



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:

T. Lewis, M. Faubel, B. Winter, J. C. Hemminger\*

**CO<sub>2</sub> Capture in an Aqueous Solution of an Amine: Role of the Solution Interface**

Y. H. Kim, S. Banta\*

**Complete Oxidation of Methanol in an Enzymatic Biofuel Cell by a Self-Assembling Hydrogel Created from Three Modified Dehydrogenases**

L. Furst, J. M. R. Narayanan, C. R. J. Stephenson\*

**Total Synthesis of (+)-Gliocladin C Enabled by Visible-Light Photoredox Catalysis**

Y. Kitagawa, H. Segawa, K. Ishii\*

**Magnetochiral Dichroism of Organic Compounds**



Educating Chemists for the Future

## Editorial

P. Atkins \_\_\_\_\_ 8442–8443



*“If I could be any age I would be 47. No point in fretting about the passage of time.*

*The biggest challenge facing scientists is reversing the growing sense from the general public that science is not a worthy area of pursuit ...”*

This and more about Paul Floreancig can be found on page 8468.

## Author Profile

Paul Floreancig \_\_\_\_\_ 8468



P. G. Bruce



F. Diederich



H.-J. Freund



A. Pfaltz



F. Schüth

## News

Arfvedson Schlenk Prize:

P. G. Bruce \_\_\_\_\_ 8469

Baeyer Medal:

F. Diederich \_\_\_\_\_ 8469

Karl Ziegler Prize:

H.-J. Freund \_\_\_\_\_ 8469

Heilbronner Hückel Lecture:

A. Pfaltz \_\_\_\_\_ 8469

Wöhler Prize:

F. Schüth \_\_\_\_\_ 8469

## Books

Energy Production and Storage

Robert H. Crabtree

reviewed by S. Campagna \_\_\_\_\_ 8471

Artificial Receptors for Chemical Sensors

Vladimir M. Mirsky, Anatoly Yatsimirsky

reviewed by W. Nau,

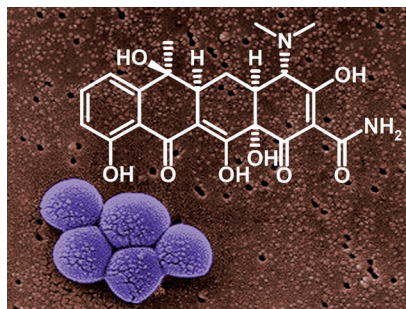
A. I. Lazar, S. Joshi \_\_\_\_\_ 8472

## Highlights

### Tetracycline Antibiotics

B. Heasley\* — 8474–8477

Isoxazole Functionalization Technologies Enable Construction of Tetracycline Derivatives

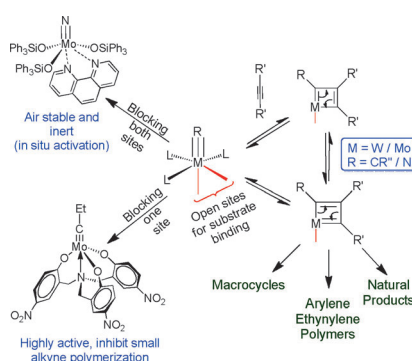


**Reactive response:** Tetracyclines are potent antimicrobial agents—however, their high consumption level has contributed to the emergence of widespread bacterial resistance, which in turn stimulates the systematic search for new tetracycline analogues. In recent years, new synthetic methods have emerged that provide access to a broad range of tetracycline analogues.

### Alkyne Metathesis

K. Jyothish, W. Zhang\* — 8478–8480

Towards Highly Active and Robust Alkyne Metathesis Catalysts: Recent Developments in Catalyst Design



**Switch it up:** Recent developments in alkyne metathesis catalysts are described, with particular emphasis on the rational design of ligands that can improve the catalyst activity and stability (see scheme; M = W, Mo; R = CR', N) by probing the electrophilicity and the substrate binding sites at the transition-metal center.

## Essays

### Responsibility in Science

H. Frank,\* L. Campanella, F. Dondi, J. Mehlich, E. Leitner, G. Rossi, K. Ndjoko Ioset, G. Bringmann\* — 8482–8490

Ethics, Chemistry, and Education for Sustainability

**Why do scientists avoid considerations about ethics** and categorically deny precautionary principles? Is it because they do not adequately understand the emotional needs and fears of the general public? The authors argue that a central challenge in chemical education is conveying the philosophy of empathy; with-

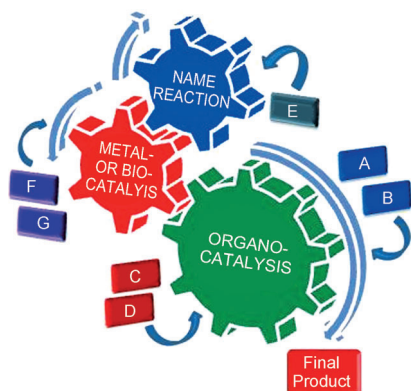
out it, the exclusively intellectual training of chemists results in heartless individuals who forget human needs and dreams. In addition, concrete examples are given from a course in applied ethics for chemistry students and a scholarship program in the Congo.

**For the USA and Canada:** ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals

postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. Annual subscription price for institutions: US\$ 11,738/10,206 (valid for print and electronic / print or electronic delivery); for

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

## Minireviews



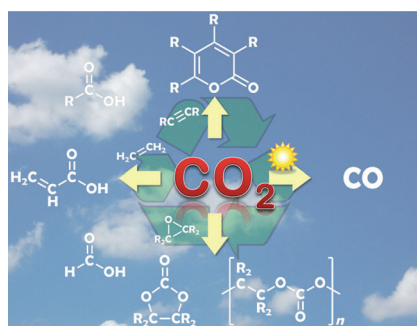
### It's great, but what shall we call it?

Asymmetric organocatalysis has been successfully incorporated in many multi-step one-pot sequences (see picture; A–G are reagents). In this Minireview, an easy-to-use classification system for the systematic and informative description of one-pot reactions is introduced. Selected important contributions within the field of organocatalytic one-pot reactions are reviewed according to this new system.

### One-Pot Reactions

Ł. Albrecht, H. Jiang,  
 K. A. Jørgensen\* ————— 8492–8509

A Simple Recipe for Sophisticated Cocktails: Organocatalytic One-Pot Reactions—Concept, Nomenclature, and Future Perspectives



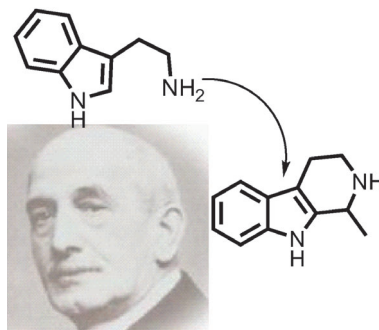
**Renewable carbon resources**, such as carbon dioxide, are of enormous interest as an entry into industrially relevant chemicals, such as formic or salicylic acids, urea, and (poly)carbonates. This Review highlights the use of CO<sub>2</sub> as a C<sub>1</sub> feedstock as well as its transformation with homogeneous molecular transition-metal catalysts.

### CO<sub>2</sub> Activation

M. Cokoja, C. Bruckmeier, B. Rieger,\*  
 W. A. Herrmann,  
 F. E. Kühn\* ————— 8510–8537

Transformation of Carbon Dioxide with Homogeneous Transition-Metal Catalysts: A Molecular Solution to a Global Challenge?

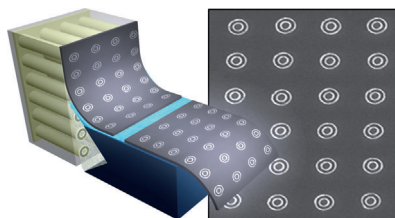
**100 years ago** Pictet and Spengler discovered the most important method for the synthesis of alkaloid scaffolds—the condensation of aryl ethylamines and aldehydes. Today, efficient enzymatic and non-enzymatic methods are both available for the Pictet–Spengler reaction.



### Alkaloid Synthesis

J. Stöckigt,\* A. P. Antonchick, F. Wu,  
 H. Waldmann\* ————— 8538–8564

The Pictet–Spengler Reaction in Nature and in Organic Chemistry



**Nanoskiving** is a simple and inexpensive method of nanofabrication which makes it possible to fabricate nanostructures from materials, and of geometries, to which more familiar methods of nanofabrication are not applicable. Three steps are required: 1) deposition of a thin film onto an epoxy substrate, 2) embedding this film in an epoxy block, and 3) sectioning the epoxy block into slabs with an ultramicrotome.

### Nanofabrication

D. J. Lipomi, R. V. Martinez,  
 G. M. Whitesides\* ————— 8566–8583

Use of Thin Sectioning (Nanoskiving) to Fabricate Nanostructures for Electronic and Optical Applications

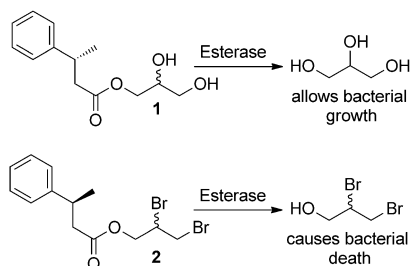
## Communications

### Protein Engineering

E. Fernández-Álvaro, R. Snajdrova,  
H. Jochens, T. Davids, D. Böttcher,\*  
U. T. Bornscheuer\* — 8584–8587



A Combination of In Vivo Selection and  
Cell Sorting for the Identification of  
Enantioselective Biocatalysts



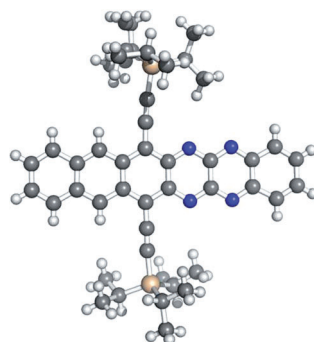
The “carrot and stick” principle could be combined with cell sorting to enable the selection of enantioselective esterase variants from a mutant library. Hence, the enormous diversity generated in directed evolution experiments is now easily accessible by this high-throughput system. In line with the principle, the hydrolysis of **1** glycerin supports cell growth, whereas the hydrolysis of **2** leads to cell death.

### Heteroacenes

B. D. Lindner, J. U. Engelhart, O. Tverskoy,  
A. L. Appleton, F. Rominger,  
A. Peters, H.-J. Himmel,  
U. H. F. Bunz\* — 8588–8591



Stable Hexacenes through Nitrogen  
Substitution



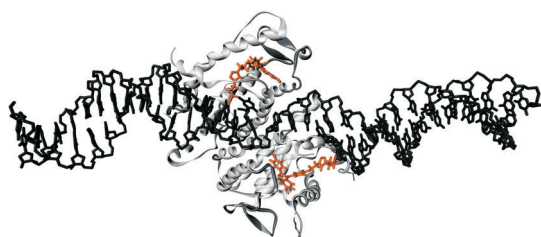
**Give me an N:** Tetraazahexacenes (see picture, N blue, Si brown) are easily prepared in high yields. Their modular synthesis allows the introduction of any substituent by the choice of suitable quinoxaline derivatives.

### DNA Complexes

F. Abendroth, A. Bujotzek, M. Shan,  
R. Haag, M. Weber,  
O. Seitz\* — 8592–8596



DNA-Controlled Bivalent Presentation of  
Ligands for the Estrogen Receptor



**Molecular ruler:** Steroid analogues were conjugated to DNA by using click chemistry, and self-assembly provided ternary DNA complexes with bivalent ligand presentation. The distance between the bound ligands was measured by

spatial screening of the estrogen receptor, and a second hydrophobic binding site was postulated. The picture shows the DNA(black)–raloxifene(orange) complex in the ligand binding domain of the receptor.

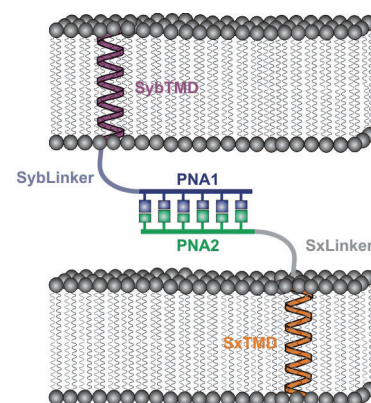
### Membrane Fusion Model

A. S. Lygina, K. Meyenberg, R. Jahn,  
U. Diederichsen\* — 8597–8601

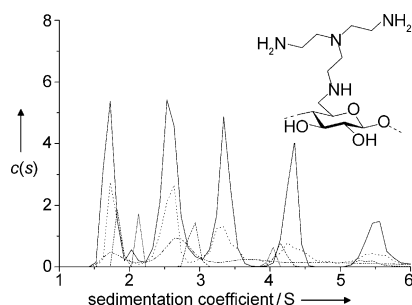


Transmembrane Domain Peptide/Peptide  
Nucleic Acid Hybrid as a Model of a  
SNARE Protein in Vesicle Fusion

**Artificial models** of the natural SNARE proteins containing the native linker regions (light blue/gray) and the transmembrane domains (TMDs) of synaptobrevin (Syb, violet) and syntaxin-1A (Sx, orange) along with a peptide nucleic acid (PNA) recognition motif can align with either an antiparallel (see picture) or parallel orientation of the interacting strands. These hybrids induce the hemifusion and partial bilayer fusion of phospholipid vesicles.





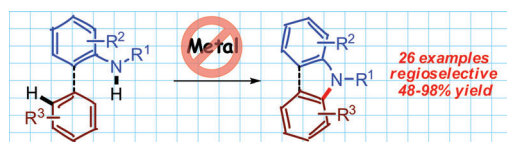


**Sugar can, too:** Many proteins form non-covalent and thermodynamically reversible oligomers, which can dictate a protein's functionality. For the first time, the presence of multiple oligomeric forms is shown in a whole class of polymeric carbohydrates, the 6-deoxy-6-aminocelluloses, using analytical ultracentrifugation as a probe.

### Carbohydrate Self-Association

T. Heinze, M. Nikolajski, S. Daus, T. M. D. Besong, N. Michaelis, P. Berlin, G. A. Morris, A. J. Rowe, S. E. Harding\* **8602–8604**

Protein-like Oligomerization of Carbohydrates



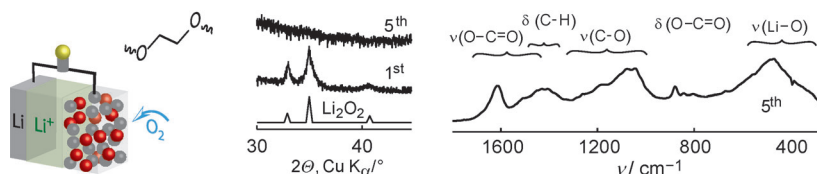
**The twinkling of an I:** In a new atom-economical and environmentally friendly organocatalytic method for intramolecular C–H amination, the C–N bond forms at ambient temperature by abstraction of

two atoms of hydrogen; only acetic acid and water are formed as by-products. The method has also been extended to the unprecedented metal-free cross-amination of nonactivated arenes.

### C–H Functionalization

A. P. Antonchick,\* R. Samanta, K. Kulikov, J. Lategahn **8605–8608**

Organocatalytic, Oxidative, Intramolecular C–H Bond Amination and Metal-free Cross-Amination of Unactivated Arenes at Ambient Temperature



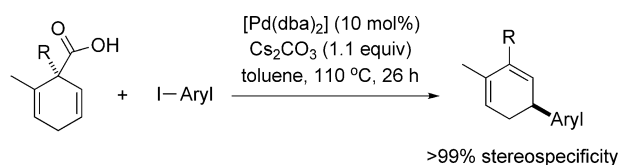
**Electrolyte puts up a fight:** The electrolyte is one of the greatest challenges facing the development of the non-aqueous Li–O<sub>2</sub> battery. Although ether-based electrolytes do from Li<sub>2</sub>O<sub>2</sub> on the first discharge, it is

shown by various techniques that they also decompose and that decomposition increases while Li<sub>2</sub>O<sub>2</sub> decreases on cycling (see picture). Thus, these electrolytes are not suitable.

### Lithium–Oxygen Batteries

S. A. Freunberger, Y. Chen, N. E. Drewett, L. J. Hardwick, F. Bardé, P. G. Bruce\* **8609–8613**

The Lithium–Oxygen Battery with Ether-Based Electrolytes



**Walk on the same side!** The title reaction occurs by means of highly stereospecific 1,3-metal migration. The starting carboxylic acids are readily prepared by Birch

reduction, and the developed protocol provides an efficient route to enantiomerically pure 5-arylated-1,3-cyclohexadiene derivatives (see scheme).

### Decarboxylative Coupling

C.-M. Chou, I. Chatterjee, A. Studer\* **8614–8617**

Stereospecific Palladium-Catalyzed Decarboxylative C(sp<sup>3</sup>)–C(sp<sup>2</sup>) Coupling of 2,5-Cyclohexadiene-1-carboxylic Acid Derivatives with Aryl Iodides

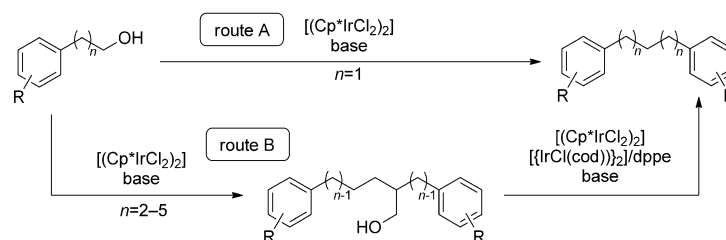


## $\alpha,\omega$ -Diarylalkanes

Y. Obora,\* Y. Anno, R. Okamoto,  
T. Matsu-ura, Y. Ishii\* — 8618–8622



Iridium-Catalyzed Reactions of  $\omega$ -Arylalkanols to  $\alpha,\omega$ -Diarylalkanes



**The long and the short of it:** An atom-economical route to  $\alpha,\omega$ -diarylalkanes from  $\omega$ -arylalkanols was achieved by a direct one-step method, or a sequential two-step method depending on the alkyl

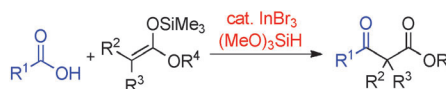
chain length. The reaction proceeded through the formation of  $\beta$ -methylhydroxy- $\alpha,\omega$ -diarylalkanes by dehydrogenation/ $\beta$ -alkylation, followed by dehydrogenation/decarbonylation.

## Synthetic Methods

Y. Nishimoto, A. Okita, M. Yasuda,  
A. Baba\* — 8623–8625



Indium Tribromide Catalyzed Cross-Claisen Condensation between Carboxylic Acids and Ketene Silyl Acetals Using Alkoxyhydrosilanes



**Acylation achieved:** The title reaction between carboxylic acids and ketene silyl acetals has been accomplished (see scheme). The additive,  $(\text{MeO})_3\text{SiH}$ , is believed to play an important role in the

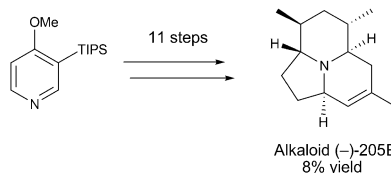
promotion of the condensation reaction. This reaction system was compatible with a diverse range of functional groups, including alkenes, alkynes, chlorides, alcohols, esters, and nitro groups.

## Natural Products

S. V. Tsukanov,  
D. L. Comins\* — 8626–8628



Concise Total Synthesis of the Frog Alkaloid (–)-205 B



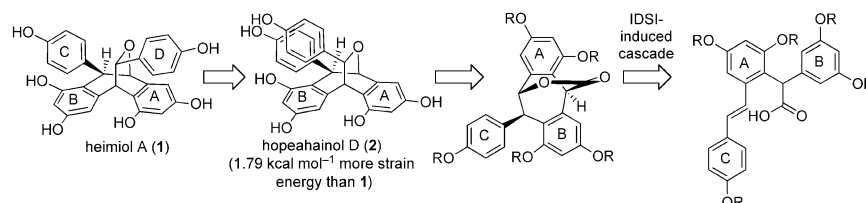
**Highly stereocontrolled:** The total synthesis of frog alkaloid (–)-205B features a chiral *N*-acylpyridinium salt reaction and an unprecedented trifluoroacetic anhydride mediated addition of an allylstannane to a vinylogous amide. The core was assembled using a Tsuji–Trost allylic amination reaction and a ring-closing metathesis. TIPS = triisopropylsilyl.

## Natural Products

S. A. Snyder,\* N. E. Wright, J. J. Pflueger,  
S. P. Breazzano — 8629–8633



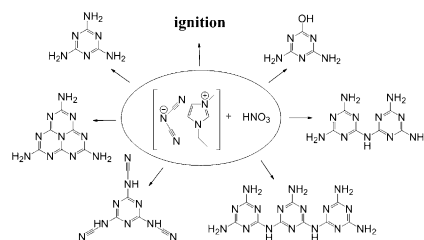
Total Syntheses of Heimiol A, Hopeahainol D, and Constrained Analogues



**IDSI to the rescue:** Use of a carefully designed cascade process empowered by the unique reagent IDSI  $[(\text{Et}_2\text{Si})_2\text{Cl-SbCl}_6]$  provided the entire [3.2.2] bicyclic core of

both targets **1** and **2** in a single, stereocontrolled operation. Use of strain energies assisted in the completion of the natural products.

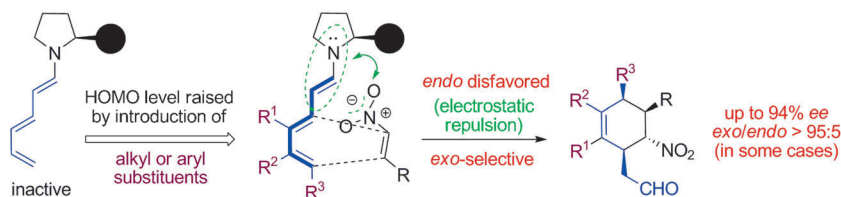
**The reaction of dicyanamide ionic liquids** with nitric acid results in hypergolic ignition and the formation of a stable precipitate. The precipitate consists of cyclic triazines, including melamine and its polymers, such as melam and melem (see scheme). This study introduces a novel approach to the synthesis of cyclic azines without resorting to high temperatures and pressures.



### Hypergolic Ionic Liquids

K. Chingin, R. H. Perry, S. D. Chambreau, G. L. Vaghjiani, R. N. Zare\* **8634–8637**

Generation of Melamine Polymer Condensates upon Hypergolic Ignition of Dicyanamide Ionic Liquids



**Raising the HOMO:** 2,4-Dienals can react with nitroalkenes in trienamine-catalyzed asymmetric Diels–Alder reactions (see scheme). Crucial for the success is raising the HOMO energy of the diene through the introduction of appropriate substitu-

ents. The reaction exhibits unusually high enantioselectivity and *exo* selectivity; *endo* addition is possibly disfavored because of the electrostatic repulsion shown in the scheme.

### Diels–Alder Reaction

Z.-J. Jia, Q. Zhou, Q.-Q. Zhou, P.-Q. Chen, Y.-C. Chen\* **8638–8641**

*exo*-Selective Asymmetric Diels–Alder Reaction of 2,4-Dienals and Nitroalkenes by Trienamine Catalysis



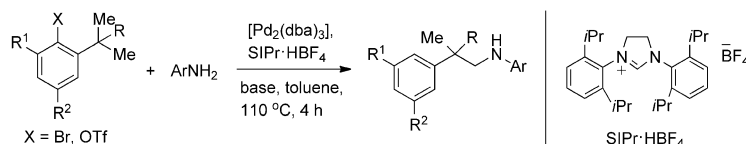
**AFM nanoindentation** was used to demonstrate that millimeter- and nanometer-sized organic cocrystals exhibit changes in the mechanical properties before, during, and after a single-crystal-to-single-crystal

[2+2] photodimerization of olefins. Millimeter-sized crystals become 40% softer, whereas nanocrystals of the same material become 40% harder following the photoreaction.

### Supramolecular Chemistry

C. Karunatilaka, D.-K. Bučar, L. R. Ditzler, T. Friščić, D. C. Swenson, L. R. MacGillivray,\* A. V. Tivanski\* **8642–8646**

Softening and Hardening of Macro- and Nano-Sized Organic Cocrystals in a Single-Crystal Transformation



**Filling out the space:** The title reaction of unactivated  $C_{sp^3}$ –H bonds using aryl amines as the nitrogen source is disclosed (see scheme; dba = dibenzylideneacetone, Tf = trifluoromethanesul-

fonyl). Either the C–N cross-coupling product or the C–H amination product could be accessed selectively by adjusting the steric environment of the substrate.

### C–H Amination

J. Pan, M. Su, S. L. Buchwald\* **8647–8651**

Palladium(0)-Catalyzed Intermolecular Amination of Unactivated  $C_{sp^3}$ –H Bonds



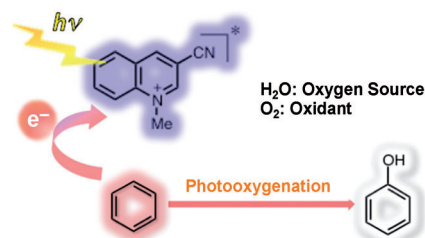
## Photocatalysis

K. Ohkubo, T. Kobayashi,  
S. Fukuzumi\* 8652–8655



Direct Oxygenation of Benzene to Phenol  
Using Quinolinium Ions as  
Homogeneous Photocatalysts

**Photocatalytic oxygenation** of benzene with oxygen and water to phenol has been achieved under ambient conditions by using the 3-cyano-1-methylquinolinium ion as a photocatalyst (see picture). The mechanism was clarified by detecting the  $\pi$ -dimer benzene radical cation produced by photoinduced electron transfer from benzene to the photocatalyst, and by monitoring the reaction of the radical cations with water molecules.

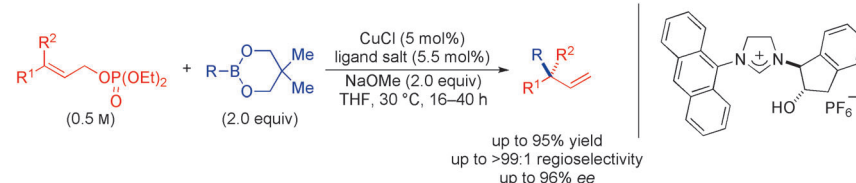


## Asymmetric Catalysis

R. Shintani,\* K. Takatsu, M. Takeda,  
T. Hayashi\* 8656–8659



Copper-Catalyzed Asymmetric Allylic  
Substitution of Allyl Phosphates with Aryl-  
and Alkenylboronates



**The asymmetric allylic** substitution of allyl phosphates with aryl- and alkenylboronates catalyzed by a copper/N-heterocyclic carbene complex was developed and the  $\gamma$ -substitution products were obtained

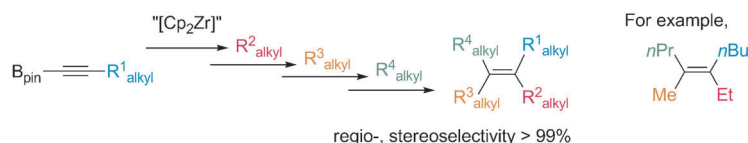
with high enantioselectivity (see scheme). To account for the observed influence of the reaction parameters a possible catalytic cycle for this process was proposed.

## Cross-Coupling

Y. Nishihara,\* Y. Okada, J. Jiao,  
M. Suetsugu, M.-T. Lan, M. Kinoshita,  
M. Iwasaki, K. Takagi 8660–8664



Highly Regio- and Stereoselective  
Synthesis of Multialkylated Olefins  
through Carbozirconation of  
Alkynylboronates and Sequential Negishi  
and Suzuki–Miyaura Coupling Reactions



**Two Nobel couplings:** The synthesis of tri- and tetraalkylated olefins has been achieved (see scheme). These multialkylated olefins were prepared by the zirconocene-mediated carbometalation of 1-alkynylboronates and subsequent sequential

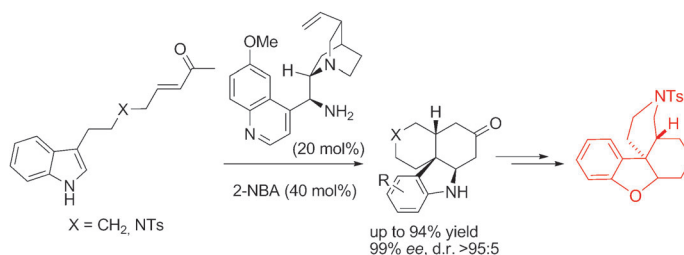
C–C bond formation with Negishi and Suzuki–Miyaura cross-coupling reactions using  $\beta$ -hydrogen-containing alkylzinc reagents and alkyl electrophiles as coupling partners.

## Asymmetric Catalysis

Q. Cai, C. Zheng, J.-W. Zhang,  
S.-L. You\* 8665–8669



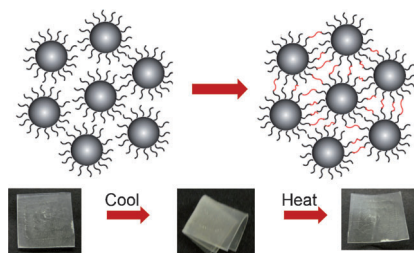
Enantioselective Michael/Mannich  
Polycyclization Cascade of Indolyl Enones  
Catalyzed by Quinine-Derived Primary  
Amines



**Three's a crowd:** The title reaction provides a tetracyclic core bearing three chiral centers (see scheme; Ts = 4-toluenesulfonyl) with excellent enantioselectivity and

good diastereoselectivity. The reaction was used to efficiently construct the (+)-kresigine skeleton.



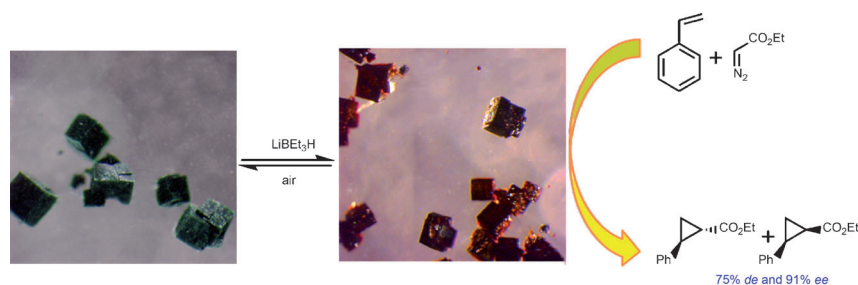


**Forget-me-not:** Nanoparticle fillers in shape-memory polymers usually improve mechanical properties at the expense of shape-memory performance. A new approach overcomes these drawbacks by cross-linking the functionalized poly(ethylene glycol) tethers on silica nanoparticles (see picture).

### Shape-Memory Polymers

P. Agarwal, M. Chopra,  
 L. A. Archer\* 8670–8673

Nanoparticle Netpoints for Shape-Memory Polymers



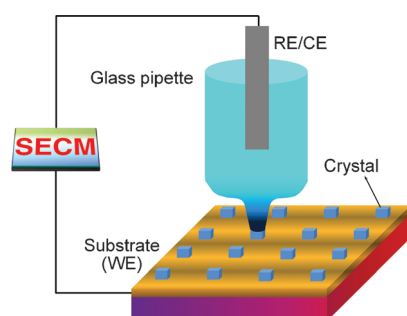
**To and fro:** Chiral metal–organic frameworks (CMOFs) derived from redox-active ruthenium/salen building blocks exhibited reversible single-crystal to single-crystal reduction and reoxidation. The catalytically inactive Ru<sup>III</sup> CMOFs (green;

see picture) were reduced to Ru<sup>II</sup> CMOFs (red) that were highly active for the asymmetric cyclopropanation of alkenes with very high diastereo- and enantioselectivities.

### Asymmetric Catalysis

J. M. Falkowski, C. Wang, S. Liu,  
 W. Lin\* 8674–8678

Actuation of Asymmetric Cyclopropanation Catalysts: Reversible Single-Crystal to Single-Crystal Reduction of Metal–Organic Frameworks

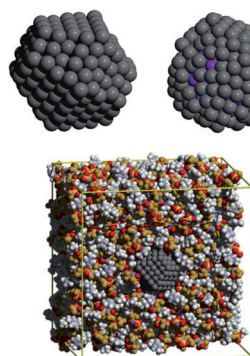


**On solid ground:** Mix-valent iron hexacyanides (Fe<sup>III</sup>, Fe<sup>II</sup>, and Prussian blue) can replace NaCl crystal lattice units to form a solid-state solution. A scanning electrochemical microcapillary (SECM) technique has been developed for the controllable microfabrication of the microcrystals. In situ confocal Raman spectra can also be obtained without exposure to any liquid environment. WE=working electrode, RE/CE=reference/counter electrode.

### Solid-State Reactions

D. Yang, L. Han, Y. Yang, L.-B. Zhao,  
 C. Zong, Y.-F. Huang, D. Zhan,\*  
 Z.-Q. Tian 8679–8682

Solid-State Redox Solutions: Microfabrication and Electrochemistry



**Not thick-skinned:** The solvation of a metallic nanoparticle in the ionic liquid [C<sub>4</sub>C<sub>1</sub>im][Ntf<sub>2</sub>] was investigated by molecular simulation with a specific interaction potential. The interfacial layer of ionic liquid is only one ion thick, and thus excludes a stabilization mechanism based on an electrostatic double layer.

### Nanoparticles in Ionic Liquids

A. S. Pensado,  
 A. A. H. Pádua\* 8683–8687

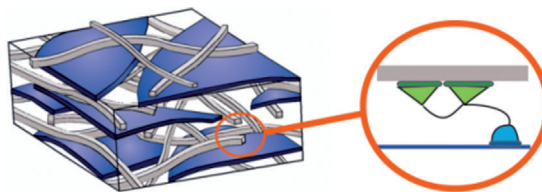
Solvation and Stabilization of Metallic Nanoparticles in Ionic Liquids

## Nanomaterials

P. Laaksonen,\* A. Walther, J.-M. Malho,  
M. Kainlahti, O. Ikkala,  
M. B. Linder\* ————— 8688–8691



Genetic Engineering of Biomimetic  
Nanocomposites: Diblock Proteins,  
Graphene, and Nanofibrillated Cellulose



**A tough nut:** A new approach to making biomimetic nanocomposites, involving engineered proteins (see scheme; green and blue), reinforcing graphene sheets (purple), and nanofibrillated cellulose (gray), is presented. The aligned co-

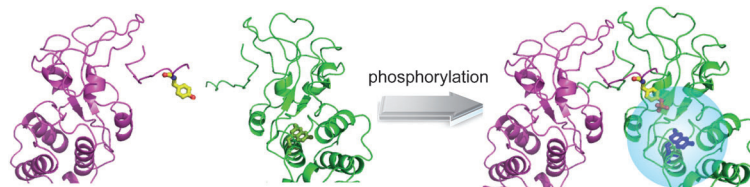
assembly of these components leads to a composite with remarkably good mechanical properties, which potentially arises from the role of the adhesive matrix proteins.

## Phosphorylation

V. K. Lacey, A. R. Parrish, S. Han, Z. Shen,  
S. P. Briggs, Y. Ma,  
L. Wang\* ————— 8692–8696



A Fluorescent Reporter of the  
Phosphorylation Status of the Substrate  
Protein STAT3



**Roving reporter:** A reversible biosensor reports the phosphorylation status of full-length substrate protein STAT3 by genetically incorporating 7-hydroxycoumarin into its phosphotyrosine binding pocket

(see picture). A large fluorescence increase with characteristic emission and excitation properties results as a response to phosphorylation of STAT3 in vitro and endogenously in nuclear extracts.

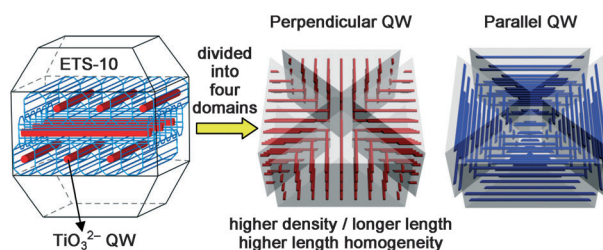


## Vibrational Spectroscopy

N. C. Jeong, H. Lim, H. Cheong,  
K. B. Yoon\* ————— 8697–8701



Distribution Pattern of Length, Length  
Uniformity, and Density of  $\text{TiO}_3^{2-}$   
Quantum Wires in an ETS-10 Crystal  
Revealed by Laser-Scanning Confocal  
Polarized Micro-Raman Spectroscopy



**Inner beauty:** The titanate molecular sieve ETS-10 has  $\text{TiO}_3^{2-}$  quantum wires (QWs) of varying length and local density along the  $[110]$  and  $[1\bar{1}0]$  directions (see picture). Analysis of the distribution of the

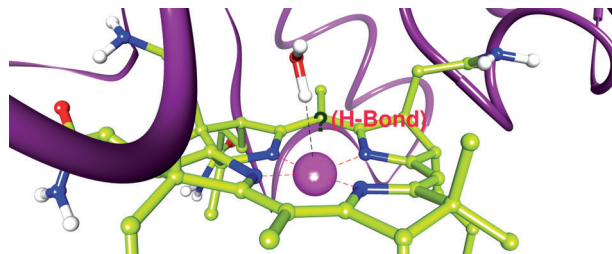
QWs within a crystal using laser-scanning confocal polarized micro-Raman spectroscopy shows that they are not distributed evenly but in a symmetrical manner in an interesting pattern.

## Hydrogen Bonds

M. Kumar,  
P. M. Kozłowski\* ————— 8702–8705

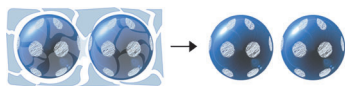


A Biologically Relevant  $\text{Co}^{1+}\cdots\text{H}$  Bond:  
Possible Implications in the Protein-  
Induced Redox Tuning of  $\text{Co}^{2+}/\text{Co}^{1+}$   
Reduction



**Reduced circumstances:** A hydrogen bond induced by the  $\text{Co}^+$  ion has been identified theoretically (see picture). It plays a vital role in explaining the mechanistic base of

protein-induced tuning of the  $\text{Co}^{2+}/\text{Co}^+$  redox process, a common catalytic event in a wide variety of methyltransferases and adenosyltransferases.



**Useful contacts:** A new method to achieve regular patterns generates anisotropic, “patchy” microspheres by using interfacial condensation of a liquid mask and the proximity of the particles to their neighbors to determine a mask pattern.

The microspheres are separated from the scaffold and labeled with a first protein at non-mask regions (green) followed by removal of the mask and immobilization of a second protein (red).

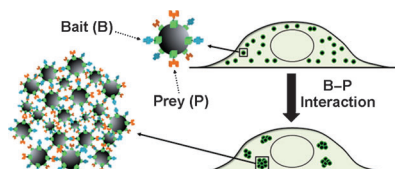
### Patchy Particles

K. Kamalasanan, S. Jhunjhunwala, J. Wu, A. Swanson, D. Gao, S. R. Little\* \_\_\_\_\_ **8706–8708**

Patchy, Anisotropic Microspheres with Soft Protein Islets



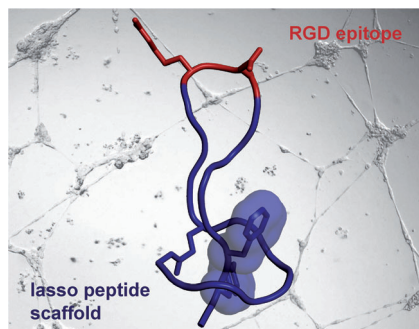
**Seeing into cells:** Genetically engineered, labeled ferritin is used to form biological nanoparticles displaying bait (B) and prey (P) molecules inside cells (see picture). Specific bait–prey interactions induce the interconnected assembly of nanoparticles into nanoclusters on a timescale of seconds. This phenotypic readout with a small molecule as an inducible switch was used to directly visualize dynamic molecular interactions within living cells.



### Biological Nanoparticles

S. Lee, K. H. Lee, J.-S. Ha, S.-G. Lee, T. K. Kim\* \_\_\_\_\_ **8709–8713**

Small-Molecule-Based Nanoassemblies as Inducible Nanoprobes for Monitoring Dynamic Molecular Interactions Inside Live Cells



**Tightening the noose:** Lasso peptides are a class of stable bacterial peptides with unique characteristics that encourage their application in drug design. Epitope grafting of the integrin binding motif RGD onto the lasso structure of microcin J25 converts the knotted peptide into a nanomolar integrin antagonist (see picture). Engineered lasso peptides can therefore be used for pharmacophore presentation.

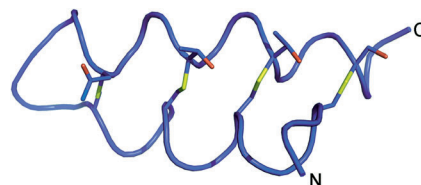
### Lasso Peptides

T. A. Knappe, F. Manzenrieder, C. Mas-Moruno, U. Linne, F. Sasse, H. Kessler, X. Xie, M. A. Marahiel\* \_\_\_\_\_ **8714–8717**

Introducing Lasso Peptides as Molecular Scaffolds for Drug Design: Engineering of an Integrin Antagonist



**Problem solved:** Thurincin H is an anti-microbial peptide with suspected post-translational modifications. MS/MS sequencing identified the residues that were modified, and NMR spectroscopic studies in solution led to the 3D structure of thurincin H, which features four S–C<sub>α</sub> thioether crosslinks (yellow in schematic representation). This structure may be representative of several other bacteriocins with identical masses.



### Bacteriocin Structure


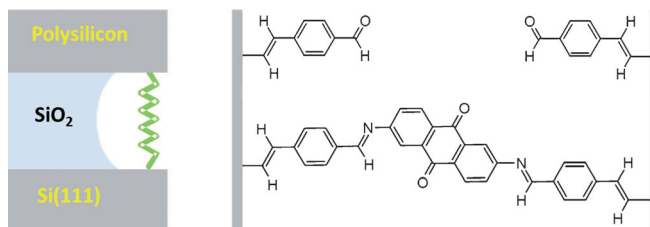
C. S. Sit, M. J. van Belkum, R. T. McKay, R. W. Worobo, J. C. Vederas\* \_\_\_\_\_ **8718–8721**

The 3D Solution Structure of Thurincin H, a Bacteriocin with Four Sulfur to  $\alpha$ -Carbon Crosslinks



## Silicon Nanogaps

G. J. Ashwell,\* L. J. Phillips,  
B. J. Robinson, S. A. Barnes,  
A. T. Williams, B. Urasinska-Wojcik,  
C. J. Lambert, I. M. Grace, T. I. Cox,  
I. C. Sage \_\_\_\_\_ **8722–8726**

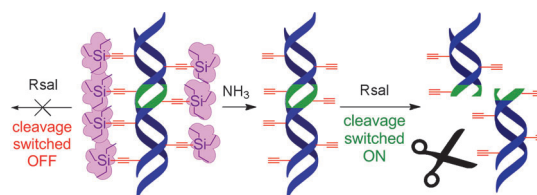
 Synthesis of Covalently Linked Molecular Bridges between Silicon Electrodes in CMOS-Based Arrays of Vertical Si/SiO<sub>2</sub>/Si Nanogaps


**Silicon nanogaps** were bridged in situ by grafting 4-ethynylbenzaldehyde to activate the electrodes and coupling 2,6-diaminoanthra-9,10-quinone to link the coatings. The bridged structures

exhibit currents of 11–14 nA at 1 V. The process is reversed by soaking in acidified solution, which causes the current to diminish.

## DNA Protection

P. Kielkowski, H. Macíčková-Cahová,  
R. Pohl, M. Hocek\* 8727–8730




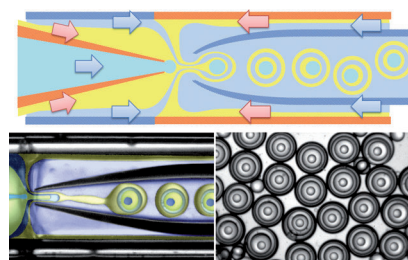
 Transient and Switchable  
(Triethylsilyl)ethynyl Protection of DNA  
against Cleavage by Restriction  
Endonucleases

**Restricted access to DNA:** (Triethylsilyl)-ethynyl-modified 7-deaza-dATP is readily incorporated into DNA by primer extension or polymerase chain reaction using KODXL polymerase. The silylethynyl-

protected DNA resists the cleavage by restriction endonucleases (REs), such as RsaI (see scheme), but after it is treated with  $\text{NH}_3$ , the resulting deprotected DNA is fully cleavable by the REs.

## Microfluidics

S.-H. Kim, D. A. Weitz\* — 8731–8734

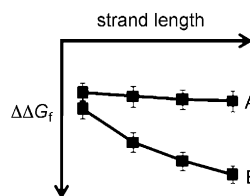
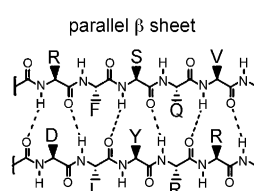


# One-Step Emulsification of Multiple Concentric Shells with Capillary Microfluidic Devices

**Polymeric onions:** A facile method to produce monodisperse multiple emulsion drops of high order is developed using a capillary microfluidic device. Coaxial multiphase flows are stabilized by confinement in microcapillary and emulsified to multiple emulsion drops. The breakup of coaxial interfaces, triggered by the core-drop, facilitates the making of multiple emulsion drops of onionlike configuration.

## Protein Substructures

F. Freire, A. M. Almeida, J. D. Fisk,  
J. D. Steinkruger,  
S. H. Gellman\* \_\_\_\_\_ **8735–8738**

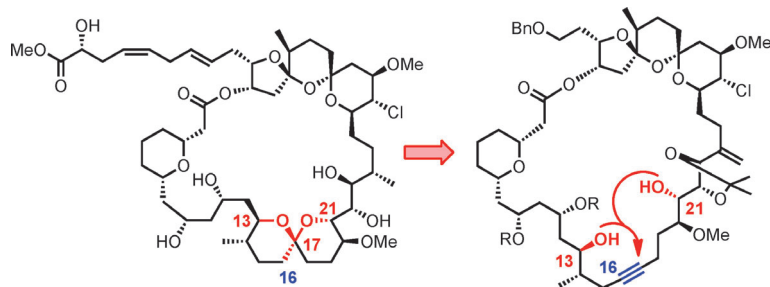


## Impact of Strand Length on the Stability of Parallel- $\beta$ -Sheet Secondary Structure

**Molecular design** can be used to investigate whether the parallel- $\beta$ -sheet secondary structure is subject to length-dependent cooperative stabilization along the strand direction (see picture). Extending

strands by adding high-propensity residues (B) leads to a steady increase in parallel- $\beta$ -sheet stability, but inclusion of low-propensity residues (A) can negate this stabilization.





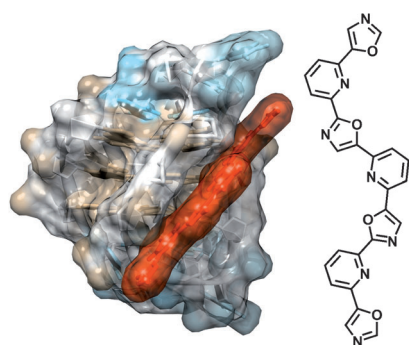
**Outlandish:** The spiroketal embedded in spirastrellolide F methyl ester is a daring site for ring closure, yet it has allowed the power of catalytic alkyne scission and

activation to be showcased (see scheme). An improved strategy for the introduction of the labile side chain was also developed.

## Natural Product Synthesis

S. Benson, M.-P. Collin, A. Arlt, B. Gabor, R. Goddard, A. Fürstner\* — **8739–8744**

Second-Generation Total Synthesis of Spirastrellolide F Methyl Ester: The Alkyne Route

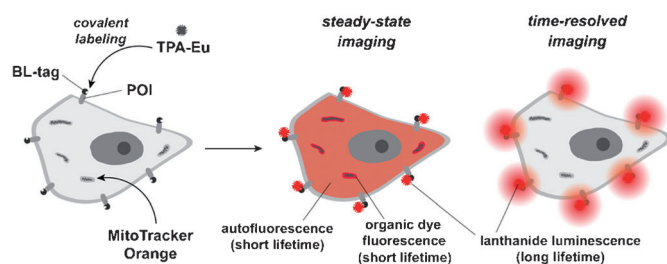


**Feeling groovy:** A family of nonmacrocyclic G-quadruplex binders with alternate oxazole and pyridine motifs was prepared. The shown heptacyclic derivative exhibits an unprecedented binding preference for certain quadruplex topologies: it recognizes exclusively the human telomeric quadruplex in Na<sup>+</sup> buffer but not in K<sup>+</sup> buffer. This unique quadruplex binding profile is strongly dependent on the size of the ligand and may result from groove interactions.

## G-Quadruplexes

F. Hamon, E. Largy, A. Guédin-Beaurepaire, M. Rouchon-Dagois, A. Sidibe, D. Monchaud, J.-L. Mergny, J.-F. Riou, C.-H. Nguyen, M.-P. Teulade-Fichou\* — **8745–8749**

An Acyclic Oligoheteroaryle That Discriminates Strongly between Diverse G-Quadruplex Topologies



**Better late ...** Lanthanide-based time-resolved luminescence imaging of proteins is a promising technology. A novel luminescent lanthanide probe (see picture, TPA-Eu) for mutant  $\beta$ -lactamase-

based protein labeling system (BL-tag) is used to selectively image cell-surface proteins (POIs) in the presence of autofluorescent background signals, thus enabling imaging with serum.

## Cell Imaging Technology

S. Mizukami, T. Yamamoto, A. Yoshimura, S. Watanabe, K. Kikuchi\* — **8750–8752**

Covalent Protein Labeling with a Lanthanide Complex and Its Application to Photoluminescence Lifetime-Based Multicolor Bioimaging







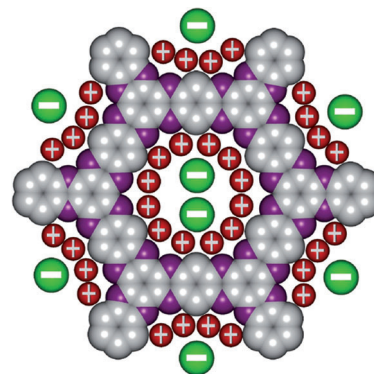
## Porous Frameworks

Y. Kou, Y. Xu, Z. Guo,  
D. Jiang\* \_\_\_\_\_ **8753–8757**



Supercapacitive Energy Storage and  
Electric Power Supply Using an Aza-Fused  
 $\pi$ -Conjugated Microporous Framework

**Supercapacitor:** A  $\pi$  conjugated microporous polymer with an aza-fused framework is reported. The porous framework is conductive and allows electrolyte ions to move into the pores because of structural features (see picture). The material becomes highly co-operative in the formation of electrostatic charge-separation layers, shows exceptional capacitance in supercapacitive energy storage, provides high energy densities, and offers an excellent cycle life.



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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## Corrigendum

Asymmetric Total Synthesis of  
(–)-Cribrostatin 4 (Renieramycin H)

G. Vincent, R. M. Williams\* **1517–1520**

*Angew. Chem. Int. Ed.* **2007**, 46

DOI 10.1002/anie.200604126

In Scheme 3 of this Communication, the configuration of compound **18** was drawn incorrectly and should be corrected as shown here (corrections in red).

