent aromatic-ring cleavage of gen-

tisate and 1,4-dihydroxy-2-naphthoate mimicking the function of gentisate-1,2-dioxygenase.

## Functional Models

R. Rahaman, B. Chakraborty, T. K. Paine\* — **13838–13842**

Mimicking the Aromatic-Ring-Cleavage Activity of Gentisate-1,2-Dioxygenase by a Nonheme Iron Complex



**'Kene activation':** A novel method for intermolecular oxycarbonylation of terminal and internal alkenes has been designed. The electrophilic reagent,

hypervalent iodine, plays a key role in this process by activating the alkene bond for nucleophilic addition of the palladium catalyst.

## Carbonylation

M. Li, F. Yu, X. Qi, P. Chen, G. Liu\* — **13843–13848**

A Cooperative Strategy for the Highly Selective Intermolecular Oxycarbonylation Reaction of Alkenes using a Palladium Catalyst



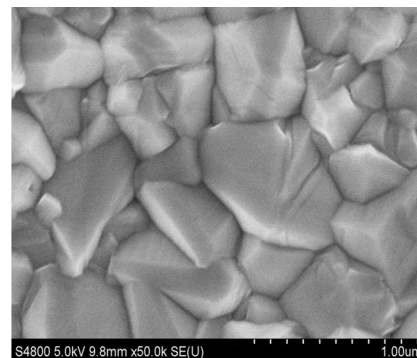
## Electrocatalysts

Q. Jiang, L. Xu, N. Chen, H. Zhang,\*  
L. Dai,\* S. Wang\* — 13849–13853



Facile Synthesis of Black Phosphorus: an Efficient Electrocatalyst for the Oxygen Evolving Reaction

**Black phosphorus** supported on titanium foil is highly efficient in the oxygen evolving reaction, with an onset potential of 1.48 V and a current density of 10 mA cm<sup>-2</sup> at 1.6 V. The electrocatalytic activity of black phosphorus materials prepared by a thermal-vaporization transformation method is comparable to that of commercial RuO<sub>2</sub> electrocatalysts.

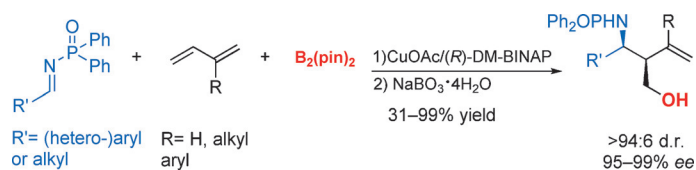


## Asymmetric Catalysis

L. Jiang, P. Cao,\* M. Wang, B. Chen,  
B. Wang, J. Liao\* — 13854–13858



Highly Diastereo- and Enantioselective Cu-Catalyzed Borylative Coupling of 1,3-Dienes and Aldimines



**A multitude of syns:** A Cu-catalyzed borylative coupling reaction of 1,3-dienes with imines was realized. Branched homoallylic amines are readily prepared in a *syn*-selective manner with high regio-,

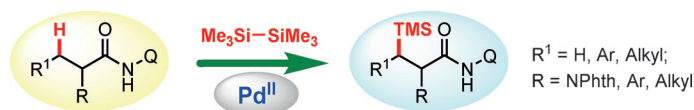
diastereo- and enantioselectivity. Moreover, these three-component coupling reactions feature good functional-group compatibility and easy access to the substrates and catalyst.

## Silylation

Y.-J. Liu, Y.-H. Liu, Z.-Z. Zhang, S.-Y. Yan,  
K. Chen, B.-F. Shi\* — 13859–13862



Divergent and Stereoselective Synthesis of  $\beta$ -Silyl- $\alpha$ -Amino Acids through Palladium-Catalyzed Intermolecular Silylation of Unactivated Primary and Secondary C–H Bonds



**Good to Si you:** A general and practical Pd<sup>II</sup>-catalyzed intermolecular silylation of primary and secondary C–H bonds of  $\alpha$ -amino acids and simple aliphatic acids is reported. This method provides divergent and stereoselective access to a variety of

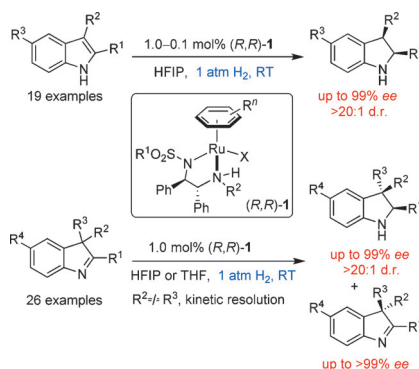
optical pure  $\beta$ -silyl- $\alpha$ -amino acids. Furthermore, the late-stage functionalization of biological small molecules such as (–)-santonin and  $\beta$ -cholic acid is demonstrated.

## Heterocycles

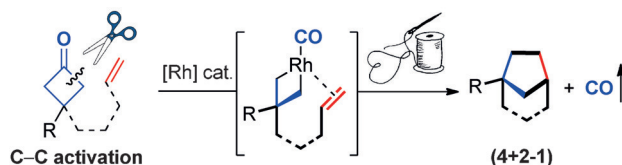
Z. Yang, F. Chen,\* Y.-M. He, N. Yang,  
Q.-H. Fan\* — 13863–13866



Highly Enantioselective Synthesis of Indolines: Asymmetric Hydrogenation at Ambient Temperature and Pressure with Cationic Ruthenium Diamine Catalysts



**Setting the ambiance:** The title reaction was achieved in the presence of chiral cationic ruthenium diamine complexes at ambient temperature and pressure. The method provides a promising approach for obtaining a broad range of enantioenriched indolines and 3H-indoles with excellent stereoselectivities. HFIP = hexafluoroisopropanol, THF = tetrahydrofuran.



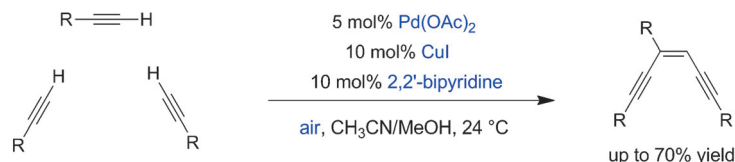
**Decarbonylative “cut and sew”:** An intramolecular decarbonylative coupling between cyclobutanones and alkenes has been developed that proceeds by rhodium-catalyzed C–C activation and pro-

vides a distinct approach to a diverse range of saturated bridged cyclopentanes. In this formal (4+2–1) transformation, cyclobutanones serve as cyclopropane surrogates.

### C–C Activation

X. Zhou, H. M. Ko,\*  
G. Dong\* — 13867 – 13871

Synthesis of Bridged Cyclopentane Derivatives by Catalytic Decarbonylative Cycloaddition of Cyclobutanones and Olefins



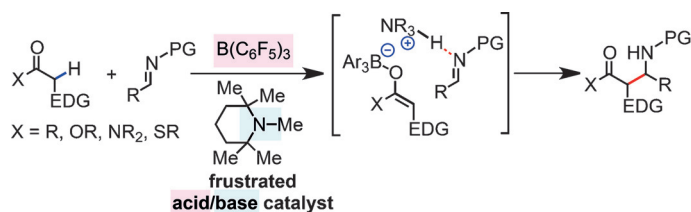
**Mix and go:** Presented herein is a mild, operationally simple, mix-and-go procedure for the synthesis of acyclic trisubstituted Z-enediynes from readily available terminal alkynes in good yields. This method stems from a serendipitous dis-

covery, and makes use of cooperative palladium/copper bimetallic catalysis and air as an oxidant to effect an intriguing alkyne trimerization to yield the valuable Z-enediyne moiety.

### Alkynes

J. T. D. Lee, Y. Zhao\* — 13872 – 13876

Access to Acyclic Z-Enediynes by Alkyne Trimerization: Cooperative Bimetallic Catalysis Using Air as the Oxidant



**It pays to be direct if you're frustrated:** A sterically frustrated Lewis acid/Brønsted base pair was found to serve as a potent cooperative acid/base catalyst for direct Mannich-type reactions (see scheme; EDG = electron-donating group, PG =

protecting group). An array of ketone, ester, amide, and thioester pronucleophiles underwent enolization by the catalyst and reaction with aldimines to afford both  $\alpha$ - and  $\beta$ -amino esters.

### Frustrated Lewis Pairs

J. Z. Chan, W. Yao, B. T. Hastings,  
C. K. Lok, M. Wasa\* — 13877 – 13881

Direct Mannich-Type Reactions Promoted by Frustrated Lewis Acid/Brønsted Base Catalysts



### Illuminating dynamic covalent chemistry!

A photoswitch, which makes it possible to modulate the reactivity of aldehyde functionalities by light irradiation, was developed to control the exchange kinetics in a dynamic imine-based polysiloxane network. In this way soft materials were obtained with remote control over their intrinsic properties, most notably their ability to self-heal.



### Dynamic Covalent Chemistry

M. Kathan, P. Kovaříček, C. Jurissek,  
A. Senf, A. Dallmann, A. F. Thünemann,  
S. Hecht\* — 13882 – 13886

Control of Imine Exchange Kinetics with Photoswitches to Modulate Self-Healing in Polysiloxane Networks by Light Illumination



Inside Back Cover



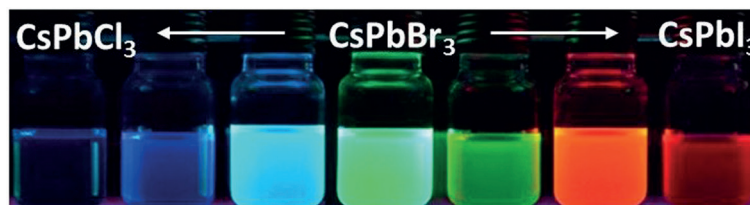


## Perovskite Nanostructures

Y. Tong, E. Bladt, M. F. Aygüler, A. Manzi,  
K. Z. Milowska, V. A. Hintermayr,  
P. Docampo, S. Bals,\* A. S. Urban,\*  
L. Polavarapu,\*  
J. Feldmann 13887 – 13892



Highly Luminescent Cesium Lead Halide Perovskite Nanocrystals with Tunable Composition and Thickness by Ultrasonication



**Under ultrasonication:** Perovskite nanocrystals and nanoplatelets with controlled halide composition and thickness were prepared by direct ultrasonication of the corresponding precursor solutions in the

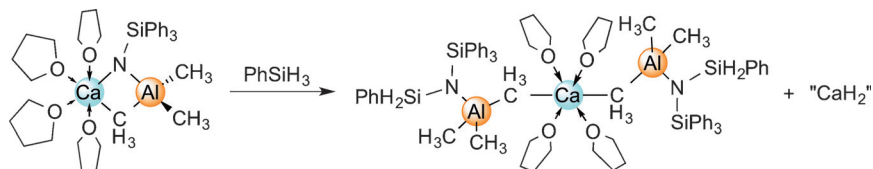
presence of organic capping molecules. The optical properties of the as-prepared  $\text{CsPbX}_3$  NCs can be tuned across the entire visible range by changing either the composition or thickness.

## Alkaline Earth Metals

B. M. Wolf, C. Maichle-Mössmer,  
R. Anwander\* 13893 – 13897



Synthesis and Reactivity of Discrete Calcium Imides



**Tandem salt metathesis/protonolysis** reactions of  $[\text{Ca}(\text{AlMe}_4)_2]_n$  and  $[\text{K}\{\text{NH}(\text{SiPh}_3)\}]$  provide access to Lewis acid

$(\text{AlMe}_3)_3$  stabilized calcium imides. Their  $\text{Ca}=\text{NR}$  multiple-bond character was revealed by  $\text{Si}-\text{H}$  addition (see scheme).



Supporting information is available on [www.angewandte.org](http://www.angewandte.org) (see article for access details).



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



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

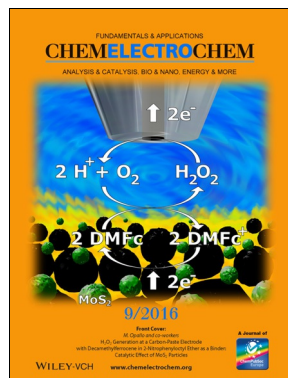


The Very Important Papers, marked VIP, have been rated unanimously as very important by the referees.

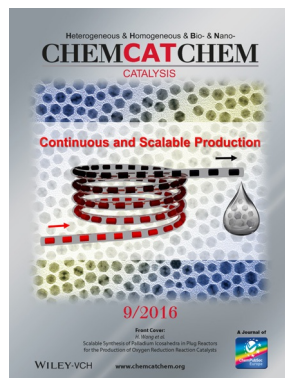


The Hot Papers are articles that the Editors have chosen on the basis of the referee reports to be of particular importance for an intensely studied area of research.

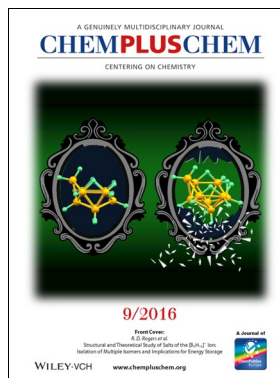
## Check out these journals:



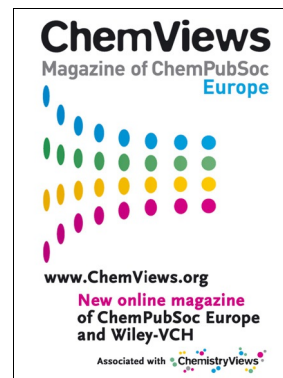
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[www.chemcatcher.org](http://www.chemcatcher.org)



[www.chempluschem.org](http://www.chempluschem.org)



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