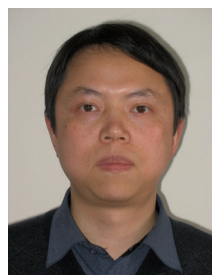


Spotlight on Angewandte's Sister Journals

## Service

11194 – 11196



*"My favorite name reaction is the Diels–Alder reaction. The secret of being a successful scientist is to keep reading and thinking ..."*

This and more about Ying-Chun Chen can be found on page 11198.

## Author Profile

Ying-Chun Chen \_\_\_\_\_ 11198



B. K. Kobilka



R. J. Lefkowitz

## News

Nobel Prizes 2012: Cells and Sensitivity—  
GPCR Heroes Honored \_\_\_\_\_ 11199

## Books

Modern Gold Catalyzed Synthesis

A. Stephen K. Hashmi, F. Dean Toste

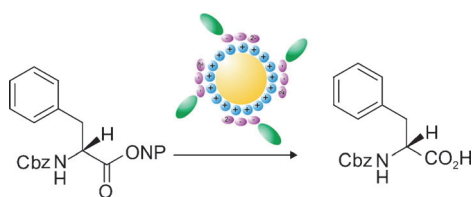
reviewed by V. Gandon \_\_\_\_\_ 11200

## Highlights

### Peptide Nanoparticles

M. Stodulski, T. Gulder\* – 11202 – 11204

Nanoparticles and Peptides: A Fruitful  
Liaison for Biomimetic Catalysis



**Inspired by nature:** Self-assembled peptide nanoparticles have been designed that accelerate ester hydrolysis (see picture; Cbz = carbobenzyloxy, NP =  $p$ -NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>). The concerted interplay of the

multivalent surface with the catalytically active peptide and the substrate at the same time combines several aspects decisive for the catalyst's efficiency, a property characteristic of enzymes.

## Nanorings

M. Pawlicki,  
L. Latos-Grażyński\* — 11205–11207

A Dynamic Library of Porphyrinic True  
Nanorings



**Behind the wheel:** A 10 nm diameter nanoring, containing 24 porphyrin units, has been created by a Vernier-templating self-organization of hexa- or octadentate templating units and linear covalently linked porphyrin oligomers. Coordination of a bidentate ligand triggers a conversion of the molecular nanocylinder into a molecular nanoannulus to afford the dimeric species, which can adopt a water wheel structure (see picture).

## Essays

### Microscopy

T. Mappes,\* N. Jahr, A. Csaki, N. Vogler,  
J. Popp, W. Fritzsche — 11208–11212



The Invention of Immersion  
Ultramicroscopy in 1912—The Birth of  
Nanotechnology?



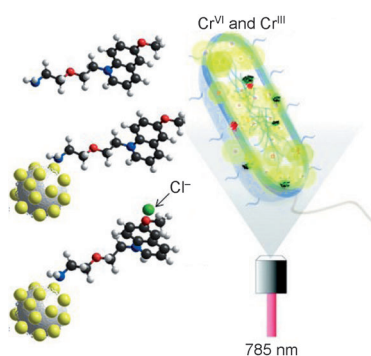
**Dawn of nanotechnology:** The immersion ultramicroscope was patented a century ago. When an analyte was examined with an antique instrument and with state-of-the-art technology, the historic assumptions were confirmed: the size and shape of the nanoparticles are in the same range as that described 100 years ago. The spectra of the Tyndall cones caused by the shape of the nanoparticles were also described correctly—long before electron microscopy was able to image single nanoparticles.

## Minireviews

### Sensing Using SERS

R. A. Alvarez-Puebla,\*  
L. M. Liz-Marzán\* — 11214–11223

SERS Detection of Small Inorganic  
Molecules and Ions



**SERS you right:** Surface-enhanced Raman scattering (SERS) can be used for the direct or indirect detection of inorganic molecules and even ions, in spite of their intrinsically low Raman scattering cross-sections. Recent advances even allow ion sensing and localization within living organisms (see picture).

**For the USA and Canada:**  
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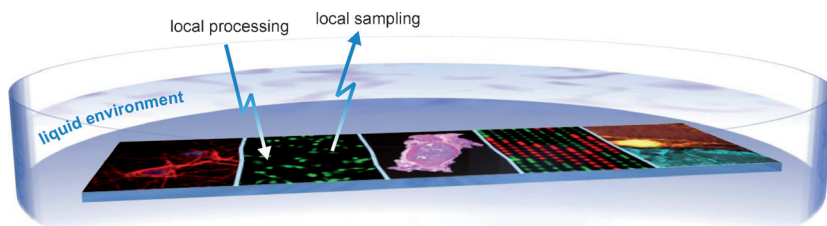
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a national chemical society prices are available  
on request. Postage and handling charges  
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## Reviews

### Microfluidics

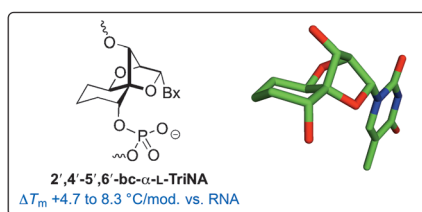
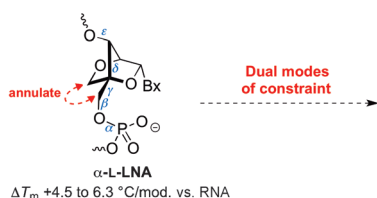
G. V. Kaigala,\* R. D. Lovchik,  
E. Delamarche\* — 11224–11240

Microfluidics in the “Open Space” for  
Performing Localized Chemistry on  
Biological Interfaces



**Space, the final frontier?** Microfluidic technologies for controlling liquid dispensing and handling will become central for localizing (bio)chemical reactions/functions on biological interfaces. However, microfluidic systems must then

operate in the “open space”, that is, without the sealed channels and chambers commonly used (see picture). The development of such open-space microfluidic technologies is reported.



**Dual conformational restriction:** A new, highly constrained modification of the  $\alpha$ -L-locked nucleic acid ( $\alpha$ -L-LNA) scaffold that locks the sugar furanose ring in an N-type configuration and also restricts rota-

tion around torsion angle  $\gamma$  was synthesized (see scheme). This new modification increases the thermostability of an oligonucleotide duplex compared to using a single mode of constraint alone.

## Communications

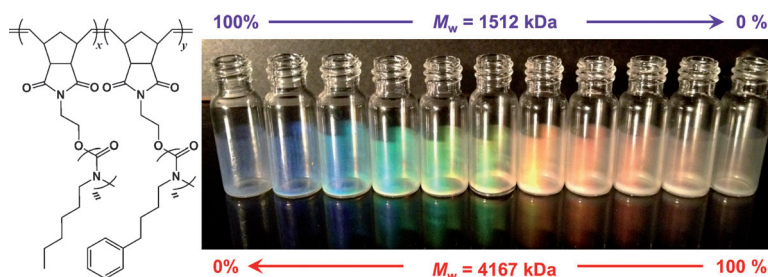
### Modified Nucleotides

S. Hanessian,\* B. R. Schroeder,  
R. D. Giacometti, B. L. Merner,  
M. Østergaard, E. E. Swayze,  
P. P. Seth\* — 11242–11245

Structure-Based Design of a Highly  
Constrained Nucleic Acid Analogue:  
Improved Duplex Stabilization by  
Restricting Sugar Pucker and Torsion  
Angle  $\gamma$



Frontispiece



**Colorful:** Enabled by their reduced capacity for chain entanglement, high-molecular-weight brush block copolymers can rapidly self-assemble to photonic crystals. The blending of two polymers of

different molecular weight can predictably modulate the sizes of the polymer domains, giving rise to a facile means of precision tuning of these photonic-band-gap materials.

### Block Copolymers

G. M. Miyake, V. A. Piunova,  
R. A. Weitekamp,  
R. H. Grubbs\* — 11246–11248

Precisely Tunable Photonic Crystals From  
Rapidly Self-Assembling Brush Block  
Copolymer Blends



Front Cover





The German Chemical Society (GDCh) invites you to:



# Angewandte Anniversary Symposium

GDCh  
125 JAHRE Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Tuesday, March 12, 2013

Henry Ford Building / FU Berlin

## Speakers



Carolyn R.  
Bertozzi



François  
Diederich



Alois  
Fürstner



Roald Hoffmann  
(Nobel Prize 1981)



Susumu  
Kitagawa



Jean-Marie Lehn  
(Nobel Prize 1987)



E.W. "Bert"  
Meijer



Frank  
Schirrmacher  
(Publisher, FAZ)



Robert  
Schlögl



George M.  
Whitesides



Ahmed Zewail  
(Nobel Prize 1999)

More information:



[angewandte.org/symposium](http://angewandte.org/symposium)



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**Yanking the chain:** A general method for the preparation of colloidal analogues of polymer chains was developed (see picture). The flexibility of these chains can be tuned by applying electric fields in combination with their subjection to simple linkage-forming procedures.

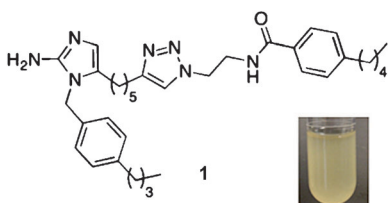
### Colloids

H. R. Vutukuri,\* A. F. Demirörs, B. Peng, P. D. J. van Oostrum, A. Imhof, A. van Blaaderen\* — 11249–11253

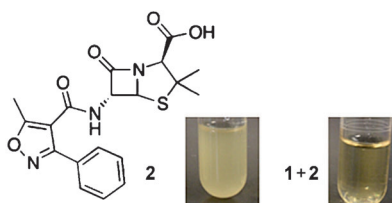
Colloidal Analogues of Charged and Uncharged Polymer Chains with Tunable Stiffness



Inside Back Cover



**Shields down!** Adjuvant molecules that have the ability to restore the susceptibility of multi-drug-resistant bacteria, such as MRSA, to clinically available antibiotics are a promising alternative to the development of novel antimicrobials. Pictured



is a potent small molecule (**1**) that, at sub-minimum inhibitory concentration (sub-MIC) levels, lowers the MIC of oxacillin (**2**) against a number of MRSA strains by up to 512-fold.

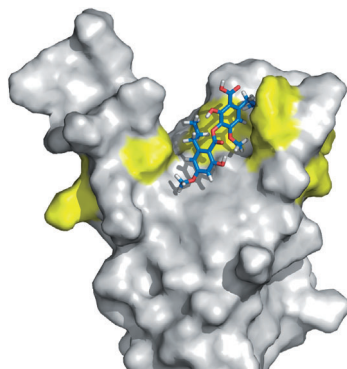
### Disarming Bacterial Resistance

T. L. Harris, R. J. Worthington, C. Melander\* — 11254–11257

Potent Small-Molecule Suppression of Oxacillin Resistance in Methicillin-Resistant *Staphylococcus aureus*



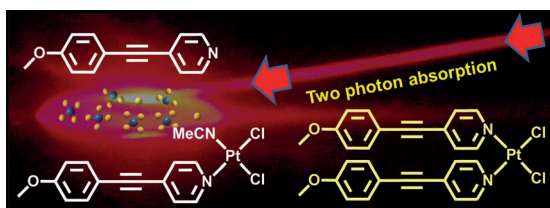
**Capturing a coactivator, naturally:** The natural products sekikaic acid and lobaric acid, isolated after a high-throughput screen of a structurally diverse extract collection, effectively target the dynamic binding interfaces of the GACKIX domain of the coactivator CBP/p300 (see structure). These molecules are the most effective inhibitors of the GACKIX domain yet described and are uniquely selective for this domain.



### Protein–Protein Interactions

C. Y. Majmudar, J. W. Højfeldt, C. J. Arevang, W. C. Pomerantz, J. K. Gagnon, P. J. Schultz, L. C. Cesa, C. H. Doss, S. P. Rowe, V. Vásquez, G. Tamayo-Castillo, T. Cierpicki, C. L. Brooks, III, D. H. Sherman, A. K. Mapp\* — 11258–11262

Sekikaic Acid and Lobaric Acid Target a Dynamic Interface of the Coactivator CBP/p300



**Two photons are better than one:** A square-planar Pt<sup>II</sup> complex with derivatized pyridine ligands was synthesized (see scheme), which undergoes two-photon-induced ligand substitution with 600–

740 nm light. Linear and quadratic density functional response theory allowed identification of the electronic transitions involved.

### Platinum Chemistry

Y. Zhao, G. M. Roberts, S. E. Greenough, N. J. Farrer, M. J. Paterson, W. H. Powell, V. G. Stavros,\* P. J. Sadler\* — 11263–11266

Two-Photon-Activated Ligand Exchange in Platinum(II) Complexes

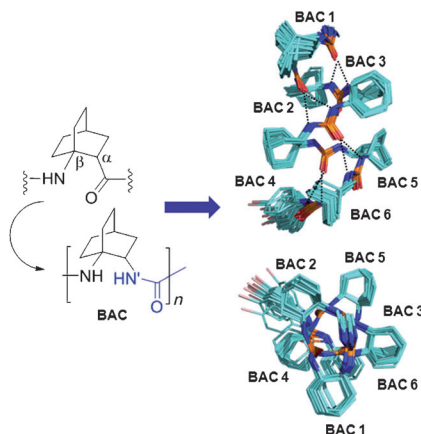


## Oligourea Foldamers

B. Legrand, C. André, E. Wenger,  
C. Didierjean, M. C. Averlant-Petit,  
J. Martinez, M. Calmes,\*  
M. Amblard\* — 11267 – 11270



Robust Helix Formation in a New Family  
of Oligoureas Based on a Constrained  
Bicyclic Building Block



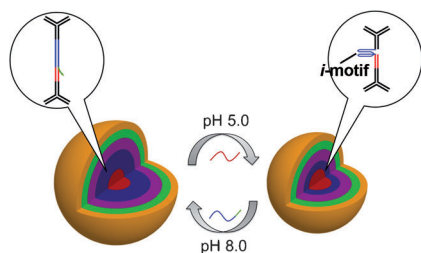
**BAC for more:** A constrained bicyclic building block with urea linkages is an efficient combination for the formation of a highly rigid helical system. This type of bicyclic amino carbamoyl (BAC) foldamer was studied both in solution (see scheme) and in the solid state. A robust H-bond (dotted line) network was found between the carbonyl oxygen atoms (red) and the amino groups (dark blue) within the helix.

## DNA Nanostructures

T. Zhou, P. Chen, L. Niu, J. Jin, D. Liang,  
Z. Li, Z. Yang, D. Liu\* — 11271 – 11274



pH-Responsive Size-Tunable Self-  
Assembled DNA Dendrimers



**Putting the DNA in dendrimers:** A strategy to swiftly prepare DNA dendrimers based solely on DNA self-assembly is presented. This technique produces highly pure DNA dendrimers with an excellent yield of high generation dendrimers. The incorporation of molecular motors (*i*-motifs) into the DNA dendrimers allows for a change in size (up to 30%) in response to changing pH values (see scheme).

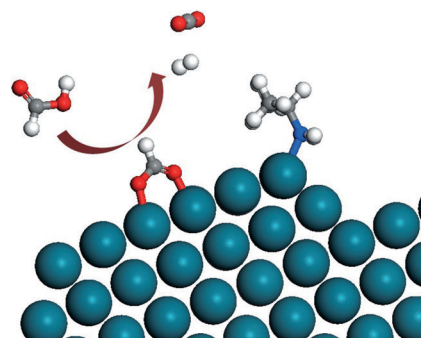
## Organic–Metal Particulate Catalysts

S. Jones, J. Qu, K. Tedsree, X.-Q. Gong,  
S. C. E. Tsang\* — 11275 – 11278



Prominent Electronic and Geometric  
Modifications of Palladium Nanoparticles  
by Polymer Stabilizers for Hydrogen  
Production under Ambient Conditions

**A remarkable effect** from the modification of electronic and geometric properties of Pd nanoparticles by the use of polymer pendant groups bound to the surface of palladium nanoparticles is reported. The degree of electron promotion to the Pd nanoparticles under ambient conditions was found to be dependent on the availability of the lone pair electrons of the pendant groups.

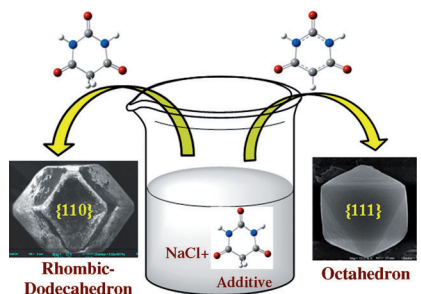


## Crystal Growth

A. Sen, B. Ganguly\* — 11279 – 11283



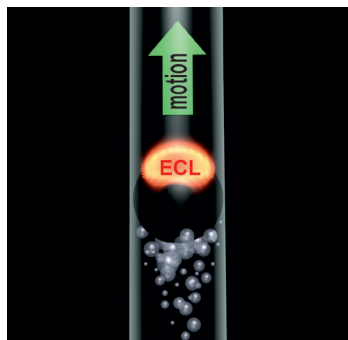
Is Dual Morphology of Rock-Salt Crystals  
Possible with a Single Additive? The  
Answer Is Yes, with Barbituric Acid



**Crystal face lift:** Barbituric acid is shown to be a new crystal-habit modifier for sodium chloride crystals (see scheme). Two morphologies of salt crystals can be prepared separately with this new additive. It is of the few additives able to induce rhombic dodecahedron crystals for NaCl, and is required only a trace of amount, unlike other additives, such as glycine.



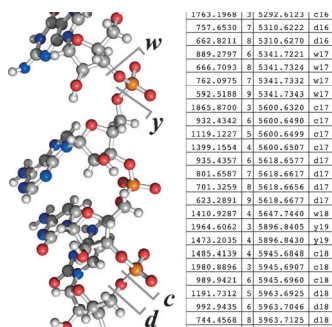
**Swimmer in the dark:** Propulsion of a conducting object is intrinsically coupled with light emission using bipolar electrochemistry. Asymmetric redox activity on the surface of the swimmer (black bead; see picture) causes production of gas bubbles to propel the swimmer in a glass tube with simultaneous electrochemiluminescence (ECL) emission to monitor the progress of the swimmer.



## Luminescent Motion

M. Sentic, G. Loget, D. Manojlovic, A. Kuhn, N. Sojic\* — 11284–11288

Light-Emitting Electrochemical “Swimmers”



**Characteristic mass differences** between fragment ions from backbone cleavage of RNA by electron detachment (*d*, *w*) and fragment ions from collisionally activated dissociation (*c*, *y*) provide extensive sequence information (see picture). Structure analysis by this approach should be especially useful for the detailed characterization of synthetic or post-transcriptionally modified RNA.

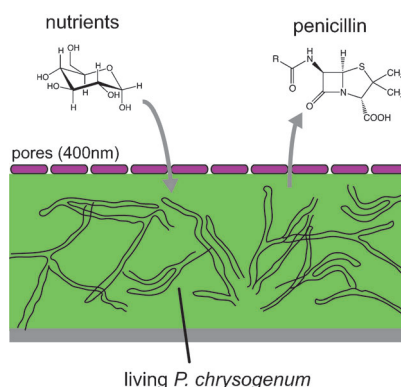
## RNA Sequencing

M. Taucher, K. Breuker\* — 11289–11292

Characterization of Modified RNA by Top-Down Mass Spectrometry



**Living materials:** Artificial biological niches are loaded with the penicillin-producing mold *Penicillium chrysogenum*. This living material consumes food through a nanoporous top layer and releases the antibiotic on-site. No reloading of the active compound is needed. Gram-positive bacteria were efficiently killed if nearby, whereas Gram-negative bacteria (control experiment, not sensitive to penicillin) were not affected.



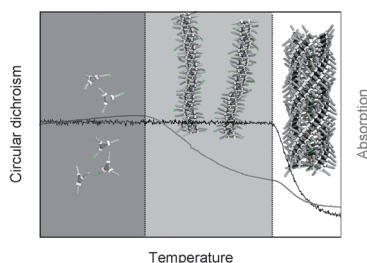
## Living Materials

L. C. Gerber, F. M. Koehler, R. N. Grass, W. J. Stark\* — 11293–11296

Incorporation of Penicillin-Producing Fungi into Living Materials to Provide Chemically Active and Antibiotic-Releasing Surfaces



**The interplay** of two subsequent aggregation processes results in a symmetry-breaking phenomenon in an achiral self-assembling system. Partially fluorinated benzene-1,3,5-tricarboxamide molecules self-assemble into a racemic mixture of one-dimensional *P*- and *M*-helical aggregates, followed by bundling into optically active higher-order aggregates or fibers (see picture).



## Chirality

P. J. M. Stals, P. A. Korevaar, M. A. J. Gillissen, T. F. A. de Greef, C. F. C. Fitié, R. P. Sijbesma,\* A. R. A. Palmans,\* E. W. Meijer\* — 11297–11301

Symmetry Breaking in the Self-Assembly of Partially Fluorinated Benzene-1,3,5-tricarboxamides

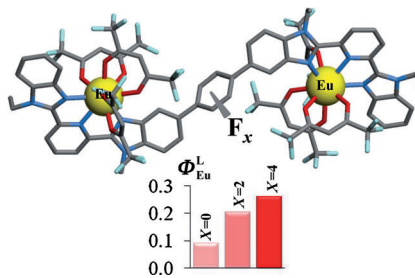


## Energy Transfer

J.-F. Lemonnier, L. Babel, L. Guénée,  
P. Mukherjee, D. H. Waldeck,\*  
S. V. Eliseeva, S. Petoud,\*  
C. Piguet\* 11302–11305



Perfluorinated Aromatic Spacers for  
Sensitizing Europium(III) Centers in  
Dinuclear Oligomers: Better than the  
Best by Chemical Design?



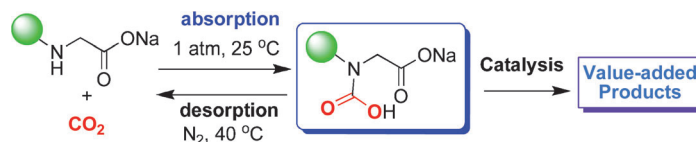
**Transfer news:** The use of a simple method allows the various sensitization steps in Eu<sup>III</sup>-containing complexes to be deciphered. Incorporation of an increasing number of electron-withdrawing fluorine atoms on the rigid and electronically tunable phenyl spacer between two tridentate binding units (see picture, red O, dark blue N) affects the quantum yield, intersystem crossing, and energy-transfer processes in a rational way.

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

A.-H. Liu, R. Ma, C. Song, Z.-Z. Yang,  
A. Yu,\* Y. Cai, L.-N. He,\* Y.-N. Zhao, B. Yu,  
Q.-W. Song 11306–11310



Equimolar CO<sub>2</sub> Capture by N-Substituted  
Amino Acid Salts and Subsequent  
Conversion



**Steric bulk controls CO<sub>2</sub> absorption:** N-substituted amino acid salts in poly(ethylene glycol) reversibly absorb CO<sub>2</sub> in nearly 1:1 stoichiometry. Carbamic acid is thought to be the absorbed form of CO<sub>2</sub>;

this was supported by NMR and in situ IR spectroscopy, and DFT calculations. The captured CO<sub>2</sub> could be converted directly into oxazolidinones and thus CO<sub>2</sub> desorption could be sidestepped.



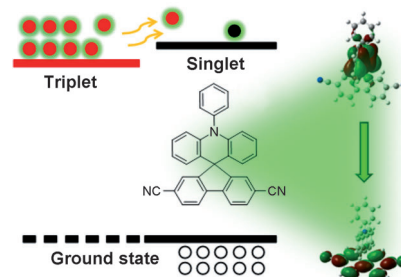
## Organic Light-Emitting Diodes

G. Méhes, H. Nomura, Q. Zhang,  
T. Nakagawa, C. Adachi\* 11311–11315



Enhanced Electroluminescence Efficiency  
in a Spiro-Acridine Derivative through  
Thermally Activated Delayed Fluorescence

**Make your OLED fluorescent:** An aromatic molecule based on a spiro-acridine derivative was designed (see picture), and its photoluminescence and electroluminescence were characterized. By combining the donor and acceptor moieties a small energy gap between the lowest singlet and triplet states was achieved. This design leads to an organic light-emitting diode (OLED) that rivals phosphorescent devices regarding exciton generation efficiency.

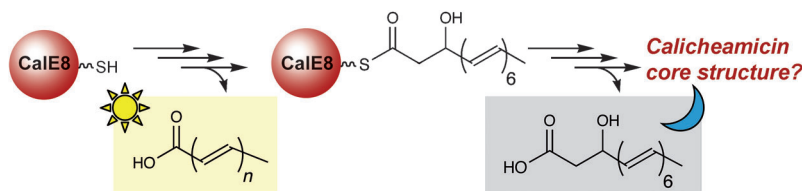


## Enediynes Biosynthesis

K. Belecki,  
C. A. Townsend\* 11316–11319



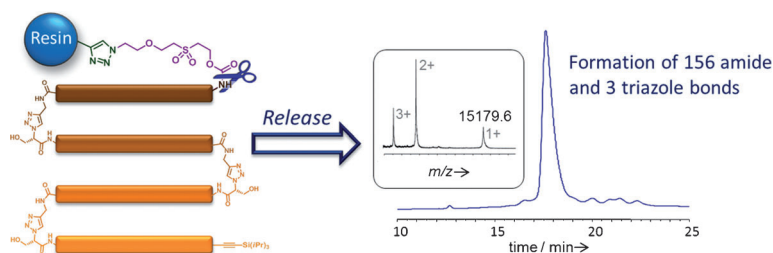
Environmental Control of the  
Calicheamicin Polyketide Synthase Leads  
to Detection of a Programmed Octaketide  
and a Proposal for Enediynes Biosynthesis



**A light in the dark:** The fermentation products of the polyketide synthase CalE8 (without its cognate thioesterase) were identified and gave some insight into the elusive early steps of calicheamicin bio-

synthesis. Fermentation in either the light or dark resulted in different proportions of a new octaketide (see scheme) and led to an updated mechanistic proposal.





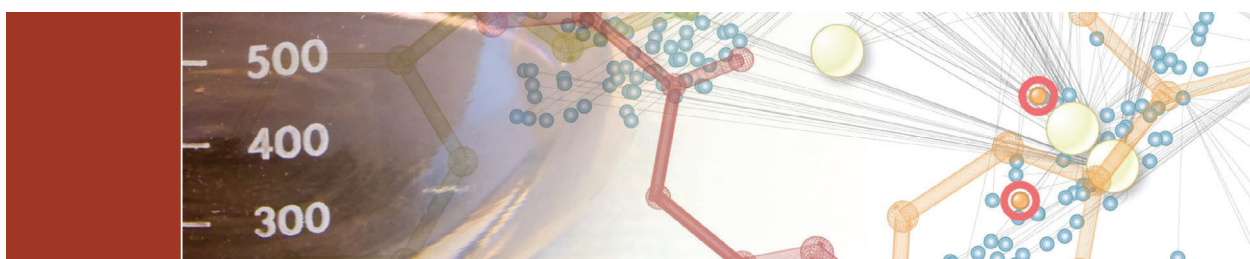
**Please release me:** A new linker for the temporary tagging of peptides at their N-terminus after solid-phase elongation, and its potential for capture/release purification is demonstrated. This concept is extended to a remarkably efficient self-

purifying N-to-C iterative triazole ligation strategy, which is applied to the synthesis of a polypeptide having 160 residues, in a high purity without the need for chromatographic purification (see picture; orange blocks: peptide segments).

### Solid-Phase Chemical Ligation

V. Aucagne,\* I. E. Valverde, P. Marceau,  
M. Galibert, N. Dendane,  
A. F. Delmas\* 11320–11324

Towards the Simplification of Protein  
Synthesis: Iterative Solid-Supported  
Ligations with Concomitant Purifications



## Novartis Chemistry Lectureship

Novartis is pleased to announce the following Novartis Chemistry Lecturers for 2012 – 2013.

### Martin D. Burke

University of Illinois  
Urbana-Champaign, IL, USA

### Vy Maria Dong

University of California  
Irvine, CA, USA

### Kai Johnsson

Ecole Polytechnique  
Fédérale de Lausanne  
Lausanne, Switzerland

### Benjamin List

Max-Planck-Institut für  
Kohlenforschung  
Mülheim an der Ruhr,  
Germany

### Andrew J. Phillips

Yale University  
New Haven, CT, USA

### Mark S.P. Sansom

University of Oxford  
Oxford, UK

The Novartis Chemistry Lectureship is awarded to scientists in recognition of outstanding contributions to organic and computational chemistry, including applications to biology.



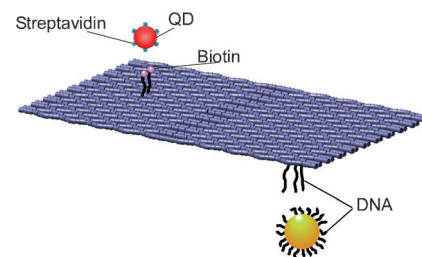
## DNA Nanotechnology

R. Wang,\* C. Nuckolls,  
S. J. Wind\* 11325–11327



Assembly of Heterogeneous Functional  
Nanomaterials on DNA Origami Scaffolds

**One on each side:** Gold nanoparticles (AuNPs) and semiconducting quantum dots (QDs) are integrated on a single DNA origami scaffold. Streptavidin-functionalized QDs bind to biotin anchors on one side of the DNA origami, while DNA-coated AuNPs bind through DNA hybridization to single-stranded DNA on the other side of the scaffold. This approach offers a new path toward the organization of complex systems consisting of disparate materials.

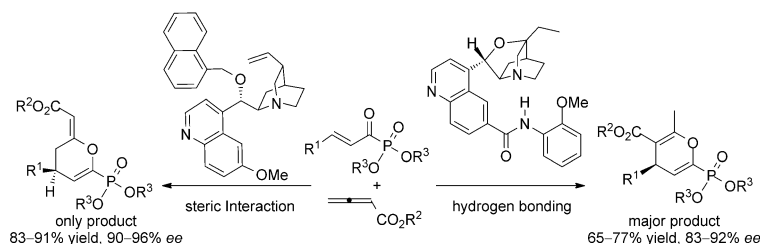


## Asymmetric Organocatalysis

C.-K. Pei, Y. Jiang, Y. Wei,\*  
M. Shi\* 11328–11332



Enantioselective Synthesis of Highly  
Functionalized Phosphonate-Substituted  
Pyrans or Dihydropyrans Through  
Asymmetric [4+2] Cycloaddition of  
 $\beta,\gamma$ -Unsaturated  $\alpha$ -Ketophosphonates  
with Allenic Esters



**Tell me which you want:** Catalytic asymmetric [4+2] cycloadditions of  $\beta,\gamma$ -unsaturated  $\alpha$ -ketophosphonates with allenic esters catalyzed by organocatalysts derived from different cinchona alkaloids have been developed, affording phospho-

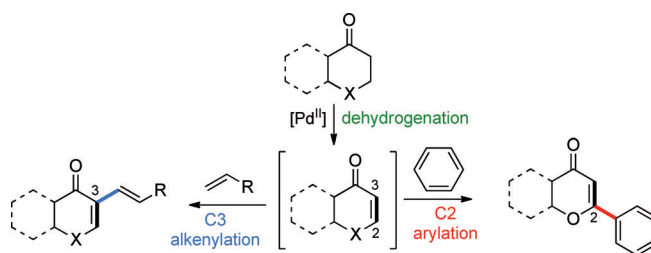
nate-substituted functionalized pyran and dihydropyran derivatives in excellent yields with high enantioselectivities under mild conditions. The choice of product is controlled by the hydrogen bonding characteristics of the chosen catalyst.

## Synthetic Methods

Y. Moon, D. Kwon,  
S. Hong\* 11333–11336



Palladium-Catalyzed Dehydrogenation/  
Oxidative Cross-Coupling Sequence of  
 $\beta$ -Heteroatom-Substituted Ketones



**Concise and selective:** The title one-pot sequence allows formation of the enone functionality and subsequent cross-coupling. The process provides access to

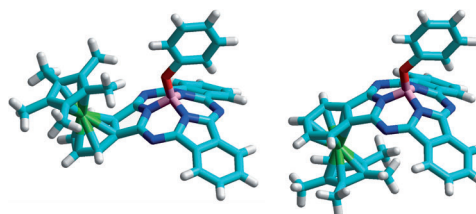
highly functionalized cyclic enones and enamines from readily accessible  $\beta$ -heteroatom-substituted cyclic ketones.

## $\pi$ Complexes

E. Caballero, J. Fernández-Ariza,  
V. M. Lynch, C. Romero-Nieto,  
M. S. Rodríguez-Morgade,\* J. L. Sessler,\*  
D. M. Guldi,\* T. Torres\* 11337–11342

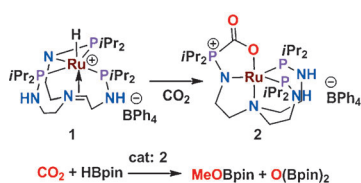


Cyclopentadienylruthenium  $\pi$  Complexes  
of Subphthalocyanines: A “Drop-Pin”  
Approach To Modifying the Electronic  
Features of Aromatic Macrocycles



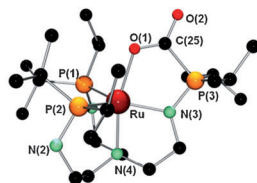
**Facing facts:** Coordination of  $\text{Cp}^*\text{Ru}$  ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ) to the concave and convex  $\pi$  surfaces of subphthalocyanines constitutes a new approach to the functionalization of subazaporphyrins. While the

convex face shows higher reactivity, coordination to the concave side produces a stronger diatropic influence on the  $\text{Cp}^*$  ligand and a greater perturbation of the macrocyclic  $\pi$ -electronic features.



**Frustrating ruthenium:** The ruthenium complex **1** is shown to bind carbon dioxide or aldehyde in a manner similar to a frustrated Lewis pair. Compound **2** catalyzes the reduction of  $\text{CO}_2$  in the

presence of pinacolborane (HBpin), yielding MeOBpin and  $\text{O}(\text{Bpin})_2$  (see picture; Ru red, P orange, N green, O light red, C black).



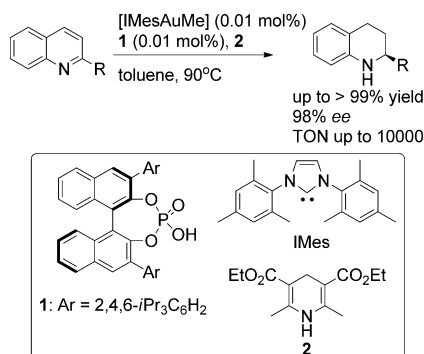
## CO<sub>2</sub> Reduction

M. J. Sgro,  
D. W. Stephan\* 11343–11345

Frustrated Lewis Pair Inspired Carbon Dioxide Reduction by a Ruthenium Tris(aminophosphine) Complex



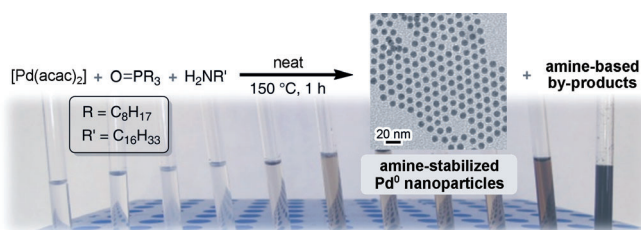
**A little gold goes a long way:** As little as 0.01 mol% of chiral gold phosphate is sufficient to afford the asymmetric transfer hydrogenation of quinolines with high stereoselectivity (up to 98% *ee*). The achiral ligands on gold were found to have considerable effect on the catalytic efficiency.



## Gold Catalysis

X.-F. Tu, L.-Z. Gong\* 11346–11349

Highly Enantioselective Transfer Hydrogenation of Quinolines Catalyzed by Gold Phosphates: Achiral Ligand Tuning and Chiral-Anion Control of Stereoselectivity



**Small and cool:** The mechanism of formation of amine-capped Pd nanoparticles from  $[\text{Pd}(\text{acac})_2]$  (acac = acetylacetonate) is elucidated, and shown to involve Pd-amido and Pd-hydride intermediates. The

addition of a Lewis base results in a significant reduction in the temperature at which highly monodisperse nanoparticles are isolated.

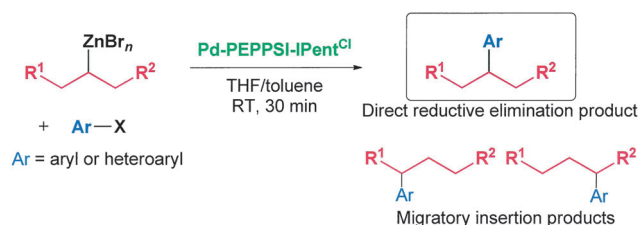
## Nanoparticle Formation

R. W. Y. Man, A. R. C. Brown,  
M. O. Wolf\* 11350–11353

Mechanism of Formation of Palladium Nanoparticles: Lewis Base Assisted, Low-Temperature Preparation of Monodisperse Nanoparticles



Back Cover



**No migration? No problem!** A series of new N-heterocyclic carbene based Pd complexes has been created and evaluated in the Negishi cross-coupling of aryl and heteroaryl chlorides, bromides, and

triflates with a variety of secondary alkyl-zinc reagents (see scheme). The direct elimination product is nearly exclusively formed; in most examples there is no migratory insertion at all.

## Homogeneous Catalysis

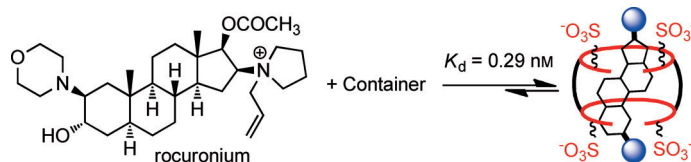
M. Pompeo, R. D. J. Froese, N. Hadei,  
M. G. Organ\* 11354–11357

Pd-PEPPSI-IPent<sup>Cl</sup>: A Highly Effective Catalyst for the Selective Cross-Coupling of Secondary Organozinc Reagents



## Host–Guest Chemistry

D. Ma, B. Zhang, U. Hoffmann,  
M. G. Sundrup, M. Eikermann,\*  
L. Isaacs\* ————— 11358 – 11362



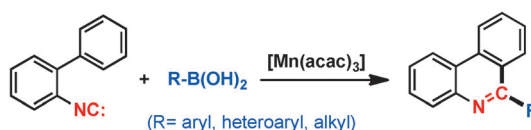
Acyclic Cucurbit[n]uril-Type Molecular  
Containers Bind Neuromuscular  
Blocking Agents In Vitro and Reverse  
Neuromuscular Block In Vivo

**Be My Guest:** Two acyclic cucurbit[n]uril-type receptors that carry  $\text{SO}_3^-$ -groups bind tightly to several commonly used neuromuscular blocking agents, such as rocuronium, in aqueous solution as

revealed by direct and competitive UV/Vis binding assays. One of these containers functions as a potent reversal agent for rocuronium-induced neuromuscular block in rats.

## Heterocycle Synthesis

M. Tobisu,\* K. Koh, T. Furukawa,  
N. Chatani\* ————— 11363 – 11366



Modular Synthesis of Phenanthridine  
Derivatives by Oxidative Cyclization of  
2-Isocyanobiphenyls with Organoboron  
Reagents

**Where HAS you been?** A manganese-mediated annulation of 2-isocyanobiaryls with organoboronic acids is developed for the synthesis of a broad range of phenanthridine derivatives (see scheme).

Mechanistic studies indicate that the reaction proceeds by the intramolecular homolytic aromatic substitution (HAS) of an imidoyl radical intermediate.

DOI: 10.1002/anie.201206408

# 50 Years Ago ...

*Angewandte Chemie International Edition* was first published in 1962, the mother journal first in 1888. In this monthly flashback, we feature some of the articles that appeared 50 years ago. This look back can open our eyes, stimulate discussion, or even raise a smile.

Are the noble gases really inert? This question was answered 50 years ago with the synthesis of noble-gas compounds, and Rudolf Hoppe et al. reported the synthesis of  $\text{XeF}_2$  when a 1:2 mixture of purified Xe and  $\text{F}_2$  was subjected to an electric discharge in a sealed vessel. This report followed work reported in the same year by Neil Bartlett on  $\text{XePtF}_6$  and Howard H. Claassen on  $\text{XeF}_4$  and launched a new field of research, thus paving the way for classic chemistry textbooks to be rewritten. For a Review on the discovery of noble-gas compounds, see P. Laszlo, G. J. Schrobilgen,

*Angew. Chem.* **1988**, 100, 495; *Angew. Chem. Int. Ed. Engl.* **1988**, 27, 479.

The Review by R. Brill was on a “cool” topic: the structure of ice. Hydrogen bridges, disorder in the crystal structure, and mixed crystals were discussed in order to give an overview on the complex structure of such a well-known substance—a topic that is as “hot” today as it was 50 years ago.

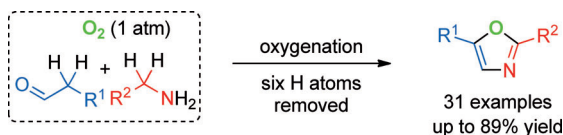
G. Wittig and D. Hellwinkel described the synthesis of bis(diphenylene)arylsoranes. This synthesis, which involved

the reaction of spirobis(diphenylene)arsonium salts, provides an alternative route to that reported by the same authors in Issue 1/1962.

The complaints from workers in a veneer factory about skin irritation led W. Sandermann and M. H. Simatupang to investigate the active principle of teak wood. Analysis of golden yellow crystals that were deposited on teak veneers showed them to contain the toxic 2- $\gamma$ , $\gamma$ -dimethylallyl-1,4-naphthaquinone.

[Read more in Issue 11/1962](#)





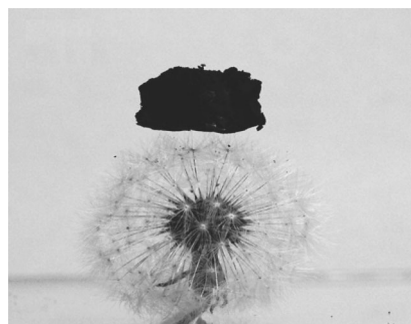
A fragment-assembling strategy is used to form oxazoles from aryl acetaldehydes, amines, and molecular oxygen under mild conditions (see scheme). The transfor-

mation is highly efficient with the removal of six hydrogen atoms, including the cleavage of four  $\text{C}(\text{sp}^3)\text{---H}$  bonds.

## Oxygenation

Z. Xu, C. Zhang, N. Jiao\* 11367–11370

Synthesis of Oxazoles through Copper-Mediated Aerobic Oxidative Dehydrogenative Annulation and Oxygenation of Aldehydes and Amines



**Graphene lite:** A density of  $(2.1 \pm 0.3) \text{ mg cm}^{-3}$ , the lowest to date for a graphene framework architecture, is achieved by preparing an ultralight, N-doped, 3D graphene framework (see photo of a block of the material balancing on a dandelion). Its adsorption capacity for oils and organic solvents is much higher than that of the best carbonaceous sorbents, and it is a promising electrode material for supercapacitors ( $484 \text{ F g}^{-1}$ ) and as a metal-free catalyst for the oxygen reduction reaction.

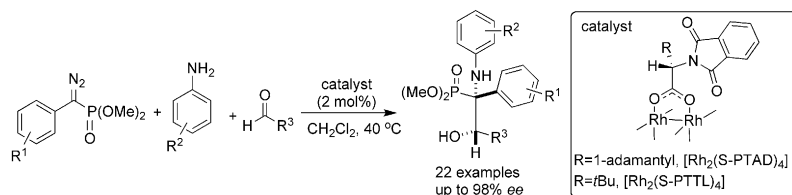
## Ultralight Graphene

Y. Zhao, C. Hu, Y. Hu, H. Cheng, G. Shi, L. Qu\* 11371–11375

A Versatile, Ultralight, Nitrogen-Doped Graphene Framework



Inside Cover



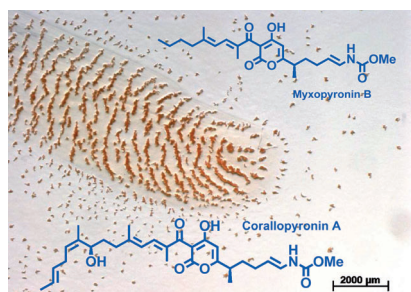
**Chiral dirhodium carboxylate complexes** ( $[\text{Rh}_2(\text{S-PTAD})_4]$  or  $[\text{Rh}_2(\text{S-PTTL})_4]$ , see scheme) efficiently catalyze asymmetric three-component coupling reactions of  $\alpha$ -diazophosphonates, anilines, and elec-

tron-deficient aldehydes to give  $\alpha$ -amino- $\beta$ -hydroxyphosphonates. The high level of enantiocontrol provides evidence for the intermediacy of metal-bound ammonium ylide in the product-forming step.

## Asymmetric Catalysis

C.-Y. Zhou, J.-C. Wang, J. Wei, Z.-J. Xu, Z. Guo, K.-H. Low, C.-M. Che\* 11376–11380

Dirhodium Carboxylates Catalyzed Enantioselective Coupling Reactions of  $\alpha$ -Diazophosphonates, Anilines, and Electron-Deficient Aldehydes



**Leading the way:** The synthesis of natural products with new biological targets is one of the driving forces for the development of new antibiotics. The synthesis of the two secondary metabolites coralopyronin and myxopyronin (see picture) have been achieved, which are prominent leads for the inhibition of bacterial RNA polymerase.

## Natural Products

A. Rentsch, M. Kalesse\* 11381–11384

The Total Synthesis of Coralopyronin A and Myxopyronin B



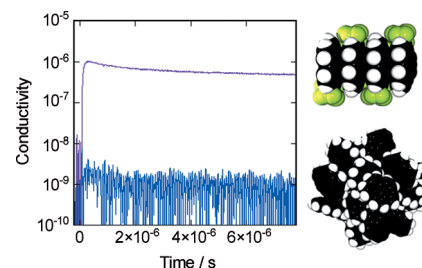
**Nanostructures**

B. M. Schmidt, S. Seki, B. Topolinski,  
K. Ohkubo, S. Fukuzumi, H. Sakurai,  
D. Lentz\* 11385–11388



Electronic Properties of  
Trifluoromethylated Corannulenes

**With great stacking comes great conductivity:** Trifluoromethylated corannulenes are unexpectedly strong electron acceptors in solution. Even a polycrystalline film of 1,2-(F<sub>3</sub>C)<sub>2</sub>-corannulene (top structure and curve in the plot) exhibits conductivity three orders of magnitude higher than that of pristine corannulene!



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)  
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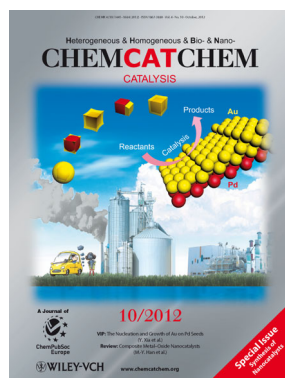


This article is accompanied by a cover picture (front or back cover, and inside or outside).

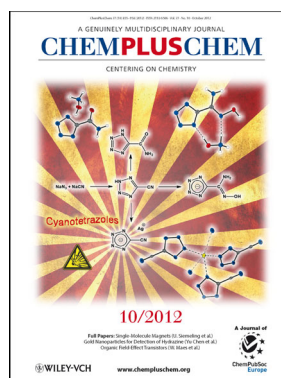
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