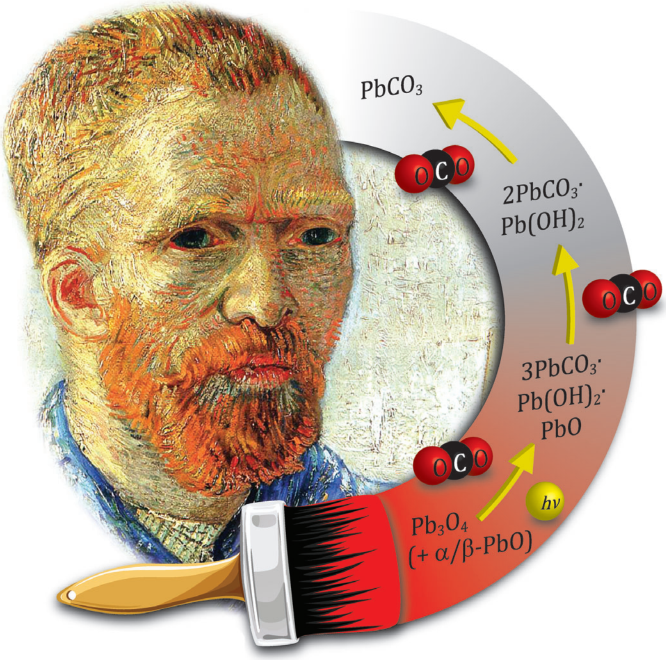
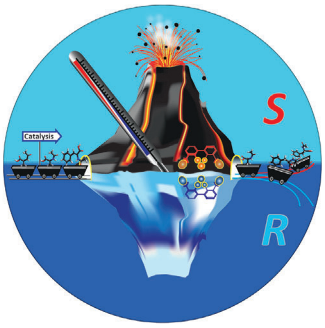
# Red lead ...

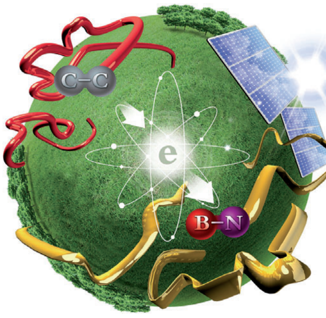


… a pigment that has been used by artists since antiquity, is known to change its color over time. Using (sub)micrometer X-ray powder diffraction tomography on a minute sample from a Van Gogh painting, a very rare lead compound (plumbonacrite, $3PbCO_3 \cdot Pb(OH)_2 \cdot Pb$) was found in the inner structure of the sample. In their Communication on page 3607 ff., K. Janssens et al. explain how an additional step in the photochemical degradation pathway of red lead could be identified.

### Asymmetric Catalysis

G. Storch and O. Trapp describe in their Communication on page 3580 ff. how the enantioselectivity in the asymmetric hydrogenation of prochiral (Z)-α-acetamidocinnamates and α-substituted acrylates depends on the thermal treatment of the catalyst.



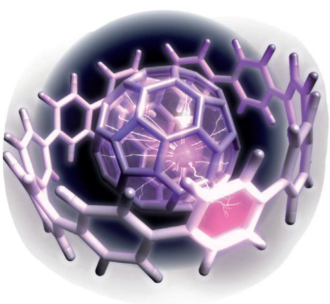


### Electron Transport

In their Communication on page 3648 ff., J. Liu and co-workers report how conjugated polymers can be transformed from electron donors to electron acceptors through lowering the HOMO and LUMO levels by replacement of a C–C unit with a B←N unit.

### Supramolecular Cations

K. Itami and co-workers show in their Communication on page 3707 ff. that in the supramolecule formed between [10]cycloparaphenylene (CPP) and $Li^+@C_{60}$, the charge on $Li^+$ is delocalized not only onto the fullerene cage, but also onto the surrounding CPP ring.



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## Service

## Author Profile

*"In a spare hour, I play the Stratocaster.*
*The natural talent I would like to be gifted with is being really good at playing the Stratocaster …"*
This and more about Gisbert Schneider can be found on page 3548.

## News


J. K. Barton


K. R. Dunbar


W. J. Evans

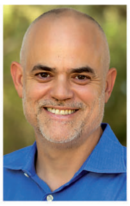

L. E. Overman


M. A. Marletta


E. T. Kool


H. I. Kenttämaa


T. R. Hoye


F. Romesberg


C. L. Perrin


J. G. Chen


M. Brookhart

## Books

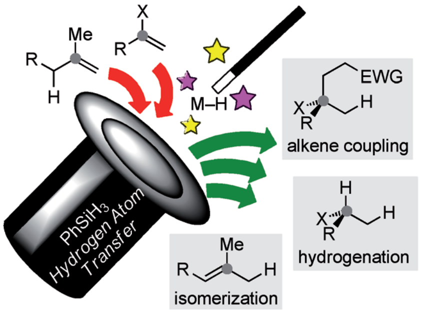
# Highlights

### Radical Chemistry

A. Simonneau,
M. Oestreich* ______ 3556 – 3558

Fascinating Hydrogen Atom Transfer Chemistry of Alkenes Inspired by Problems in Total Synthesis

**The magical HAT**: Radical hydrofunctionalization processes of alkenes recently witnessed tremendous progress. The coupling of heteroatom-substituted alkenes was achieved by means of catalytic hydrogen atom transfer (HAT), enabling the construction of functionalized quaternary centers with unusual ease. Challenging thermodynamically controlled hydrogenations and isomerizations of alkenes as well as reductions of vinyl halides were accomplished using HAT processes.

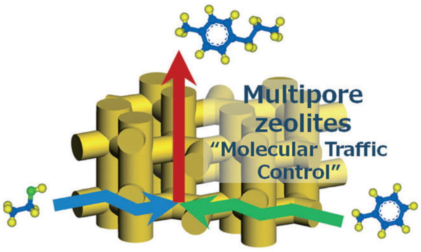


# Reviews

### Zeolite Structures and Catalysis

M. Moliner, C. Martínez,
A. Corma* ______ 3560 – 3579

Multipore Zeolites: Synthesis and Catalytic Applications



**Molecular traffic control**: Multipore zeolites contain channels of different sizes. They can be prepared in a planned manner and their channel structure offers advantages in shape- and size-selective catalysis. The different rates molecules diffuse through the different channels is termed molecular traffic control.

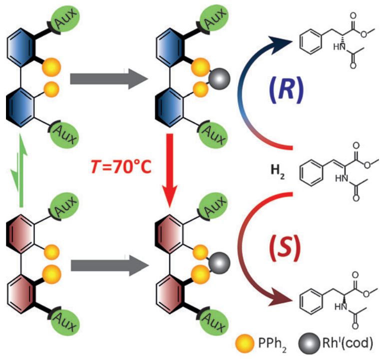
# Communications

### Asymmetric Catalysis

G. Storch, O. Trapp* ______ 3580 – 3586

Temperature-Controlled Bidirectional Enantioselectivity in a Dynamic Catalyst for Asymmetric Hydrogenation

**Frontispiece**



**Temperature switches enantioselectivity!** A stereochemically flexible diastereomeric rhodium(I) catalyst has been designed for the asymmetric hydrogenation of prochiral (*Z*)-α-acetamidocinnamates and α-substituted acrylates. The catalyst changes its enantioselectivity depending on the temperature to produce each single enantiomer in high yield and a constant high enantioselectivity.

**For the USA and Canada:**
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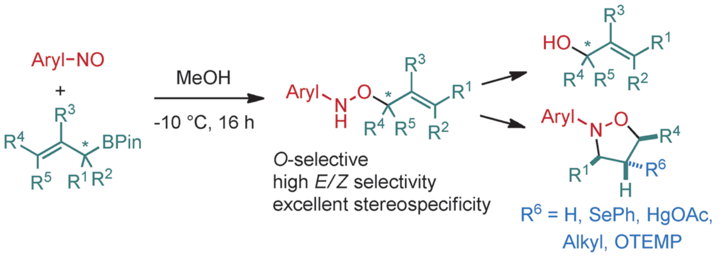
## Nitrosoarenes

Y. Li, S. Chakrabarty,
A. Studer* ______ 3587 – 3591

An Efficient Approach to Chiral Allyloxyamines by Stereospecific Allylation of Nitrosoarenes with Chiral Allylboronates

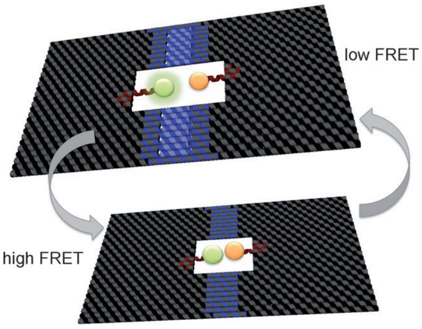


**Stereospecific and regioselective**: Allylborations of nitrosoarenes with readily available $\alpha$-chiral allylboronates occur with high stereoselectivity to provide allyloxyamines. These allyloxyamines can be readily transformed into various isoxazolidines and allylalcohols.

## DNA Nanotechnology

B. Saccà,* Y. Ishitsuka, R. Meyer,
A. Sprengel, E. C. Schöneweiß,
G. U. Nienhaus,*
C. M. Niemeyer* ______ 3592 – 3597

Reversible Reconfiguration of DNA Origami Nanochambers Monitored by Single-Molecule FRET

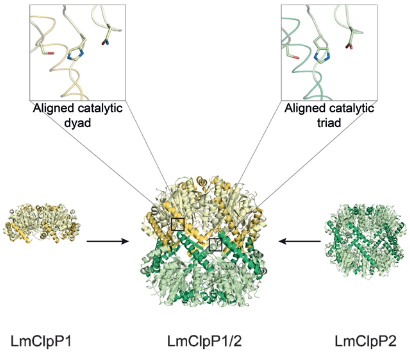


**Inspired by their natural counterparts**, dynamic compartmentalization systems were realized, in which the switchable mechanical movement of small DNA motifs was integrated into a DNA origami scaffold. The kinetics of the movement was determined by distance-dependent energy transfer between two fluorophores.

## Protein Structure

M. Dahmen, M.-T. Vielberg, M. Groll,*
S. A. Sieber* ______ 3598 – 3602

Structure and Mechanism of the Caseinolytic Protease ClpP1/2 Heterocomplex from *Listeria monocytogenes*

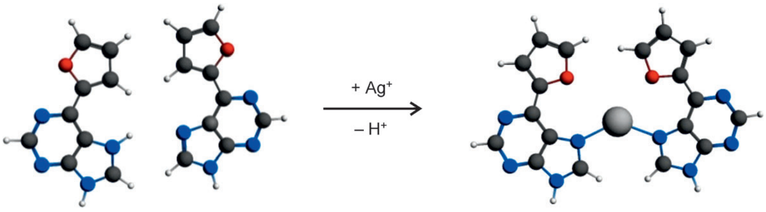


**All together now**: The crystal structure of the heterooligomeric ClpP1 and ClpP2 complex from *Listeria monocytogenes* was solved. Taken together with biochemical data, the structure provides insights into the catalysis and transient stability of the complex, as well as its interaction with the associated ClpX chaperone. Subtle differences in the S1 pockets could be predicted and are the basis for the development of specific inhibitors.

## Metal-Mediated Base Pairs

I. Sinha, C. Fonseca Guerra,*
J. Müller* ______ 3603 – 3606

A Highly Stabilizing Silver(I)-Mediated Base Pair in Parallel-Stranded DNA



**I'm stranded**: An artificial nucleoside forms $Ag^+$-mediated base pairs both in antiparallel-stranded duplexes with Watson–Crick-type geometry and in parallel-stranded duplexes with Hoogsteen-type geometry. The base pair within the parallel-stranded duplex is significantly more stabilizing and is the most strongly stabilizing $Ag^+$-mediated base pair reported for any type of nucleic acid.

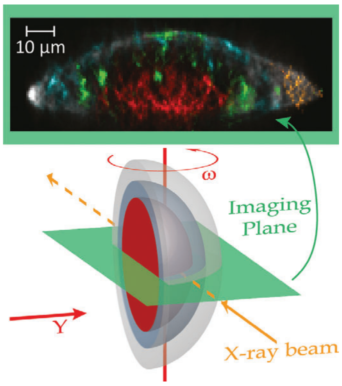
## Pigment Discoloration

F. Vanmeert, G. Van der Snickt,
K. Janssens* ———— 3607 – 3610

Plumbonacrite Identified by X-ray Powder Diffraction Tomography as a Missing Link during Degradation of Red Lead in a Van Gogh Painting

**Front Cover**

**Unravelling minium degradation**: The very rare lead carbonate mineral plumbonacrite was identified in a Van Gogh painting using combined microscopic X-ray fluorescence and X-ray powder diffraction mapping and tomography methods. Thanks to the high spatial resolution and specificity of this technique an additional step in the photochemical degradation pathway of red lead (minium) is demonstrated.



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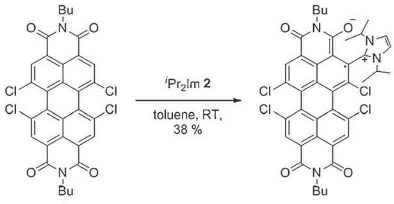
## Zwitterionic Radicals

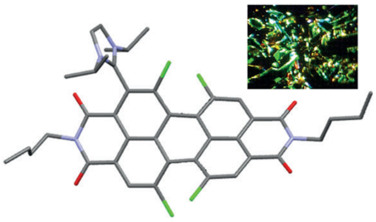
D. Schmidt, D. Bialas,
F. Würthner* ———— 3611 – 3614

Ambient Stable Zwitterionic Perylene Bisimide-Centered Radical



1

$^i$Pr$_2$Im-PBI-Cl$_4$ 4



**A zwitterionic radical** $^i$Pr$_2$Im-PBI-Cl$_4$ **4** was isolated from the reaction of PBI-Cl$_4$ **1** with the N-heterocyclic carbene 1,3-di-*iso*-propyl-imidazolin-2-ylidene ($^i$Pr$_2$Im **2**). It is stable at ambient conditions and has been characterized by UV/Vis absorption, EPR and NMR spectroscopy as well as single-crystal X-ray diffraction.

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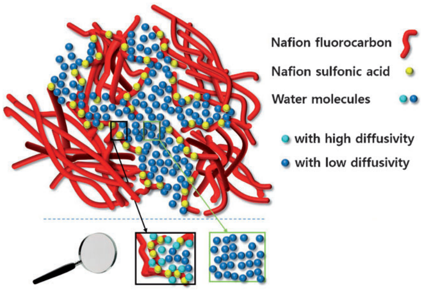
## Fuel-Cell Membranes

J. Song, O. H. Han,*
S. Han* ———— 3615 – 3620

Nanometer-Scale Water- and Proton-Diffusion Heterogeneities across Water Channels in Polymer Electrolyte Membranes



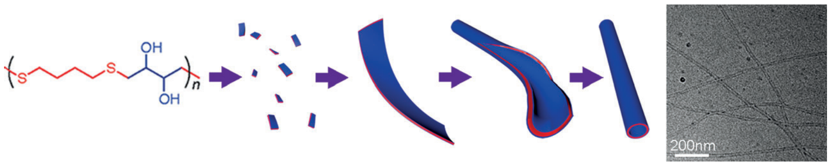
**On the surface of it…** The water/proton diffusivity in Nafion within 1 nm of spin probes located in specific heterogeneous regions of the polymer electrolyte membrane (PEM) was significantly faster near the fluorocarbon and the acidic groups lining the water channels than within the water channels (see picture). Thus, surface chemistry at the (sub-)nanometer scale dictates key transport properties and offers new design principles for PEMs.

---

## Polymeric Nanostructures

J. X. Chen, C. Y. Yu, Z. Q. Shi, S. R. Yu,
Z. Y. Lu, W. F. Jiang, M. Zhang, W. He,*
Y. F. Zhou,* D. Y. Yan ———— 3621 – 3625

Ultrathin Alternating Copolymer Nanotubes with Readily Tunable Surface Functionalities

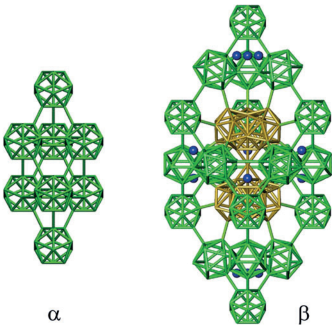


**Clicking into place**: Ultrathin nanotubes with readily tunable surface functionalities self-assemble from a novel alternative copolymer synthesized using epoxy–thiol click chemistry. The copolymer self-assembly mechanism is investigated experimentally and using dissipative particle dynamics simulations.

### Structure of Boron

M. A. White,* A. B. Cerqueira,
C. A. Whitman, M. B. Johnson,
T. Ogitsu ——— **3626–3629**

Determination of Phase Stability of Elemental Boron



**Elementary information**: Through experimental thermodynamics, the fundamental question of which structure of elemental boron is most stable has been answered: it is the unique disordered β-form.

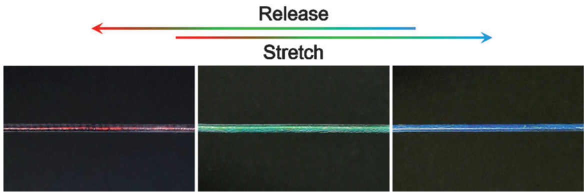
---

### Photonic Crystals

X. Sun,* J. Zhang, X. Lu, X. Fang,
H. Peng* ——— **3630–3634**

Mechanochromic Photonic-Crystal Fibers Based on Continuous Sheets of Aligned Carbon Nanotubes

**Inside Cover**



**Color play**: A new family of mechanochromic photonic-crystal fibers exhibits tunable structural colors under stretching. These fibers maintain both a high sensitivity and stability even after more than 1000 deformation cycles. These elastic photonic-crystal fibers are woven into colorful patterns and fabrics for various applications in displays and sensing devices.

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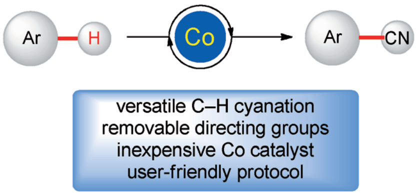
### C–H Activation

J. Li, L. Ackermann* ——— **3635–3638**

Cobalt-Catalyzed C–H Cyanation of Arenes and Heteroarenes



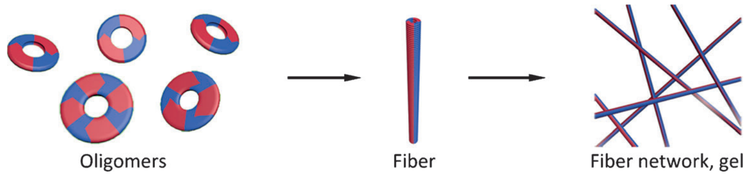
**As directed**: The title reactions were accomplished with in situ generated cobalt(III) carboxylate complexes for highly efficient C–H activations. The direct cyanation proved viable with removable directing groups and displayed a broad substrate scope and mild reaction conditions.

---

### Nanostructures

S. Liu, A. Tang, M. Xie, Y. Zhao, J. Jiang,
G. Liang* ——— **3639–3642**

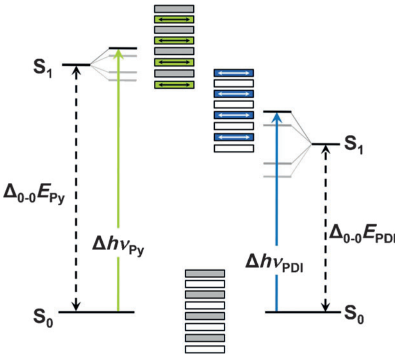
Oligomeric Hydrogels Self-Assembled from Reduction-Controlled Condensation



**Bowl full of gel**: A biocompatible condensation reaction was employed to synthesize amphiphilic macrocyclized oligomers, which instantly self-assembled into nanofibers through parallel stacking and formed oligomeric hydrogels.

## *Co-existing Excitons*

**DNA scaffolding** is used for the construction of well-defined heterochromophoric stacks. Electronic coupling among non-adjacent chromophores of the same type leads to the co-existence of independent PDI and pyrene H-aggregates in alternating multichromophores.



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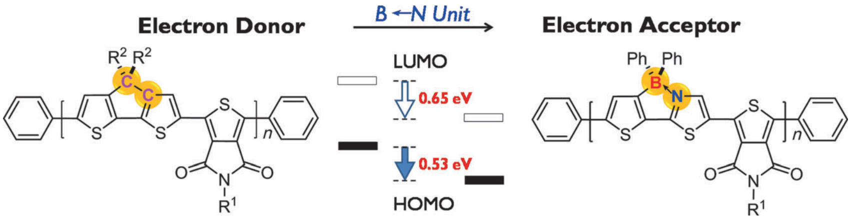
## *Electron Transport*

**Inside Back Cover**



**Transforming units**: A novel strategy decreases both LUMO and HOMO energy levels of conjugated polymers, by about 0.6 eV, through replacement of a C–C unit by a B←N unit. The replacement transforms the resulting polymer from an electron donor into an electron acceptor.

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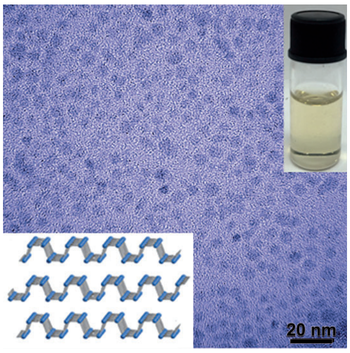
## *Black Phosphorus*



**Black** phosphorus quantum dots (BPQDs) with lateral size of 4.9 ± 1.6 nm and thickness of 1.9 ± 0.9 nm (ca. 4 ± 2 layers) are synthesized in solution by a top-down approach. The mixture of BPQDs and polyvinylpyrrolidone is successfully used as active layer in a flexible memory device with a nonvolatile rewritable memory effect.

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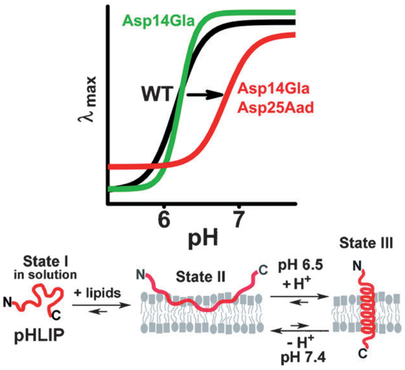
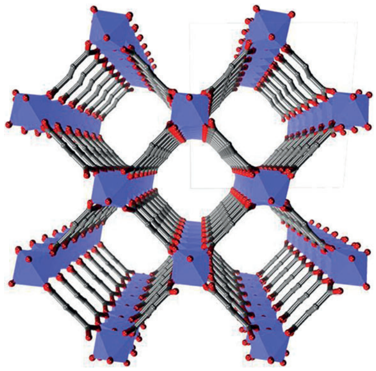
## *Drug Delivery*



**The pH low insertion peptide** (pHLIP) allows drugs to be delivered selectively to the cytoplasm of cancer cells based on tumor extracellular acidity (pH$_e$). Incorporation of noncanonical amino acids into pHLIP can increase the pH at which it inserts into membranes, thus better matching tumor pH$_e$, without compromising the sharpness of transition.

**The aluminum fumarate sample** BASF A520 synthesis has been optimized and its structure analyzed through a combination of X-ray powder diffraction, solid-state NMR spectroscopy, molecular simulation, IR spectroscopy, and thermal analysis. A520 is an analogue of the MIL-53(Al)-BDC solid, but with a more rigid behavior. The impact of the synthesis routes in terms of defects and catalytic behavior have finally been correlated.



### Metal–Organic Frameworks

E. Alvarez, N. Guillou, C. Martineau, B. Bueken, B. Van de Voorde, C. Le Guillouzer, P. Fabry, F. Nouar, F. Taulelle, D. de Vos, J.-S. Chang, K. H. Cho, N. Ramsahye, T. Devic, M. Daturi, G. Maurin,* C. Serre* ______ **3664 – 3668**

The Structure of the Aluminum Fumarate Metal–Organic Framework A520

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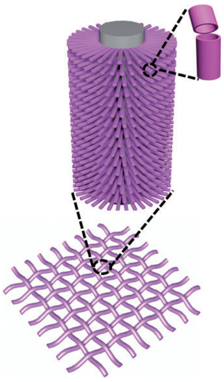

**PdCo nanotube arrays** supported on carbon fiber cloth for use as high-performance electrocatalysts were synthesized for ethanol electrooxidation. The system of nanotube arrays on carbon fiber cloth is highly flexible, and its high electrocatalytic performance is almost constant regardless of the distorted state, such as normal, bent, and twisted.

### Electrocatalysis

A.-L. Wang, X.-J. He, X.-F. Lu, H. Xu, Y.-X. Tong, G.-R. Li* ______ **3669 – 3673**

Palladium–Cobalt Nanotube Arrays Supported on Carbon Fiber Cloth as High-Performance Flexible Electrocatalysts for Ethanol Oxidation

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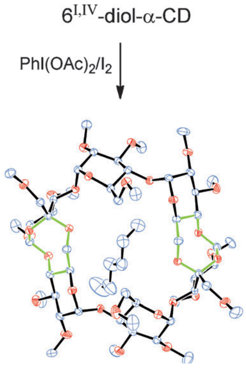

**The successful match** of cyclodextrins (CDs) with radical chemistry is reported. The di-alkoxyl radical generated from $6^{I,IV}$-diol-α-CD under oxidative conditions led to a stable crystalline bis(1,3,5-trioxocane) with a guest *n*-hexane molecule. The primary face of the bis(1,3,5-trioxocane) is severely distorted toward a narrower elliptical shape.

### Host–Guest Systems

D. Alvarez-Dorta, E. I. León, A. R. Kennedy, A. Martín,* I. Pérez-Martín, E. Suárez* ______ **3674 – 3678**

Easy Access to Modified Cyclodextrins by an Intramolecular Radical Approach

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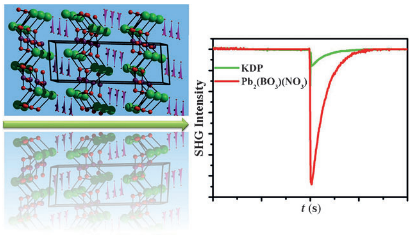


**$Pb_2(BO_3)(NO_3)$** is a new second-harmonic generation (SHG) material that contains parallel π-conjugated nitrate and borate anions. It was obtained through a facile hydrothermal reaction, shows a remarkable strong SHG response of about 9.0 times that of potassium dihydrogen phosphate (KDP), and is phase-matchable.

### Second-Harmonic Generation Materials

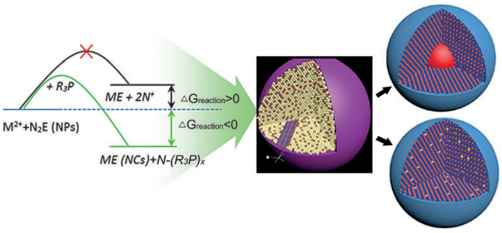
J.-L. Song, C.-L. Hu, X. Xu, F. Kong, J.-G. Mao* ______ **3679 – 3682**

A Facile Synthetic Route to a New SHG Material with Two Types of Parallel π-Conjugated Planar Triangular Units

## Core–Shell Nanocrystals

J. Gui, M. Ji, J. Liu, M. Xu, J. Zhang,*
H. Zhu ———— **3683 – 3687**

Phosphine-Initiated Cation Exchange for Precisely Tailoring Composition and Properties of Semiconductor Nanostructures: Old Concept, New Applications

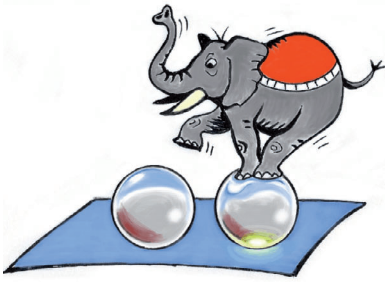


**Different phosphines** were used to modulate the thermodynamic and kinetic parameters of cation exchange in the synthesis of complex semiconductor nanostructures. Besides the preservation of the original shape and size of the semiconductor nanocrystals, this method also shows potential for precisely modulating the crystallinity and composition of the resulting nanocrystals. M = Cd, Zn, Pb, etc.; N = Ag, Cu, etc.; E = S, Se, Te.

## Fluorescent Probes

T. Suhina, B. Weber, C. E. Carpentier,
K. Lorincz, P. Schall, D. Bonn,*
A. M. Brouwer* ———— **3688 – 3691**

Fluorescence Microscopy Visualization of Contacts Between Objects

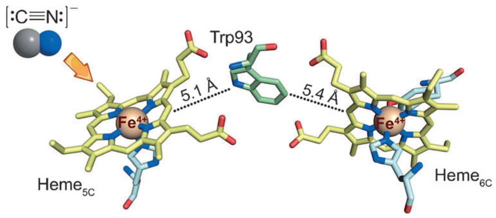


**All the fun of the surface**: By using rigidochromic fluorescent probe molecules attached to a surface, the contact area between the surface and an object can be visualized. Confinement of the molecules suppresses nonradiative decay and turns on the fluorescence.

## Biological Charge Resonance

J. Geng, I. Davis, A. Liu* —— **3692 – 3696**

Probing Bis-$Fe^{IV}$ MauG: Experimental Evidence for the Long-Range Charge-Resonance Model



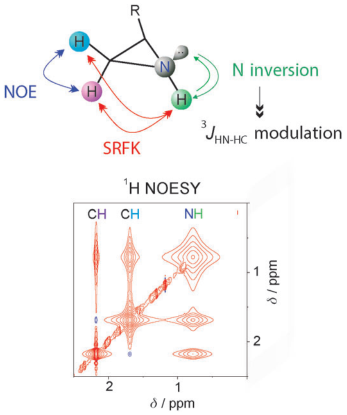
**Small molecules** were used to experimentally investigate the biological long-range charge-resonance (CR) model proposed in the high-valence bis-$Fe^{IV}$ intermediate of MauG. The chemical nature of the bis-$Fe^{IV}$ species was demonstrated to be an equilibrium of different resonance structures as predicted by the CR model. This study provides supporting evidence for the first CR phenomenon in a biological catalytic intermediate.

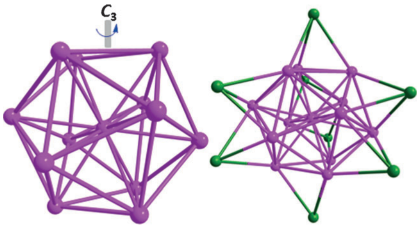
## NMR Spectroscopy

I. Kuprov, D. M. Hodgson, J. Kloesges,
C. I. Pearson, B. Odell,
T. D. W. Claridge* ———— **3697 – 3701**

Anomalous Nuclear Overhauser Effects in Carbon-Substituted Aziridines: Scalar Cross-Relaxation of the First Kind

**Scalar relaxation**: Apparently anomalous cross-peaks in 2D $^1H$ NOESY spectra of carbon-substituted aziridines are shown to arise from scalar cross-relaxation of the first kind (SRFK; see picture), due to modulation of scalar coupling constants between protons. Such effects will likely be seen in NOESY spectra of other small molecules experiencing dynamic exchange modulation of scalar $^1H$-$^1H$ coupling constants.



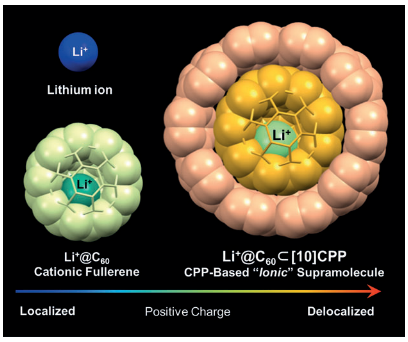


**Silver super skeleton**: A single-crystal X-ray diffraction study of a novel $[Ag_{21}\{S_2P(OiPr)_2\}_{12}](PF_6)$ nanocluster shows an unprecedented silver-centered icosahedron with additional eight capping silver atoms to generate an $Ag_{21}$ metal skeleton. DFT calculations indicate that this stable monocationic nanocluster is an eight-electron superatom.

## Superatoms

R. S. Dhayal, J.-H. Liao, Y.-C. Liu,
M.-H. Chiang, S. Kahlal, J.-Y. Saillard,*
C. W. Liu* **3702–3706**

### $[Ag_{21}\{S_2P(OiPr)_2\}_{12}]^+$: An Eight-Electron Superatom



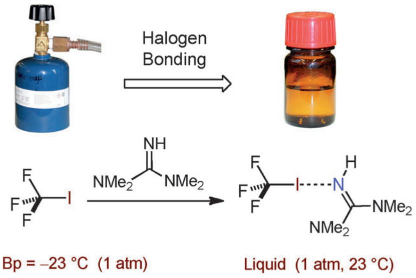
**Widen your sphere of influence**: A strong charge-transfer interaction between [10]CPP and $Li^+@C_{60}$ in the first cycloparaphenylene (CPP)-based ionic donor–acceptor supramolecule $Li^+@C_{60}\subset[10]CPP{\cdot}X^-$ is confirmed by electrochemical measurement and spectroscopic analyses. The complex is also characterized by X-ray crystallography. The charge transfer causes significant delocalization of the $Li^+$ positive charge over the entire complex.

## Ionic Supramolecules

H. Ueno, T. Nishihara, Y. Segawa,
K. Itami* **3707–3711**

### Cycloparaphenylene-Based Ionic Donor–Acceptor Supramolecule: Isolation and Characterization of $Li^+@C_{60}\subset[10]CPP$

**Back Cover**

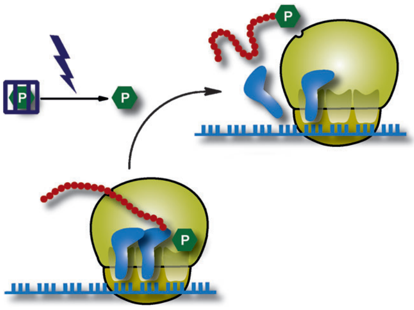


**It's (no longer) a gas!** A family of practical, liquid trifluoromethylation and pentafluoroethylation reagents enabled by halogen bonding is described. The synthetic utility of these reagents is exemplified by a novel direct arene trifluoromethylation reaction as well as adaptations of other perfluoroalkylation reactions.

## Perfluoroalkylations

F. Sladojevich, E. McNeill, J. Börgel,
S.-L. Zheng, T. Ritter* **3712–3716**

### Condensed-Phase, Halogen-Bonded $CF_3I$ and $C_2F_5I$ Adducts for Perfluoroalkylation Reactions



**On like a light**: The antibiotic puromycin (green) is a translation inhibitor that triggers the release of the nascent polypeptide chain (red) from the ribosome (yellow) and it is used in a number of applications. A photocaged puromycin derivative, NVOC-puromycin, was synthesized and characterized. Both functional recovery upon UV illumination and biological inactivity in vitro and in vivo were demonstrated.

## Photoactivation

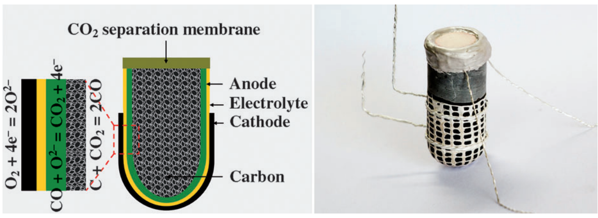
F. Buhr, J. Kohl-Landgraf, S. tom Dieck,
C. Hanus, D. Chatterjee, A. Hegelein,
E. M. Schuman, J. Wachtveitl,
H. Schwalbe* **3717–3721**

### Design of Photocaged Puromycin for Nascent Polypeptide Release and Spatiotemporal Monitoring of Translation

### Fuel Cells

B. B. Yang, R. Ran,* Y. J. Zhong, C. Su,
M. O. Tadé, Z. P. Shao* ____ 3722 – 3725

A Carbon–Air Battery for High Power Generation



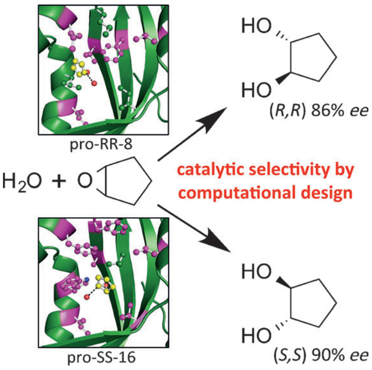
**Midair refueling**: A carbon–air battery based on a anode-supported tubular solid-oxide fuel cell integrated with a $CO_2$ separation membrane (see picture) composed of a $CO_3^{2-}$ mixture and an $O^{2-}$ conducting phase showed both high energy density and power output. A small stack composed of two batteries can be operated continuously for 200 min, which is promising for use as a portable power device.

### Biocatalyst Screening

H. J. Wijma, R. J. Floor, S. Bjelic,
S. J. Marrink, D. Baker,
D. B. Janssen* ____ 3726 – 3730

Enantioselective Enzymes by Computational Design and In Silico Screening

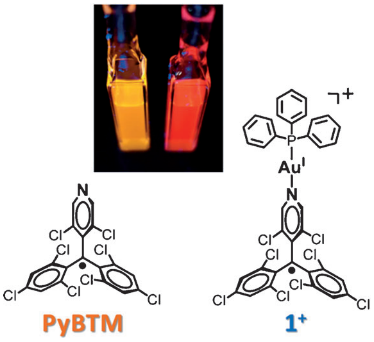
**Computational enzyme design** holds great promise for providing tailored biocatalysts. A strategy is presented that makes it possible to obtain enantiodivergent and highly enantioselective mutants of limonene epoxide hydrolase after experimental screening of only 37 variants. The results indicate that computational methods can replace a substantial amount of laboratory work when developing enantioselective enzymes.



### Radical Complexes

Y. Hattori, T. Kusamoto,*
H. Nishihara* ____ 3731 – 3734

Enhanced Luminescent Properties of an Open-Shell (3,5-Dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl Radical by Coordination to Gold

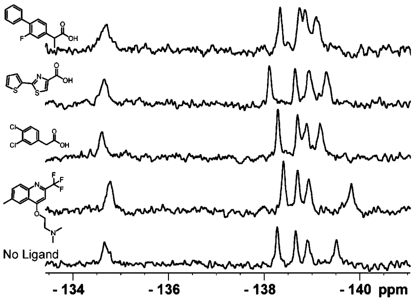


**A gold(I) complex** containing an open-shell luminescent (3,5-dichloro-4-pyridyl)-bis(2,4,6-trichlorophenyl)methyl (PyBTM) radical was prepared. The complex has fluorescence that is centered mainly on the coordinated PyBTM ligand. The photoluminescence quantum yield, fluorescence wavelength, and the stability in the photoexcited state all increased upon coordination to Au$^I$.

### NMR Spectroscopy

C. T. Gee, E. J. Koleski,
W. C. K. Pomerantz* ____ 3735 – 3739

Fragment Screening and Druggability Assessment for the CBP/p300 KIX Domain through Protein-Observed $^{19}$F NMR Spectroscopy

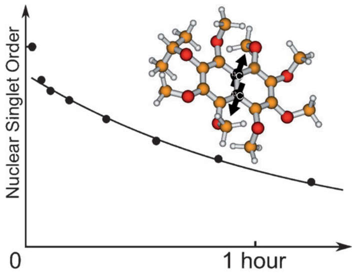


**A full small-molecule screen** has been achieved using protein-observed $^{19}$F NMR (PrOF NMR) spectroscopy of a model transcription factor binding domain of the CREB binding protein (CBP)/p300, KIX. This study demonstrates the applicability of PrOF NMR as a tool for library screening, ligand discovery, and druggability assessment.

## NMR Spectroscopy

G. Stevanato, J. T. Hill-Cousins,
P. Håkansson, S. S. Roy, L. J. Brown,
R. C. D. Brown, G. Pileio,*
M. H. Levitt* ______ **3740 – 3743**

A Nuclear Singlet Lifetime of More than One Hour in Room-Temperature Solution

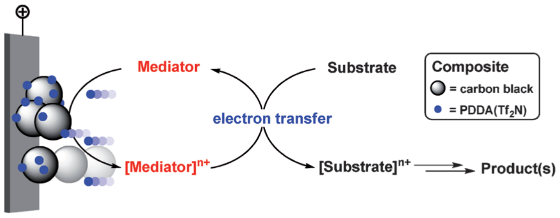


**A long-lived nuclear singlet**: A molecular system based on a $^{13}C_2$-labelled naphthalene core has been designed to support long-lived nuclear singlet order in solution. A nuclear singlet lifetime exceeding one hour has been achieved in room-temperature solution.

## Ionic Liquids

S. J. Yoo, L.-J. Li, C.-C. Zeng,
R. D. Little* ______ **3744 – 3747**

Polymeric Ionic Liquid and Carbon Black Composite as a Reusable Supporting Electrolyte: Modification of the Electrode Surface



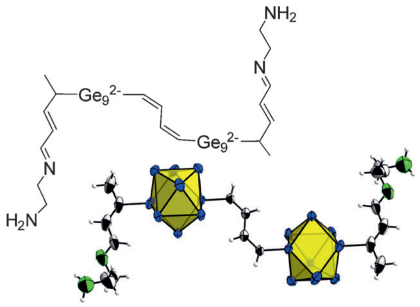
**A composite electrolyte** that combines the features of a polymeric ionic liquid with the properties of carbon nanoparticles enables electrochemical oxidations without an additional supporting electrolyte. The composite can be reused in subsequent electrolyses. In addition, the composite electrolyte can improve the kinetics through modification of the electrode surface.

## Zintl Clusters

M. M. Bentlohner, W. Klein, Z. H. Fard,
L.-A. Jantke, T. F. Fässler* __ **3748 – 3753**

Linking Deltahedral Zintl Clusters with Conjugated Organic Building Blocks: Synthesis and Characterization of the Zintl Triad [R-Ge$_9$-CH=CH−CH=CH-Ge$_9$-R]$^{4-}$

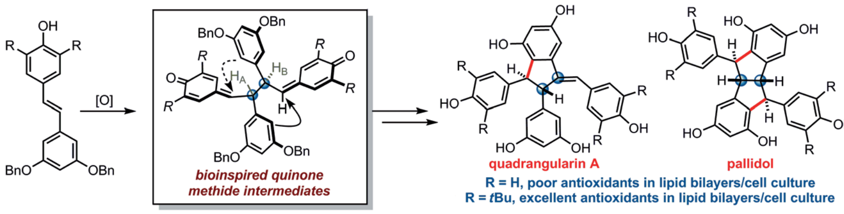
**Zintl triads**: The general possibility to synthesize electronically coupled Zintl clusters using conjugated electron π-systems as linkers in analogy to fullerene–linker–fullerene triads opens a new area of applications for Zintl clusters.



## Resveratrol

B. S. Matsuura, M. H. Keylor, B. Li, Y. Lin,
S. Allison, D. A. Pratt,*
C. R. J. Stephenson* ______ **3754 – 3757**

A Scalable Biomimetic Synthesis of Resveratrol Dimers and Systematic Evaluation of their Antioxidant Activities



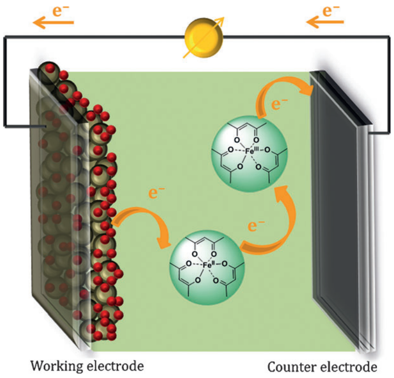
**Persistence pays off**: A concise synthesis of the resveratrol oligomers quadrangularin A and pallidol was achieved by leveraging the persistence of 2,6-di-*tert*-butyl phenol derived radical and quinone methide intermediates. Evaluation of these compounds as radical-trapping antioxidants is presented and the results demonstrate that this mode of action is unlikely to account for the observed biological activity.

### Solar Cells

I. R. Perera, T. Daeneke, S. Makuta, Z. Yu,
Y. Tachibana, A. Mishra, P. Bäuerle,
C. A. Ohlin, U. Bach,*
L. Spiccia* ______________ **3758–3762**

Application of the Tris(acetylacetonato)iron(III)/(II) Redox Couple in p-Type Dye-Sensitized Solar Cells

**Here comes the sun**: The use of an electrolyte based on the tris(acetylacetonato)iron(III)/(II) redox couple (green spheres) in p-type dye-sensitized solar cells resulted in rapid dye regeneration and an energy conversion efficiency of 2.51%. Devices were constructed using a porous NiO layer (brown spheres) on the working electrode sensitized with PMI–6T–TPA, a perylene–thiophene–triphenylamine dye (red spheres).



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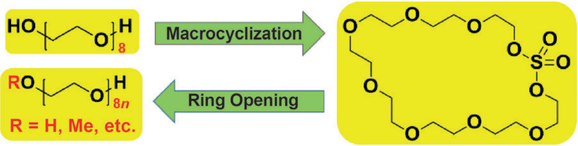
### Macrocyclic Sulfates

H. Zhang, X. Li, Q. Shi, Y. Li, G. Xia,
L. Chen, Z. Yang,
Z.-X. Jiang* ______________ **3763–3767**

Highly Efficient Synthesis of Monodisperse Poly(ethylene glycols) and Derivatives through Macrocyclization of Oligo(ethylene glycols)



**Macrocycles make synthesis easier**: Convenient macrocyclization of the OEGs provides versatile macrocyclic sulfates. These compounds are cornerstones for both monofunctionalization of OEGs and highly efficient synthesis of monodisperse PEGs and derivatives, including an unprecedented 64-mer.

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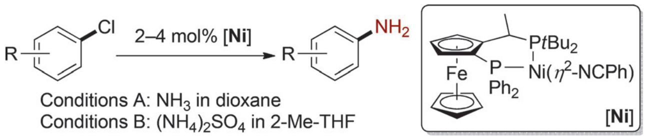
### Ammonia Coupling

R. A. Green, J. F. Hartwig* _ **3768–3772**

Nickel-Catalyzed Amination of Aryl Chlorides with Ammonia or Ammonium Salts



**Simple alternative**: The title reaction, which results in primary arylamines, is catalyzed by well-defined single-component nickel(0) precatalysts containing a Josiphos ligand and an $\eta^2$-bound benzonitrile ligand. This system also catalyzes the coupling of aryl chlorides with gaseous amines in the form of their hydrochloride salts.

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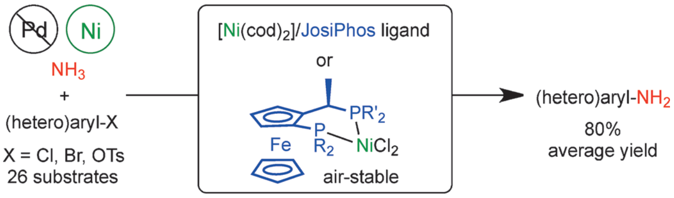
### Ammonia Coupling

A. Borzenko, N. L. Rotta-Loria,
P. M. MacQueen, C. M. Lavoie,
R. McDonald,
M. Stradiotto* ______________ **3773–3777**

Nickel-Catalyzed Monoarylation of Ammonia

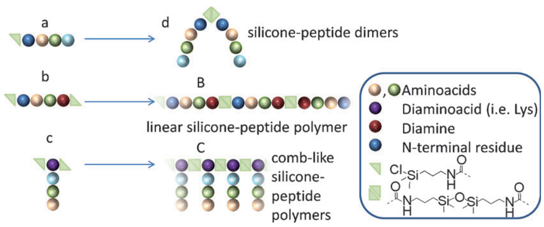


**Lighten Up**: The substrate scope of the title reaction includes (hetero)aryl chloride, bromide, and tosylate electrophiles. The versatility and potential scalability of the reported method is demonstrated by the use of either commercially available stock solutions of ammonia or ammonia gas.

## Biopolymers

S. Jebors, J. Ciccione, S. Al-Halifa,
B. Nottelet, C. Enjalbal, C. M'Kadmi,
M. Amblard, A. Mehdi,* J. Martinez,
G. Subra* **3778 – 3782**

A New Way to Silicone-Based Peptide Polymers



**Hybrid peptides**: Silicone-containing peptide polymers are obtained from hybrid hydroxydimethylsilyl peptide blocks as monomeric units. This general strategy proceeds in water and is applicable to any type of peptide, yielding linear or branched polymer chains.

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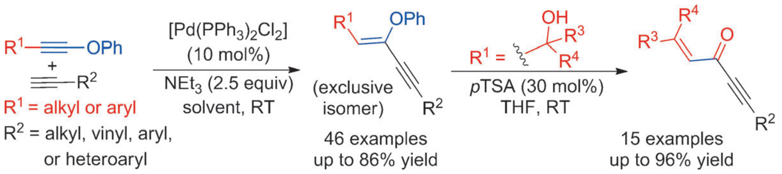
## Synthetic Methods

M. Hari Babu, V. Dwivedi, R. Kant,
M. Sridhar Reddy* **3783 – 3786**

Palladium-Catalyzed Regio- and Stereoselective Cross-Addition of Terminal Alkynes to Ynol Ethers and Synthesis of 1,4-Enyn-3-ones



**Alkyne plus alkyne**: The hydroalkynylation of phenoxy alkynes was achieved with high regio-, chemo-, and stereoselectivities. A catalytic amount of $[Pd(PPh_3)_2Cl_2]$ with 2.5 equiv. of $NEt_3$ could mediate the reaction without the need for a ligand, or a Cu catalyst for the activation of the terminal alkyne. The products with allylic hydroxy tether are convenient precursors for useful enynones. *p*TSA = *p*-toluenesulfonic acid.

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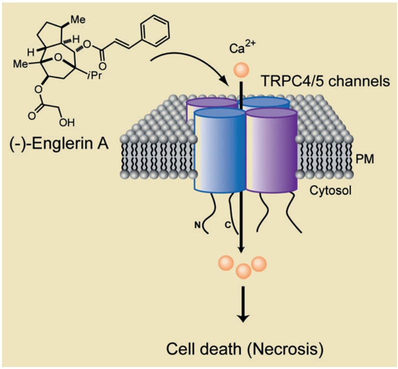
## Antitumor Agents

Y. Akbulut, H. J. Gaunt, K. Muraki,
M. J. Ludlow, M. S. Amer, A. Bruns,
N. S. Vasudev, L. Radtke, M. Willot,
S. Hahn, T. Seitz, S. Ziegler,
M. Christmann,* D. J. Beech,*
H. Waldmann* **3787 – 3791**

(−)-Englerin A is a Potent and Selective Activator of TRPC4 and TRPC5 Calcium Channels

**Natural born killer**: The sesquiterpene (−)-englerin A rapidly and selectively kills renal cancer cells through activation of calcium-permeable nonselective transient receptor potential canonical (TRPC) calcium channels. It is a highly efficient, fast-acting, potent, selective, and direct stimulator of TRPC4 and TRPC5 channels (PM = plasma membrane).



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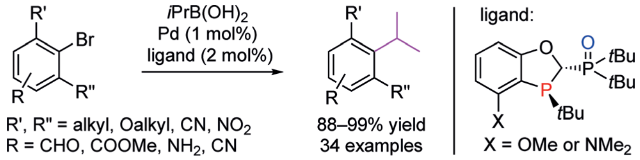
## Cross-Coupling

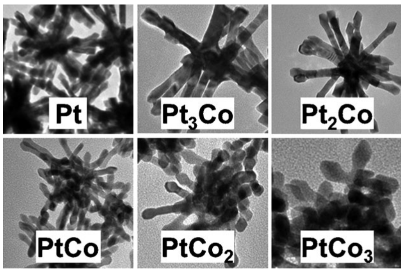
C. Li, T. Chen, B. Li, G. Xiao,
W. Tang* **3792 – 3796**

Efficient Synthesis of Sterically Hindered Arenes Bearing Acyclic Secondary Alkyl Groups by Suzuki–Miyaura Cross-Couplings



**No side reaction**: The shown bulky P,P=O ligands (right) successfully inhibit isomerization and reduction side reactions of the cross-coupling of sterically hindered substrates such as di-*ortho*-substituted aryl bromides with acyclic secondary alkylboronic acids. The method also allows the preparation of *ortho*-alkoxy di-*ortho*-substituted isopropyl arenes in excellent yields.

## Electrochemistry



**Three-dimensional** (3D) Pt–Co alloy nanostructures with tunable composition are synthesized by an effective solvothermal method. The interconnected 3D $Pt_3Co$ nanowire assembly exhibits significantly enhanced electrocatalytic activity and durability compared with commercial Pt based catalysts and a 3D Pt nanowire assembly. This is mainly attributed to the synergetic effects from composition and structural advantages.

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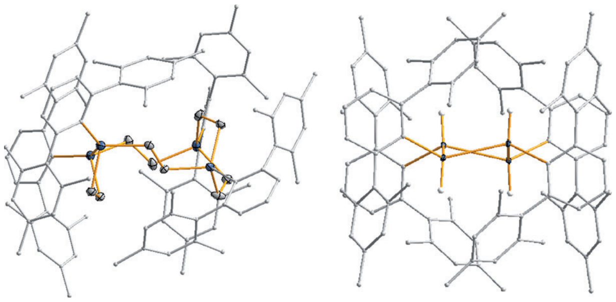
## Small Molecule Activation



**Tinned small molecules**: Reactions of the tin cluster $Sn_8(Ar^{Me_6})_4$ under mild conditions yields two new insertion compounds from incorporation of ethylene (see picture; left) or $H_2$ (right; Sn blue, C gray). These are the first reactions between a stable main-group cluster and small molecules.

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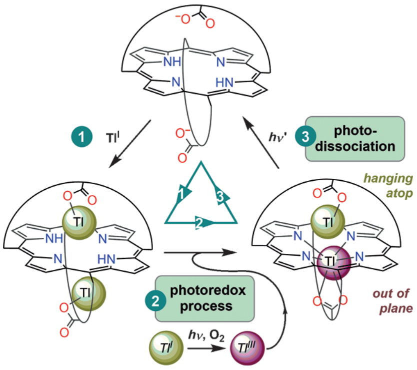
## Porphyrinoids



**Newton's cradle**: A mixed-valence thallium(III)/thallium(I) bis-strap porphyrin complex, with $Tl^{III}$ bound to the N core and $Tl^I$ attached to a strap, was generated by the addition of TlOAc to the free base and exposure to indirect sunlight. Exposure of the complex to direct sunlight leads to thallium dissociation and to the recovery of the free porphyrin.

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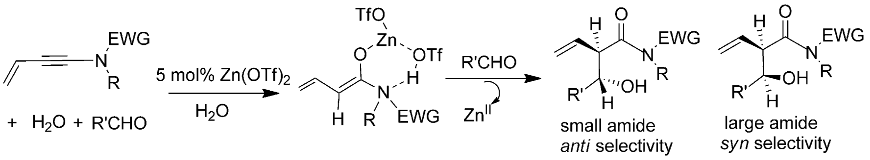
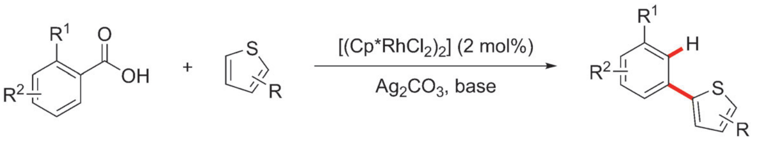
## Synthetic Methods



***EZ* switch**: The *anti* and *syn* stereoselectivity of the title reaction can be modulated by the size of the sulfonamides to yield *E*- and *Z*-configured zinc(II) dienolates selectively. This new reaction leads to enantiopure aldol products by using an inexpensive chiral sulfonamide. EWG = electron-withdrawing group.



**Who was in control?** A rhodium(III)-catalyzed carboxylic acid directed decarboxylative C–H/C–H cross-coupling of benzoic acids with thiophenes has been developed. This method provides straightforward access to biaryl scaffolds with diverse substitution patterns, many of which previously required lengthy synthetic sequences.

## *Traceless Directing Groups*

Y. Zhang, H. Zhao, M. Zhang, W. Su* ———— **3817–3821**

Carboxylic Acids as Traceless Directing Groups for the Rhodium(III)-Catalyzed Decarboxylative C–H Arylation of Thiophenes

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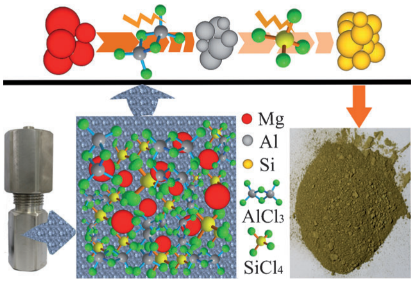

**Reduction of $SiCl_4$** with metallic Mg is realized in molten $AlCl_3$ at the low temperature of 200 °C in a stainless steel autoclave. $AlCl_3$ not only acts as a molten salt, but also participates in the reaction. The as-prepared Si nanoparticles are highly crystalline, which is highly desirable for high-performance Li-ion batteries.

## *Nanocrystalline Silicon*

N. Lin, Y. Han, L. B. Wang, J. B. Zhou, J. Zhou, Y. C. Zhu,* Y. t. Qian* ———— **3822–3825**

Preparation of Nanocrystalline Silicon from $SiCl_4$ at 200 °C in Molten Salt for High-Performance Anodes for Lithium Ion Batteries

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Supporting information is available on www.angewandte.org (see article for access details).

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

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