



The following Communications have been judged by at least two referees to be “very important papers” and will be published online at [www.angewandte.org](http://www.angewandte.org) soon:

M. A. Newton,\* M. Di Michiel, A. Kubacka, A. Iglesias-Juez, M. Fernández-García\*  
**Observing Oxygen Storage and Release at Work under Cycling Redox Conditions: Synergies between Noble Metal and Oxide Promoter**

P. Berrouard, A. Najari, A. Pron, D. Gendron, P.-O. Morin, J.-R. Pouliot, J. Veilleux, M. Leclerc\*  
**Synthesis of 5-Alkyl[3,4-c]thienopyrrole-4,6-dione-Based Polymers through Direct Heteroarylation**

J. Zeng, C. Zhu, J. Tao, M. Jin, H. Zhang, Z.-Y. Li, Y. Zhu, Y. Xia\*  
**Controlling the Nucleation and Growth of Silver on Palladium Nanocubes by Manipulating the Reaction Kinetics**

H. Chinen, K. Mawatari, Y. Pihosh, K. Morikawa, Y. Kazoe, T. Tsukahara, T. Kitamori\*  
**Enhancement of Proton Mobility in Extended Nanospace Channels**



“... In the last 30 years, the chemistry prize was given ten times for a discovery that is reasonably classified as biochemistry or molecular biology ...”  
Read more in the Editorial by Roald Hoffmann on page 1734.

## Editorial

R. Hoffmann\* \_\_\_\_\_ 1734–1735

What, Another Nobel Prize in Chemistry to a Nonchemist?



“If I could be anyone for a day, I would be Leonardo da Vinci.  
My favorite way to spend a holiday is to hike on an alpine ‘via ferrata’ ...”  
This and more about Manfred Scheer can be found on page 1756.

## Author Profile

Manfred Scheer \_\_\_\_\_ 1756–1757



S. Buchholz



A. Thomas



H. Kagan



M. Antonietti

## News

Honorary Professorship:  
S. Buchholz \_\_\_\_\_ 1758

Bayer Early Excellence in Science Award:  
A. Thomas \_\_\_\_\_ 1758

Burckhardt Helferich Prize:  
H. Kagan \_\_\_\_\_ 1758

Honorary Doctorate:  
M. Antonietti \_\_\_\_\_ 1758

## Books

Chemical Synthetic Biology

Pier Luigi Luisi, Cristiano Chiarabelli

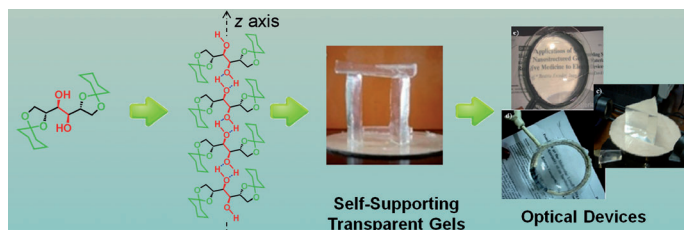
reviewed by S. Brakmann \_\_\_\_\_ 1759

## Highlights

### Molecular Gels

G. John,\* S. R. Jadhav, V. M. Menon,  
V. T. John \_\_\_\_\_ 1760–1762

Flexible Optics: Recent Developments in  
Molecular Gels



**Get smart:** Organogels based on sugar ketals have been prepared with a unique combination of properties suitable for the development of flexible optical devices and potential applications as smart

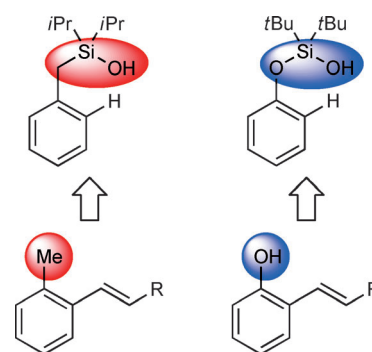
materials for the fabrication of microphtononic systems. Key features in the self-assembly of these gelators were conformational restrictions and interaction affinities.

### Palladium(II) Catalysis

M. Mewald, J. A. Schiffner,  
M. Oestreich\* \_\_\_\_\_ 1763–1765

A New Direction in C–H Alkenylation:  
Silanol as a Helping Hand

**Director's cut:** Not only conventional alcohols but also silanols can act as directing groups in oxidative palladium(II)-catalyzed C–H alkenylations. The silicon-tethered hydroxy groups are “traceless”, thereby facilitating the regioselective C–H activation of toluene derivatives as well as phenols (see scheme).



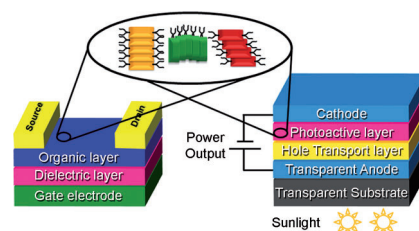
## Minireviews

### Materials Science

S. S. Babu, S. Prasanthkumar,  
A. Ajayaghosh\* \_\_\_\_\_ 1766–1776

Self-Assembled Gelators for Organic  
Electronics

**All gelled together:** Solvent-assisted gelation of functional organic molecules leading to one-dimensional fibers is an area of great interest. Recent developments in molecular self-assembly-assisted gelation of  $\pi$  systems into soft functional materials and their potential application in organic electronic devices, such as organic field-effect transistors and organic solar cells, are reviewed (see picture).



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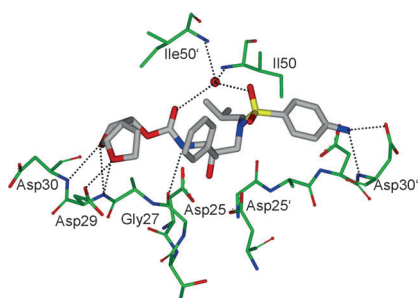
individuals who are personal members of a  
national chemical society prices are available  
on request. Postage and handling charges  
included. All prices are subject to local VAT/  
sales tax.

## Reviews

### Backbone Binding

A. K. Ghosh,\* D. D. Anderson, I. T. Weber,  
H. Mitsuya ————— 1778–1802

Enhancing Protein Backbone Binding—A  
Fruitful Concept for Combating Drug-  
Resistant HIV



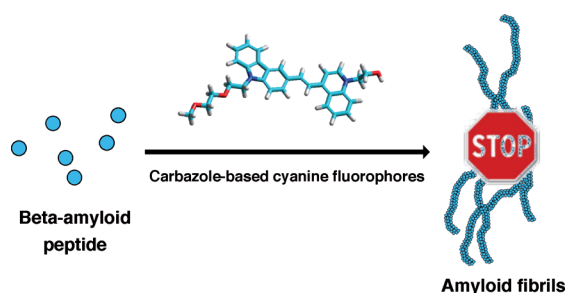
**Impeding the evolution of drug resistance:** HIV protease inhibitors are critical to antiretroviral treatment regimens. However, the rapid onset of drug resistance limits the effectiveness of most approved inhibitors. The structure-based design of inhibitors targeting atoms in the protein backbone is an attractive strategy for maintaining drug efficacy. This approach limits the enzyme's ability to evolve resistance without sacrificing its catalytic activity.

## Communications

### Alzheimer's Therapeutics

W. Yang, Y. Wong, O. T. W. Ng, L.-P. Bai,  
D. W. J. Kwong, Y. Ke, Z.-H. Jiang,  
H.-W. Li,\* K. K. L. Yung,\*  
M. S. Wong\* ————— 1804–1810

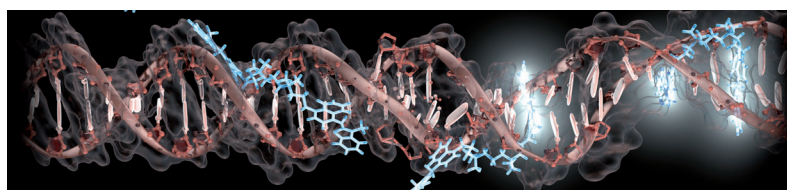
Inhibition of Beta-Amyloid Peptide  
Aggregation by Multifunctional  
Carbazole-Based Fluorophores



**Stopping aggregation:** Carbazole-based cyanine fluorophores bind selectively to the  $A\beta_{(1-40)}$  peptide and its aggregates which are responsible for causing Alzheimer's disease. One of these fluoro-

phores, SLOH, exerts a strong inhibitory effect on  $A\beta_{(1-40)}$  fibrillogenesis (see scheme) and can pass through the blood-brain barrier making it a potential therapeutic agent for Alzheimer's disease.

Frontispiece



**Lights off, but someone is home:** Single-molecule force spectroscopy was used to investigate DNA intercalation in the presence and absence of unbound dye (see picture). Force-induced intercalation, traditionally ascribed to dye from solution

binding to the DNA, occurred approximately two hours after the removal of the free dye. The results show that binding/unbinding and intercalation/deintercalation are distinct processes that occur on very different time scales.

### DNA Intercalation

D. H. Paik, T. T. Perkins\* — 1811–1815

Dynamics and Multiple Stable Binding  
Modes of DNA Intercalators Revealed by  
Single-Molecule Force Spectroscopy



Front Cover



## Hydrogels

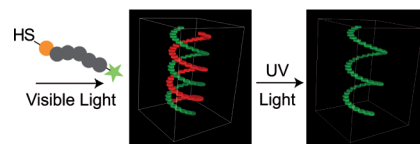


C. A. DeForest,  
K. S. Anseth\* — 1816–1819



Photoreversible Patterning of  
Biomolecules within Click-Based  
Hydrogels

**Lighting the way:** Biochemical cues have been reversibly patterned into hydrogels with full spatiotemporal control by using two photochemical reactions. The hydrogel is conjugated with a peptide by a thiolene photoaddition reaction that is initiated by visible light. Subsequent, selective photocleavage of an *o*-nitrobenzyl ether with UV light enables dynamic presentation of the peptide to cells with control in three dimensions.



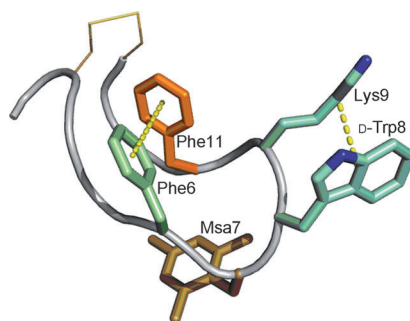
Back Cover

## Noncovalent Interactions

P. Martín-Gago, M. Gomez-Caminals,  
R. Ramón, X. Verdager,  
P. Martín-Malpartida, E. Aragón,  
J. Fernández-Carneado, B. Ponsati,  
P. López-Ruiz, M. A. Cortes, B. Colás,  
M. J. Macias,\* A. Riera\* — 1820–1825



Fine-tuning the  $\pi$ - $\pi$  Aromatic  
Interactions in Peptides: Somatostatin  
Analogues Containing Mesityl Alanine



**Going through the motions:** Somatostatin analogues having greater conformational rigidity than somatostatin have been prepared by substituting Phe residues in the native sequence with mesityl alanine (Msa; see structure). The analogues show high affinity for SSTR receptors, thus showing that fine-tuning of noncovalent interactions between amino acid side chains can modulate peptide affinity and selectivity.



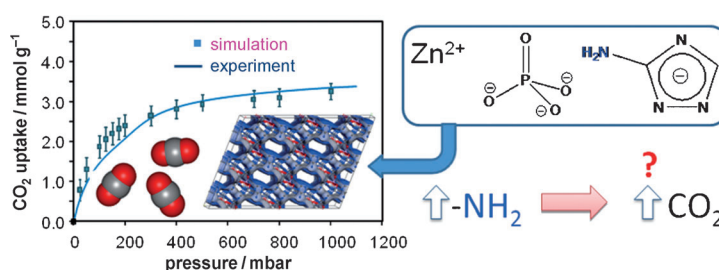
Inside Back Cover

## CO<sub>2</sub> Capture Materials

R. Vaidhyanathan, S. S. Iremonger,  
G. K. H. Shimizu,\* P. G. Boyd, S. Alavi,  
T. K. Woo\* — 1826–1829

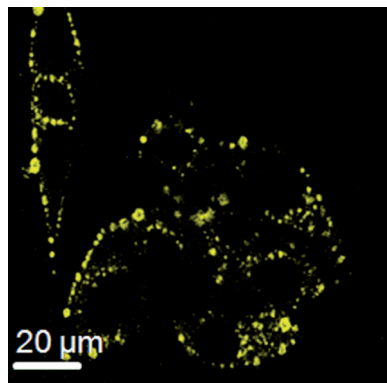


Competition and Cooperativity in Carbon  
Dioxide Sorption by Amine-Functionalized  
Metal–Organic Frameworks



**Molecular insights** into the roles of amine functionalization and cooperative CO<sub>2</sub> interactions into enhancing (and diminishing) CO<sub>2</sub> binding by metal-organic frameworks are shown both experimentally and computationally. Contrary to

popular thinking, higher amination decreases CO<sub>2</sub> binding in this system. This loss is compensated by cooperativity between CO<sub>2</sub> triads that enhances binding by over 7 kJ mol<sup>-1</sup>.

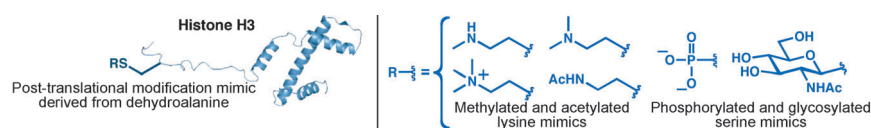


**Lasting glow:** Under femtosecond laser irradiation, graphene oxide nanoparticles (GONs) give strong two-photon luminescence (TPL; see picture). The presence of GONs also induces microbubbling, which causes cell death at an order of magnitude lower laser power than when cells are not labeled. The results show that GONs can be used for TPL-based imaging and photothermal cancer therapy.

## Bionanotechnology

J. L. Li, H. C. Bao, X. L. Hou, L. Sun, X. G. Wang,\* M. Gu\* — 1830–1834

Graphene Oxide Nanoparticles as a Nonbleaching Optical Probe for Two-Photon Luminescence Imaging and Cell Therapy



**Six for the price of one:** From a single precursor, dehydroalanine, six distinct post-translational modifications can be site-selectively installed on histone proteins (see figure), including the first site-selective phosphorylation and glycosylation of histones.

Direct observation of histone deacetylase activity on a full-length modified histone as well as its interactions with both chromatin reader and writer/eraser proteins are reported.

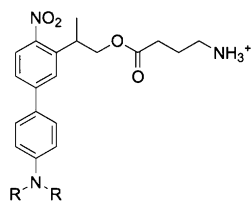
## Protein Modifications

J. M. Chalker, L. Lercher, N. R. Rose, C. J. Schofield, B. G. Davis\* — 1835–1839

Conversion of Cysteine into Dehydroalanine Enables Access to Synthetic Histones Bearing Diverse Post-Translational Modifications



**Rattling the cage:** The two  $\gamma$ -aminobutyric acid (GABA) derivatives **1** and **2** exhibit efficient and rapid ( $<5 \times 10^{-6}$  s) GABA photorelease upon one-photon excitation combined with two-photon uncaging cross-section at  $\lambda = 800$  nm. Compounds **1** and **2** were successfully used for two-photon GABA release in intact brain tissue, thus offering attractive perspectives in chemical neurosciences.

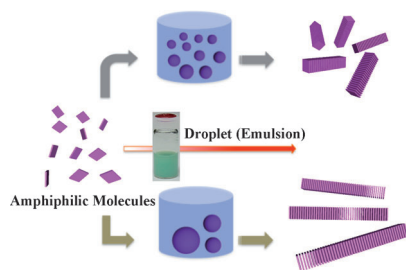


$\epsilon_{397\text{nm}} = 7500 \text{ M}^{-1} \text{ cm}^{-1}$   
1: R = carboxymethyl  
2: R = 2-(2-methoxyethoxy)ethyl

## Caged Compounds

L. Donato, A. Mourot, C. M. Davenport, C. Herbivo, D. Warther, J. Léonard, F. Bolze, J.-F. Nicoud, R. H. Kramer, M. Goeldner,\* A. Specht\* — 1840–1843

Water-Soluble, Donor–Acceptor Biphenyl Derivatives in the 2-(*o*-Nitrophenyl)propyl Series: Highly Efficient Two-Photon Uncaging of the Neurotransmitter  $\gamma$ -Aminobutyric Acid at  $\lambda = 800$  nm



**Self-assembly in a droplet:** A supramolecular system that governs self-assembly events over hierarchies from the nano- to the micrometer range has been developed by combining a bottom-up strategy based on molecular programming with top-down droplet microscience. Discrete 1D tubular structures were created by exploiting the compartment effect of the droplet, induced during dynamic shrinking under non-equilibrium conditions (see picture).

## Supramolecular Chemistry

M. Numata,\* D. Kinoshita, N. Taniguchi, H. Tamiaki, A. Ohta — 1844–1848

Self-Assembly of Amphiphilic Molecules in Droplet Compartments: An Approach Toward Discrete Submicrometer-Sized One-Dimensional Structures



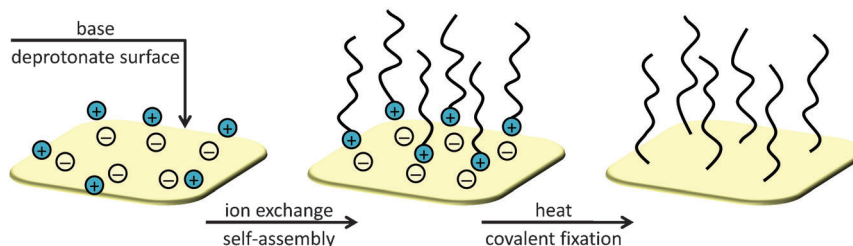


## Surface Modification

M. Foston, C. Hubbell, D.-Y. Park, F. Cook,  
Y. Tezuka, H. W. Beckham\* - 1849 – 1852



Surface Modification by Electrostatic Self-Assembly Followed by Covalent Fixation



**Sticks and bonds:** Surface-modifying agents can be functionalized with ionic groups that enable high exhaustion from a processing bath through electrostatic self-assembly. Using cyclic oniums as the

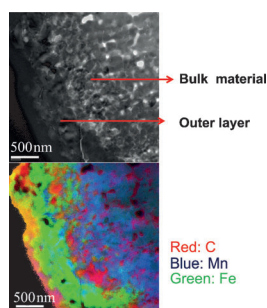
ionic functional groups, thermally induced ring-opening converts the ionic bonds to covalent bonds, thus lending permanency to the modification of the surface.

## Lithium Batteries

S.-M. Oh, S.-T. Myung, J. B. Park,  
B. Scrosati,\* K. Amine,  
Y.-K. Sun\* - 1853 – 1856



Double-Structured  $\text{LiMn}_{0.85}\text{Fe}_{0.15}\text{PO}_4$   
Coordinated with  $\text{LiFePO}_4$  for  
Rechargeable Lithium Batteries



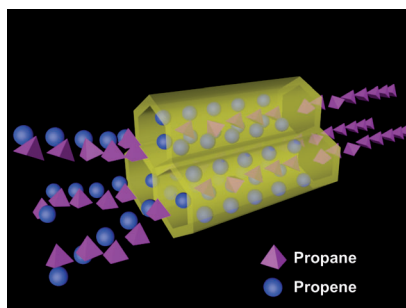
**A new coat:**  $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$  materials with a  $\text{LiFePO}_4$  outer layer of varying thickness and a  $\text{LiMn}_{0.85}\text{Fe}_{0.15}\text{PO}_4$  bulk were prepared. The physical characteristics such as tap density, porosity, and spherical morphology were fine-tuned. The double-structured micron-sized  $\text{LiMn}_{0.85}\text{Fe}_{0.15}\text{PO}_4/\text{LiFePO}_4$  material (see picture) shows properties which make this material an ideal candidate for rechargeable lithium batteries.

## Metal-Organic Frameworks

Y.-S. Bae, C. Y. Lee, K. C. Kim, O. K. Farha,  
P. Nickias, J. T. Hupp,\* S. T. Nguyen,\*  
R. Q. Snurr\* - 1857 – 1860



High Propene/Propane Selectivity in  
Isostructural Metal–Organic Frameworks  
with High Densities of Open Metal Sites



**Two go in, one comes out:** A series of isostructural M-MOF-74 materials ( $M = \text{Co}, \text{Mn}, \text{and Mg}$ ) with high densities of open metal sites have been examined for the selective adsorption of propene over propane. Co-MOF-74 exhibits the highest thermodynamic  $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$  selectivity (ca. 45) reported for any MOF to date.

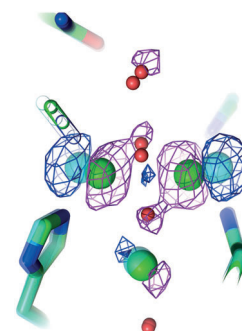
## Multicopper Oxidases

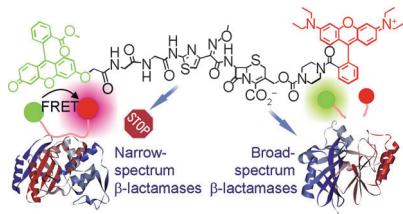
H. Komori, R. Sugiyama, K. Kataoka,  
Y. Higuchi, T. Sakurai\* - 1861 – 1864



An O-Centered Structure of the Trinuclear  
Copper Center in the Cys500Ser/  
Glu506Gln Mutant of CueO and  
Structural Changes in Low to High X-Ray  
Dose Conditions

**Right on CueO:** The O-centered structure of the trinuclear copper center in a multicopper oxidase (CueO) was shown to be an intermediate of the four-electron reduction of dioxygen (see picture). This structure was determined by in situ data collection of X-ray diffractions and copper K-edge spectra at low to high X-ray dose conditions.



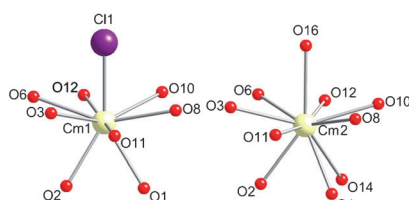


**Identification of bacteria:** A methoxyimino cephalosporin derivative containing a pair of fluorescence resonance energy transfer (FRET) fluorophores was synthesized. This probe displays selective cleavage toward different types of  $\beta$ -lactamases, thereby providing a rapid assay to distinguish bacterial cells that are either sensitive or resistant to broad-spectrum  $\beta$ -lactam antibiotics (see picture).

### $\beta$ -Lactam Antibiotics

J. X. Zhang, Y. Shen, S. L. May, D. C. Nelson, S. W. Li\* — 1865 – 1868

Ratiometric Fluorescence Detection of Pathogenic Bacteria Resistant to Broad-Spectrum  $\beta$ -Lactam Antibiotics

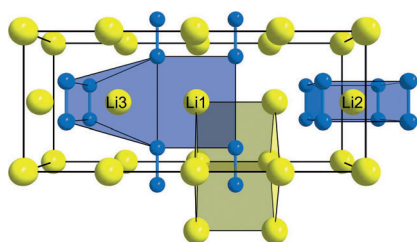


**The two faces of curium:** The first curium borate has been prepared showing a complex structure with coordination environments for  $\text{Cm}^{\text{III}}$  that are found in both  $\text{Pu}^{\text{III}}$  and  $\text{Am}^{\text{III}}$  borates (see picture). Time-resolved laser-induced photoluminescence studies as well as X-ray diffraction experiments show two distinct  $\text{Cm}^{\text{III}}$  sites with different coordination environments.

### Actinides

M. J. Polinski, S. Wang, E. V. Alekseev, W. Depmeier, G. Liu, R. G. Haire, T. E. Albrecht-Schmitt\* — 1869 – 1872

Curium(III) Borate Shows Coordination Environments of Both Plutonium(III) and Americium(III) Borates

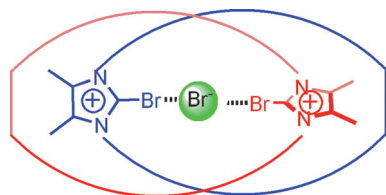


**Diazenide surprise:** The synthesis of an alkali diazenide,  $\text{Li}_2\text{N}_2$ , is presented. Lithium diazenide adopts an unprecedented structure type for compounds with  $\text{A}_2\text{B}_2$  composition (see picture). Spectroscopic analysis shows a significant feature at  $1328\text{ cm}^{-1}$  which is assigned to the stretching vibration of the  $[\text{N}_2]^{2-}$  ion. Electronic structure calculations underline the metallic character and confirm the 50% occupation of the antibonding  $\pi$  states in  $[\text{N}_2]^{2-}$ .

### Lithium Diazenide

S. B. Schneider, R. Frankovsky, W. Schnick\* — 1873 – 1875

High-Pressure Synthesis and Characterization of the Alkali Diazenide  $\text{Li}_2\text{N}_2$



**The anion-templated synthesis** of a halogen-bonding catenane, which recognizes chloride and bromide ions solely by halogen bonding, is described. The catenane's ability to optically sense halide anions using fluorescence spectroscopy is demonstrated.

### Halogen Bonding

A. Caballero, F. Zapata, N. G. White, P. J. Costa, V. Félix, P. D. Beer\* — 1876 – 1880

A Halogen-Bonding Catenane for Anion Recognition and Sensing

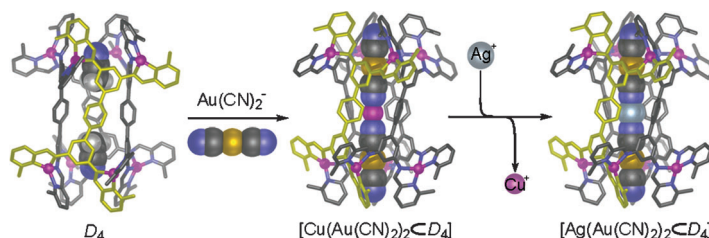


## Host–Guest Systems

W. Meng, J. K. Clegg,  
J. R. Nitschke\* — 1881 – 1884



Transformative Binding and Release of Gold Guests from a Self-Assembled  $\text{Cu}_8\text{L}_4$  Tube



**Totally tubular:** A linear  $\text{M}_8\text{L}_4^{8+}$  receptor, which binds tightly and selectively to the dicyanoaurate anion, was assembled from simple organic subcomponents and copper(I) ions. The guest complex is not bound unchanged, but instead is trans-

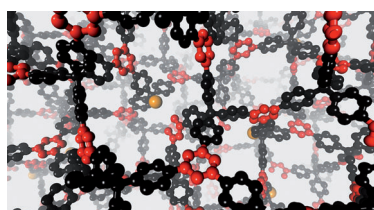
formed into a longer linear complex where two dicyanogold units are bridged by a central cation of copper/silver (see scheme). This complex optimally fills the cavity of the receptor but is not observed in the absence of the host.

## Covalent Organic Frameworks

D. N. Bunck, W. R. Dichtel\* — 1885 – 1889



Internal Functionalization of Three-Dimensional Covalent Organic Frameworks



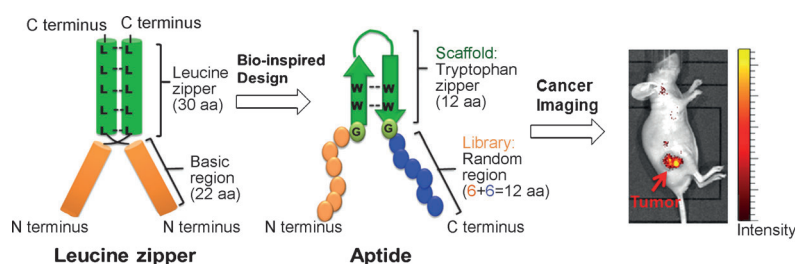
**Thinking inside the COF:** Internally functionalized, boroxine-linked, three-dimensional, covalent organic frameworks (COFs) can be synthesized by co-crystallizing a truncated, trifunctional monomer with the parent tetrafunctional building block. The functionalized COFs possess accessible functional groups and a distinct interior microenvironment. In the picture the orange sphere corresponds to an alkyl chain or an allyl group in the pore interior.

## Peptide Design

S. Kim, D. Kim, H. H. Jung, I.-H. Lee,  
J. I. Kim, J.-Y. Suh, S. Jon\* — 1890 – 1894



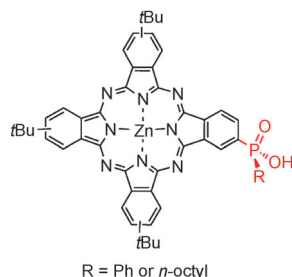
Bio-Inspired Design and Potential Biomedical Applications of a Novel Class of High-Affinity Peptides



**Two arms to hold:** Inspired by the structure of basic leucine-zipper proteins, high-affinity peptides, named aptides, were designed that contain a stabilizing scaffold (tryptophan zipper) and two target-

binding regions (orange and blue in picture). A fluorescently labeled aptide that binds to a tumor-specific protein was used for fluorescence imaging in vivo.





**Anchors away!** Two zinc phthalocyanine photosensitizers with different phosphonic acid anchor groups were synthesized (see scheme). Solar cells sensitized with these compounds have a short-circuit photo-current density of  $7.6 \pm 0.2 \text{ mA cm}^{-2}$ , an open-circuit voltage of  $559 \pm 30 \text{ mV}$ , and a fill factor of  $0.76 \pm 0.03$ , which corresponds to an overall conversion efficiency of 3.24% under 1 sun.

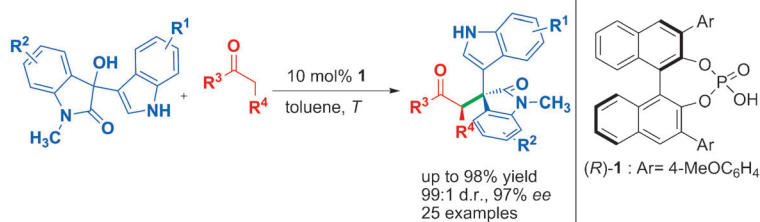
### Photosensitizers

I. López-Duarte, M. Wang, R. Humphry-Baker, M. Ince, M. V. Martínez-Díaz, M. K. Nazeeruddin,\* T. Torres,\* M. Grätzel\* — 1895 – 1898

Molecular Engineering of Zinc Phthalocyanines with Phosphonic Acid Anchoring Groups



Inside Cover



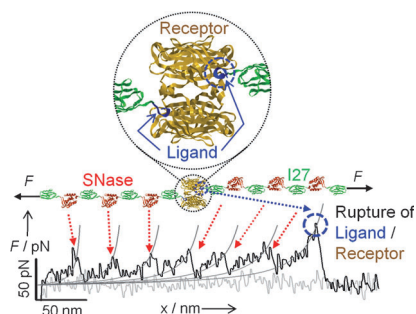
**Being direct:** A Brønsted acid catalyzed  $\alpha$  alkylation of ketones is described. The phosphoric acid 1 promotes this reaction

to afford the desired products with high yields, high diastereoselectivities, and good to excellent enantioselectivities.

### Organocatalysis

L. Song, Q.-X. Guo,\* X.-C. Li, J. Tian, Y.-G. Peng\* — 1899 – 1902

The Direct Asymmetric  $\alpha$  Alkylation of Ketones by Brønsted Acid Catalysis



**Into low force regime:** A universal molecular force probe for measuring by AFM the strength of receptor–ligand and protein–protein complexes was developed. The protein-based force probe has the sensitivity on the order of piconewtons and provides a single-molecule fingerprint for identifying mechanical rupture events of individual complexes (see picture).

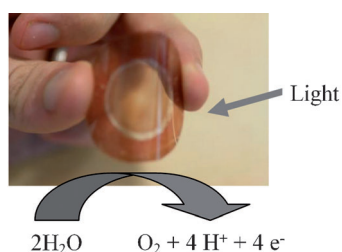
### Protein-Based Force Probe

M. Kim, C.-C. Wang, F. Benedetti, P. E. Marszalek\* — 1903 – 1906

A Nanoscale Force Probe for Gauging Intermolecular Interactions



**A flexible polymer for selective seawater splitting:** Incorporation of a monomeric Mn-porphyrin that is normally catalytically inactive, into a flexible poly(terthiophene) film yields a remarkable light-assisted water oxidation catalyst with an apparent overpotential for water oxidation of a mere 0.09 V. The catalyst generates exclusively O<sub>2</sub> and no Cl<sub>2</sub> in seawater at 0.9 V versus Ag/AgCl.



### Water Splitting

J. Chen,\* P. Wagner, L. Tong, G. G. Wallace, D. L. Officer, G. F. Swiegers\* — 1907 – 1910

A Porphyrin-Doped Polymer Catalyzes Selective, Light-Assisted Water Oxidation in Seawater

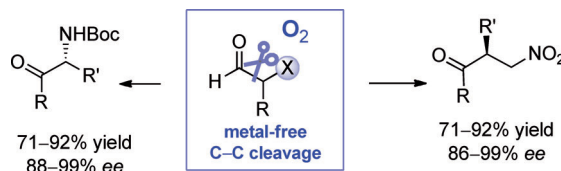


## C–C Cleavage

B. Tiwari, J. Zhang,  
Y. R. Chi\* 1911–1914



Facile Access to Chiral Ketones through  
Metal-Free Oxidative C–C Bond Cleavage  
of Aldehydes by O<sub>2</sub>



**Giving the metal the boot:** The title reaction provides facile access to functionalized chiral ketones from chiral  $\alpha,\alpha'$ -disubstituted aldehydes in the presence of molecular oxygen (see scheme). The C–C

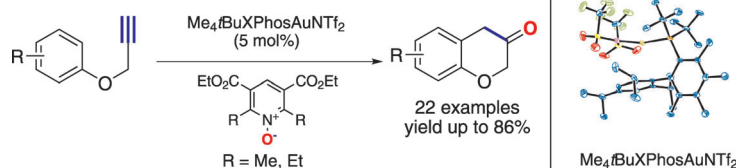
bond-cleavage approach offers an alternative or better method relative to the typical bond-forming strategies used in synthesizing chiral ketones.

## Homogeneous Catalysis

Y. Wang, K. Ji, S. Lan,  
L. Zhang\* 1915–1918



Rapid Access to Chroman-3-ones through  
Gold-Catalyzed Oxidation of Propargyl  
Aryl Ethers



**The two-step:** Chroman-3-ones are important intermediates for organic synthesis and medicinal chemistry. However, their syntheses require multiple steps and are not efficient. By using gold-catalyzed

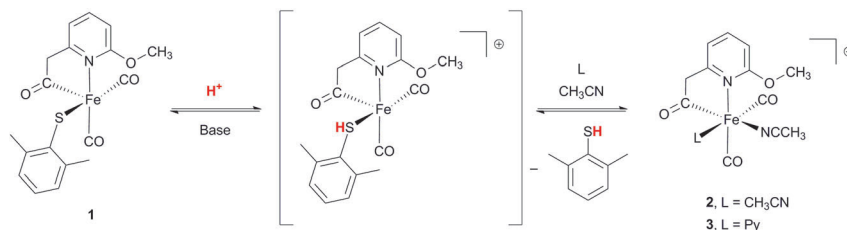
alkyne oxidation, this versatile heterocycle can be prepared in only two steps from readily available phenols and with mostly high efficiencies (see scheme).

## Biomimetic Chemistry

D. Chen, R. Scopelliti,  
X. L. Hu\* 1919–1921



Reversible Protonation of a Thiolate  
Ligand in an [Fe]-Hydrogenase Model  
Complex



**What is the channel?** The thiolate ligand in the five-coordinate model complex **1** of [Fe]-hydrogenase is preferentially and reversibly protonated, even in the presence of an acyl ligand. The results suggest

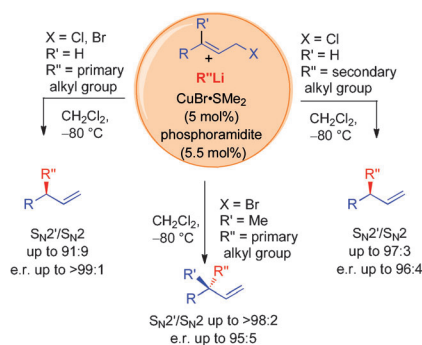
that the Cys176 thiolate ligand in [Fe]-hydrogenase can serve as the internal base to accept the proton after heterolytic splitting of H<sub>2</sub>.

## Asymmetric Catalysis

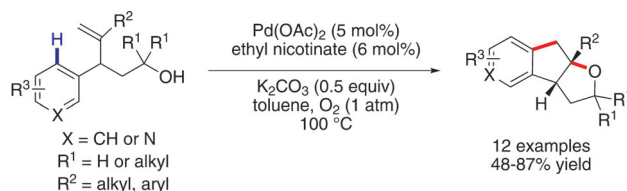
M. Fañanás-Mastral, M. Pérez, P. H. Bos,  
A. Rudolph, S. R. Harutyunyan,\*  
B. L. Feringa\* 1922–1925



Enantioselective Synthesis of Tertiary and  
Quaternary Stereogenic Centers: Copper/  
Phosphoramidite-Catalyzed Allylic  
Alkylation with Organolithium Reagents



**An efficient** and highly enantioselective copper-catalyzed allylic alkylation of disubstituted allyl halides with primary and secondary organolithium reagents using phosphoramidite ligands is reported. The use of trisubstituted allyl bromides allows, for the first time, the enantioselective synthesis of all-carbon quaternary stereogenic centers with these reactive organometallic reagents.



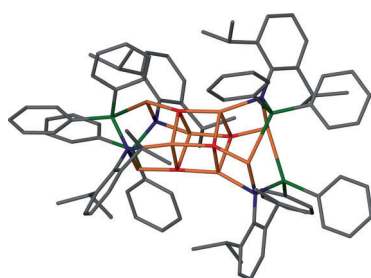
**An efficient protocol** has been developed for the intramolecular oxidative oxyarylation using a Pd<sup>II</sup>-catalyzed tandem oxy-palladation/C–H functionalization strategy. This methodology allows rapid access to tetrahydro-2*H*-indeno-[2,1-*b*]furan

frameworks from simple hydroxyalkenes. The reactivity of this process is orthogonal to that of Pd<sup>0</sup>-catalyzed transformations, enabling the divergent modification of a single molecule.

## C–H Functionalization

R. Zhu, S. L. Buchwald\* — 1926 – 1929

Combined Oxy-palladation/C–H Functionalization: Palladium(II)-Catalyzed Intramolecular Oxidative Oxyarylation of Hydroxyalkenes



**LiH-ghtweight:** The title complex having a central (LiH)<sub>4</sub> cube has been prepared and structurally characterized (see picture). The compound is stable towards LiH elimination at room temperature in solution, and can be employed for hydro-lithiation reactivity as has been demonstrated by its reaction with benzophenone.

## Cluster Compounds

A. Stasch\* — 1930 – 1933

A Hydrocarbon-Soluble Lithium Hydride Complex



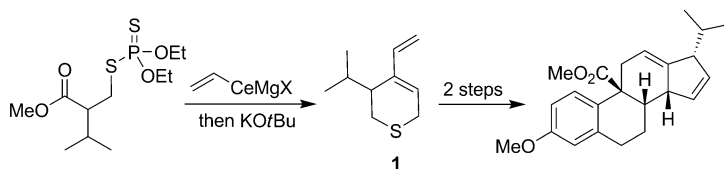
**Unusual split:** A wide variety of benzosiloles and derivatives are obtained by the Pd-catalyzed intermolecular coupling of 2-silylaryl bromides and alkynes and the accompanying selective cleavage of the C(sp<sup>3</sup>)–Si bonds as a key step (see

scheme). The product spectrum includes benzosiloles, benzothiophene-fused siloles, ladder-type  $\pi$ -conjugated benzosiloles, and thiophene-bridged 2,5-bis-benzosiloles.

## C(sp<sup>3</sup>)–Si Activation

Y. Liang, W. Geng, J. Wei,  
Z. Xi\* — 1934 – 1937

Palladium-Catalyzed Intermolecular Coupling of 2-Silylaryl Bromides with Alkynes: Synthesis of Benzosiloles and Heteroarene-Fused Siloles by Catalytic Cleavage of the C(sp<sup>3</sup>)–Si Bond



**The fifth element:** An efficient new synthetic method for accessing 3,6-dihydro-2*H*-thiopyrans **1** in one pot has been developed. This method employs an anionic cascade, which is triggered by the addition of a vinyl nucleophile to a

carbonyl group followed by S to O thiophosphate migration and an intramolecular thiolate displacement. The scope is demonstrated for a range of ketone and ester substrates.

## Synthetic Methods

F. Li, D. Calabrese, M. Brichacek, I. Lin,  
J. T. Njardarson\* — 1938 – 1941

Efficient Synthesis of Thiopyrans Using a Sulfur-Enabled Anionic Cascade

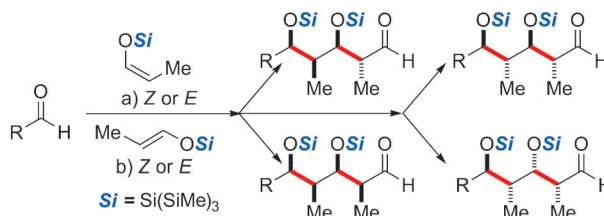


## Synthetic Methods

P. B. Brady, H. Yamamoto\* - 1942 – 1946



Rapid and Stereochemically Flexible  
Synthesis of Polypropionates: Super-Silyl-  
Governed Aldol Cascades



**Polypropionates made EZ:** The *E/Z* geometry of tris(trimethylsilyl)silyl super silyl enol ethers derived from propionaldehyde controls diastereoselectivity in the aldehyde crossed-aldol reaction. These silyl enol ethers can participate in

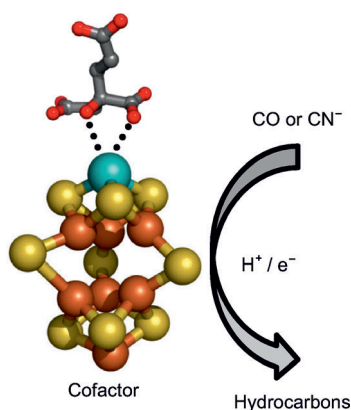
polyaldol cascade reactions, thus allowing the one-pot synthesis of four different dipropionate stereotetrads (see scheme), and polyketides bearing up to five contiguous stereocenters.

## Biocatalysis

C. C. Lee, Y. Hu,\*  
M. W. Ribbe\* - 1947 – 1949



ATP-Independent Formation of  
Hydrocarbons Catalyzed by Isolated  
Nitrogenase Cofactors



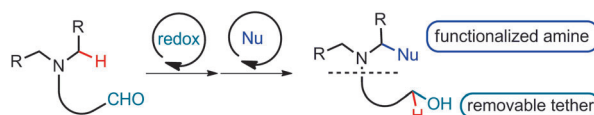
**Reduce to produce:** Molybdenum- and vanadium-nitrogenase cofactors have been isolated and shown to reduce carbon monoxide and cyanide ions to a mixture of alkanes and alkenes in the presence of a strong reductant, europium(II) diethylenetriaminepentaacetate (see scheme). Various hydrocarbons of up to seven carbon atoms in length are detected as products in these ATP-free reactions.

## Redox Reactions

I. D. Jurberg, B. Peng, E. Wöstefeld,  
M. Wasserloos,  
N. Maulide\* - 1950 – 1953



Intramolecular Redox-Triggered C–H  
Functionalization



**Sacrifice for the team:** A one-pot method achieves remote functionalization at the  $\alpha$ -position of an amine moiety through the sacrificial reduction of a neighboring group. The process takes advantage of an

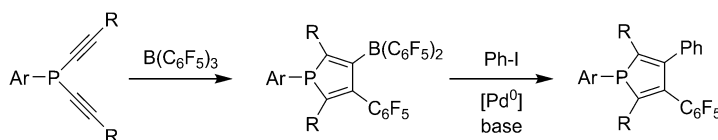
intramolecular redox reaction, thereby avoiding the need for any external oxidants. This method was applied to a concise five-step total synthesis of indolizidine 167B.

## Phosphorus Heterocycles

J. Möbus, Q. Bonnin, K. Ueda, R. Fröhlich,  
K. Itami, G. Kehr, G. Erker\* - 1954 – 1957

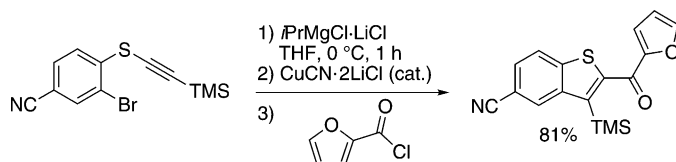


The 1,1-Carboboration of  
Bis(alkynyl)phosphanes as a Route to  
Phosphole Compounds



**Neat and tidy:**  $B(C_6F_5)_3$  efficiently converts a series of bis(alkynyl)phosphanes into highly substituted 3-borylphospholes through a twofold 1,1-carboboration

reaction sequence. The boron substituted phospholes were also used as substrates in Suzuki–Miyaura type cross-coupling reactions (see scheme).



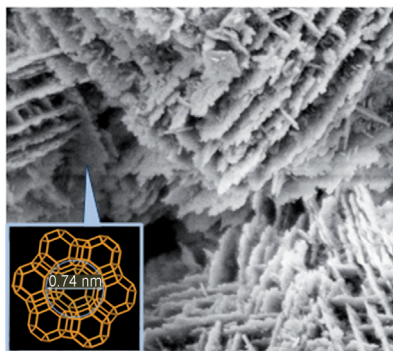
**Highly functional:** A copper(I)-catalyzed intramolecular carbomagnesiation under mild conditions transforms readily available alkynyl(aryl)thioethers into magnesiated benzothiophenes. Subsequent reaction with various electrophiles (acid

chlorides, allyl bromides, aryl halides) provides polyfunctional benzo[b]thiophenes (see scheme). Further modification of the cyclization products affords highly diversified benzothiophene derivatives and new heterocyclic scaffolds.

## Heterocycle Synthesis

T. Kunz, P. Knochel\* — 1958 – 1961

Synthesis of Functionalized Benzo[b]thiophenes by the Intramolecular Copper-Catalyzed Carbomagnesiation of Alkynyl(aryl)thioethers

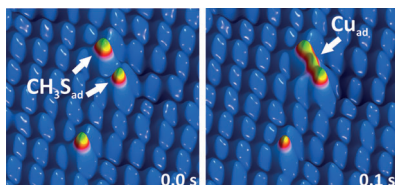


**Holey sheets:** Nanosheet assemblies of FAU-type zeolite X with intracrystalline mesopores are prepared (see picture). This material is synthesized by soft-templating and combines micro, meso, and macropores in a hierarchically interconnected manner.

## Zeolites

A. Inayat, I. Knoke, E. Spiecker, W. Schwieger\* — 1962 – 1965

Assemblies of Mesoporous FAU-Type Zeolite Nanosheets

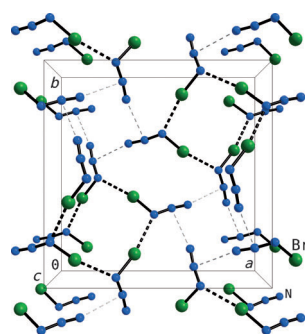


**Dynamic trapping:** Scanning tunneling microscopy video imaging of methyl thiolates on copper surfaces reveal the formation of defined metastable dimers with fluctuations on subsecond time-scales, indicating short-term trapping of copper surface atoms (see picture). This transient stabilization of metal adatoms has important implications for applications of organosulfur species as additives and in nanoscience.

## Thiolate Dynamics on Surfaces

Y.-C. Yang, A. Taranovskyy, O. M. Magnussen\* — 1966 – 1969

Thiolate-Induced Metal Adatom Trapping at Solid–Liquid Interfaces



**A new twist:** The single-crystal structural analysis of BrN<sub>3</sub> is described. In contrast to IN<sub>3</sub>, which forms chains, BrN<sub>3</sub> forms a helical structure in the solid state (see picture). Such a structural feature has not been previously observed in covalent p-block azide chemistry.

## Halogen Azides

B. Lyhs, D. Bläser, C. Wölper, S. Schulz,\* G. Jansen — 1970 – 1974

Solid-State Structure of Bromine Azide



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## Angewandte Corrigendum

Fundamental Research Needs Excellent  
Scientists and its Own Space

D. Kneißl, H. Schwarz\* — 12370–12371

Angew. Chem. Int. Ed. 2011, 50

DOI: 10.1002/anie.201108152

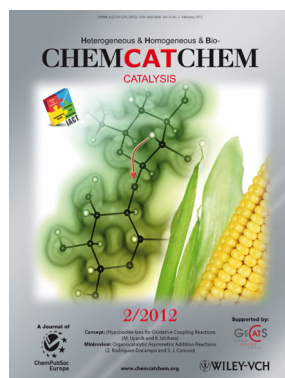
Two attentive readers have pointed out to the authors of this Editorial that Michael Faraday is referred to as “Sir Michael” and that reference was made to President Roosevelt with the wrong first name.

It is true that Faraday was offered this title, but—similar to P. M. Dirac—he declined it. Furthermore, the U.S. President that is cited in the text was “F. D. Roosevelt” and not “T. Roosevelt”. You live and learn!

## Check out these journals:



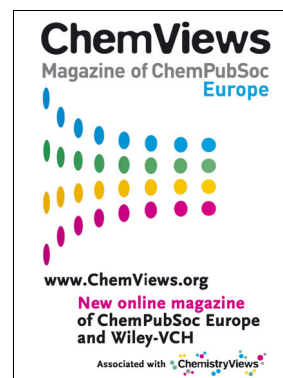
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