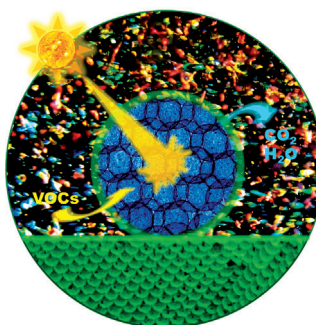


... can be used to tune the carbenoid activity of cytochrome P450 from *Bacillus megaterium*. In their Communication on page 6810 ff., F. Arnold and co-workers report the engineering of a histidine-ligated P450 enzyme that shows high catalytic activity for in vivo cyclopropanation using diazo compounds. This enzyme enables the enantioselective synthesis of a key precursor of levomilnacipran under aerobic conditions on a preparative scale. Image: Liang Zong and Yan Liang (L2Molecule.com).

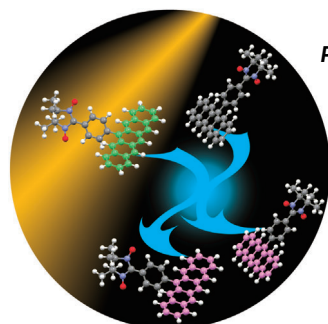
## Nanostructures

T.-O. Do and co-workers report a three-dimensional ordered assembly of thin-shell Au/TiO<sub>2</sub> hollow nanospheres in their Communication on page 6618 ff. These materials have a significantly enhanced photocatalytic activity compared to conventional nanopowders.



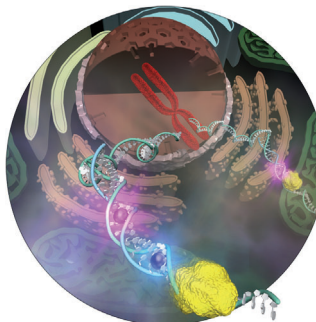
## Photophysics

In their Communication on page 6715 ff., Y. Teki et al. describe how transient absorption measurements can show that enhanced intersystem crossing and singlet fission occur in pentacene derivatives with stable radical substituents.



## Bioinorganic Chemistry

In their Communication on page 6624 ff., H. Urata and co-workers describe the incorporation of Hg<sup>II</sup> and Ag<sup>I</sup> ions into programmed sites in a DNA duplex during primer extension through the formation of T–Hg<sup>II</sup>–T and T–Ag<sup>I</sup>–C base pairs.



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6592 – 6595

## Author Profile



*"My worst nightmare is to have to suffer from more administrative nonsense.  
My biggest motivation is not the h-index, for sure. ..."*  
This and more about Carsten Bolm can be found on page 6596–6597.

Carsten Bolm ————— 6596 – 6597

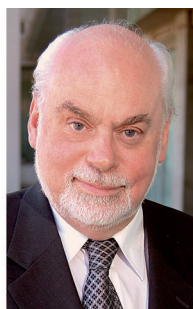
## News



G. M. Clore



G. C. Fu



J. F. Stoddart



E.-i. Negishi

New Members and Foreign Associates of the National Academy of Sciences:  
G. Marius Clore, Gregory C. Fu, Sir J. Fraser Stoddart, Ei-ichi Negishi — 6716

## Highlights

### Photochromism

J. Yoon\* ————— 6600 – 6601

Encoding Optical Signals



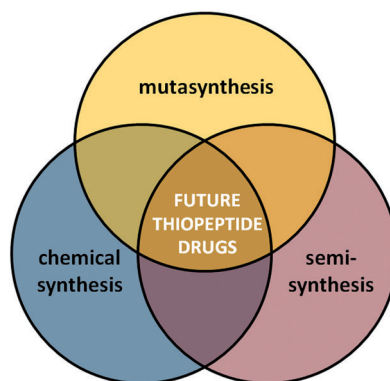
**Light up tomorrow:** A photochromic material with excellent fatigue resistance, high thermal stability, and quantitative photoswitching can be used as a linear photoswitching material to replace non-linear optical materials for encoding optical signals. Therefore, information in one light ray can be directly transmitted to another light ray without converting back to the electronic format.

## Reviews

### Thiopeptide Antibiotics

X. Just-Baringo, F. Albericio,  
M. Álvarez\* ————— 6602 – 6616

Thiopeptide Engineering: A  
Multidisciplinary Effort towards Future  
Drugs



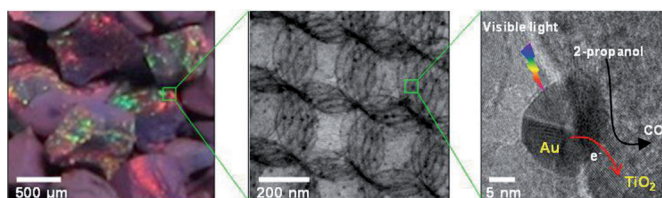
**Making a complement:** Modification of the structure of thiopeptides has produced numerous analogues that overcome some of their inherent limitations. The combined use of chemical synthesis, semisynthesis, and biosynthetic pathway engineering will allow the development of future thiopeptide-based drugs.

## Communications

### Nanostructures

C.-T. Dinh, H. Yen, F. Kleitz,  
T.-O. Do\* ————— 6618 – 6623

Three-Dimensional Ordered Assembly of  
Thin-Shell Au/TiO<sub>2</sub> Hollow Nanospheres  
for Enhanced Visible-Light-Driven  
Photocatalysis



**Order makes a difference:** A three-dimensional ordered assembly of thin-shell Au/TiO<sub>2</sub> hollow nanospheres exhibits not only a very high surface area but also photonic behavior and multiple light scattering. The designed materials show

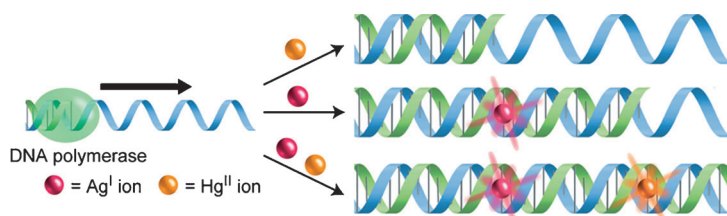
significantly enhanced visible-light absorption and a visible-light-driven photocatalytic activity several times higher than those of conventional Au/TiO<sub>2</sub> nanopowders.

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**(Quick) silver DNA:** Hg<sup>II</sup> and Ag<sup>I</sup> ions were found to specifically trigger DNA polymerase catalyzed primer extension in the absence of a Watson–Crick matched nucleotide through the formation of

T–Hg<sup>II</sup>–T and newly discovered C–Ag<sup>I</sup>–T base pairs. The strict base recognition by the metal ions enabled regulated incorporation of the two different metal ions into programmed sites in duplex DNA.

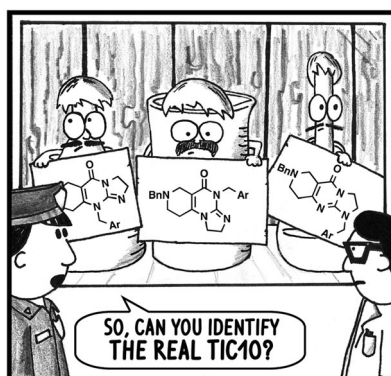
## Bioinorganic Chemistry

T. Funai, J. Nakamura, Y. Miyazaki, R. Kiri, O. Nakagawa, S. Wada, A. Ono, H. Urata\* — 6624–6627

Regulated Incorporation of Two Different Metal Ions into Programmed Sites in a Duplex by DNA Polymerase Catalyzed Primer Extension

Back Cover

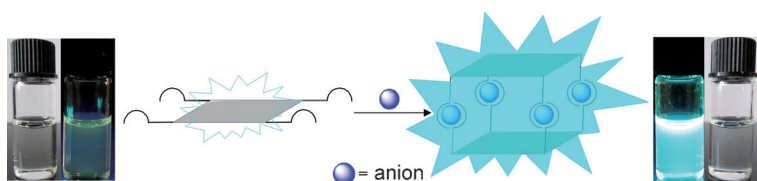
**Setting the record straight:** An investigation of an imidazolinopyrimidinone (TIC10) reported to induce expression of the immunosurveillance cytokine TRAIL led to a constitutional reassignment of the active pharmacophore. Analysis of TRAIL induction in macrophages revealed the reported structure to be inactive. The structural identity of the active compound was established. The active compound was then synthesized and its activity confirmed.



## Antitumor Agents

N. T. Jacob, J. W. Lockner, V. V. Kravchenko, K. D. Janda\* — 6628–6631

Pharmacophore Reassignment for Induction of the Immunosurveillance Cytokine TRAIL



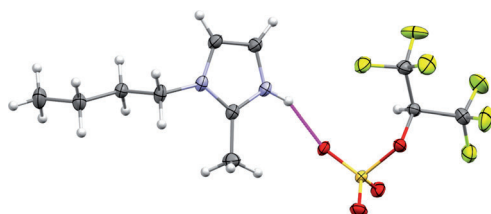
**Phosphate ions in a bind:** The tetrakis-(bisurea)-decorated tetraphenylethene (TPE) displays fluorescence “turn-on” over a wide concentration range upon phosphate coordination. The fluorescence enhancement can be attributed to the

restriction of the intramolecular rotation of TPE by anion coordination. This “anion-coordination-induced emission” (ACIE) is another approach for fluorescence turn-on.

## Anion Coordination

J. Zhao, D. Yang, Y. Zhao, X.-J. Yang, Y.-Y. Wang, B. Wu\* — 6632–6636

Anion-Coordination-Induced Turn-On Fluorescence of an Oligoureafunctionalized Tetraphenylethene in a Wide Concentration Range



**A new Superacid?** The novel Brønsted acid hfpOSO<sub>3</sub>H (hfp = C(H)(CF<sub>3</sub>)<sub>2</sub>) was prepared on the kilogram scale. In the gas phase, it is more acidic than sulfuric acid by ten orders of magnitude. Furthermore,

this acid may be used for the synthesis of air- and moisture-stable protic ionic liquids of low viscosity and high conductivity.

## Sulfur Oxoacids

W. Beichel, J. M. U. Panzer, J. Häty, X. Ye, D. Himmel, I. Krossing\* — 6637–6640

Straightforward Synthesis of the Brønsted Acid hfpOSO<sub>3</sub>H and its Application for the Synthesis of Protic Ionic Liquids

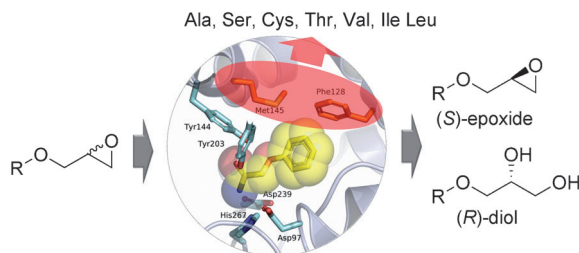


## Enzyme Catalysis

X.-D. Kong, Q. Ma, J. Zhou,\* B.-B. Zeng,\*  
J.-H. Xu\* ————— 6641 – 6644



A Smart Library of Epoxide Hydrolase Variants and the Top Hits for Synthesis of (S)- $\beta$ -Blocker Precursors



**Hot pockets:** Microtuning of the enzyme active pocket gives a smart library of epoxide hydrolase variants with an expanded substrate spectrum covering a series of typical  $\beta$ -blocker precursors.

Improved activities of 6- to 430-fold were achieved by redesigning the active site at two predicted hot spots, and enhanced activity toward bulky substrates was found.

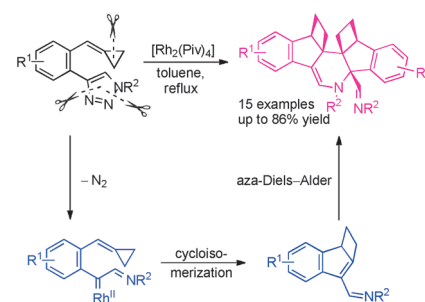
## Nitrogen Heterocycles

K. Chen, Z.-Z. Zhu, Y.-S. Zhang,  
X.-Y. Tang,\* M. Shi\* ————— 6645 – 6649



Rhodium(II)-Catalyzed Intramolecular Cycloisomerizations of Methylene cyclopropanes with *N*-Sulfonyl 1,2,3-Triazoles

The azavinyl rhodium carbenes derived from *N*-sulfonyl triazole methylenecyclopropanes were found to be very reactive in the divergent synthesis of *N*-containing heterocycles. Different types of cycloisomerizations were observed depending on the substrates. Derivatization of the products easily gave a series of diazabicyclo[3.2.1]octane derivatives. Bs = bromobenzenesulfonyl, Ms = methanesulfonyl, Piv = pivalate, Ts = 4-toluenesulfonyl.

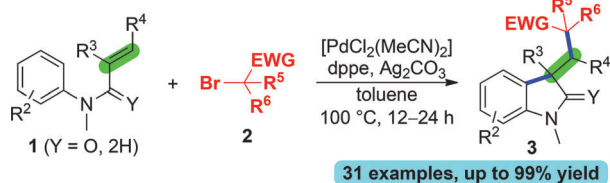


## Cross-Coupling

J.-H. Fan, W.-T. Wei, M.-B. Zhou,  
R.-J. Song, J.-H. Li\* ————— 6650 – 6654



Palladium-Catalyzed Oxidative Difunctionalization of Alkenes with  $\alpha$ -Carbonyl Alkyl Bromides Initiated through a Heck-type Insertion: A Route to Indolin-2-ones



**Indolinone synthesis:** A new palladium-catalyzed oxidative difunctionalization reaction of *N*-arylalkenes with primary, secondary, and tertiary  $\alpha$ -carbonyl alkyl bromides proceeds through a radical process and provides indolin-2-ones in

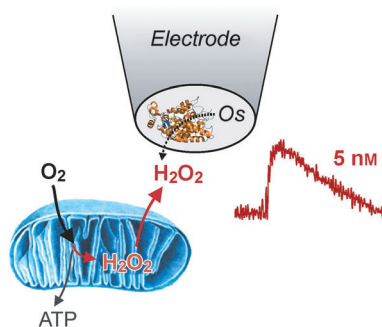
moderate to excellent yields. The reaction is initiated by a Heck insertion followed by interception of the  $\sigma$ -alkyl palladium(II) intermediate with aryl C(sp<sup>2</sup>)–H bonds. dppe = 1,2-bis(diphenylphosphino)-ethane.

## Detecting H<sub>2</sub>O<sub>2</sub> from Mitochondria

E. Suraniti, S. Ben-Amor, P. Landry,  
M. Rigoulet, E. Fontaine, S. Bottari,  
A. Devin, N. Sojic, N. Mano,\*  
S. Arbault\* ————— 6655 – 6658

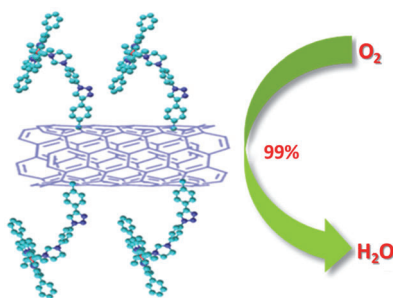


Electrochemical Monitoring of the Early Events of Hydrogen Peroxide Production by Mitochondria



**Ultrasensitive biosensors for H<sub>2</sub>O<sub>2</sub>** (1 nM limit of detection) have been developed based on peroxidase-redox polymer modified carbon electrodes (see figure; Os = polymer-bound osmium complex). They allow the monitoring of several regimes of H<sub>2</sub>O<sub>2</sub> release by mitochondria. In particular, unprecedented nanomolar-amplitude bursts of H<sub>2</sub>O<sub>2</sub> have been detected. The results offer opportunities to study the role of mitochondria as a hub of redox signaling in cells.

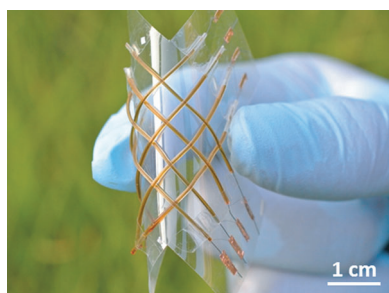
**Bio-inspired catalyst defeats Pt:** A bio-mimetic electrocatalyst for the oxygen reduction reaction (ORR) has been covalently grafted onto multiwalled carbon nanotubes. Without pyrolysis, this bio-inspired catalyst, in which an axial imidazole-coordinated porphyrin mimics the active site of O<sub>2</sub>-activating heme-containing enzymes, shows superior ORR activity and stability compared to the state-of-the-art Pt/C catalyst in both acidic and alkaline solutions.



### Oxygen Reduction

P.-J. Wei, G.-Q. Yu, Y. Naruta, J.-G. Liu\* **6659–6663**

Covalent Grafting of Carbon Nanotubes with a Biomimetic Heme Model Compound To Enhance Oxygen Reduction Reactions

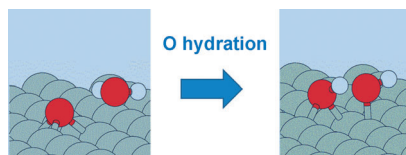


**Twisted:** A wire-shaped energy device that can perform photoelectric conversion and electrochemical storage was developed through a simple but effective twisting process. The energy wire exhibited a high energy conversion efficiency of 6.58% and specific capacitance of 85.03  $\mu\text{F cm}^{-1}$  or 2.13  $\text{mF cm}^{-2}$ , and the two functions were alternately realized without sacrificing either performance.

### Energy Conversion

H. Sun, X. You, J. Deng, X. Chen, Z. Yang, P. Chen, X. Fang, H. Peng\* **6664–6668**

A Twisted Wire-Shaped Dual-Function Energy Device for Photoelectric Conversion and Electrochemical Storage

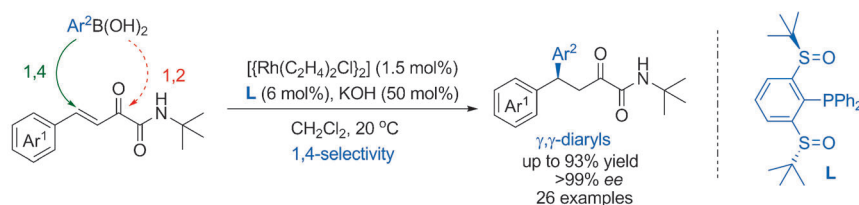


**Hydrogen fuel cell:** The oxygen reduction reaction (ORR) kinetics can be strongly accelerated by changing the solvent and its dielectric constant, a possibly general effect in electrochemical systems. The influence of the solvent dielectric constant on the reaction barriers of the ORR is studied by density functional theory (see picture).

### Oxygen Reduction

A. Fortunelli,\* W. A. Goddard,\* Y. Sha, T. H. Yu, L. Sementa, G. Barcaro, O. Andreussi **6669–6672**

Dramatic Increase in the Oxygen Reduction Reaction for Platinum Cathodes from Tuning the Solvent Dielectric Constant



**Constructing chiral carbonyls:** A simple new chiral sulfonamidophosphine ligand **L** was developed, which promoted excellent 1,4-selectivities and enantioselectivities in the rhodium-catalyzed conjugate addition of

arylboronic acids to  $\beta,\gamma$ -unsaturated  $\alpha$ -ketoamides. The desired  $\gamma,\gamma$ -diaryl- $\alpha$ -ketocarbonyl compounds were afforded with high yields and high optical purities.

### Asymmetric Catalysis

J. J. Wang, M. Wang, P. Cao, L. Y. Jiang, G. H. Chen, J. Liao\* **6673–6677**

Rhodium-Catalyzed Asymmetric Arylation of  $\beta,\gamma$ -Unsaturated  $\alpha$ -Ketoamides for the Construction of Nonracemic  $\gamma,\gamma$ -Diarylcarbonyl Compounds

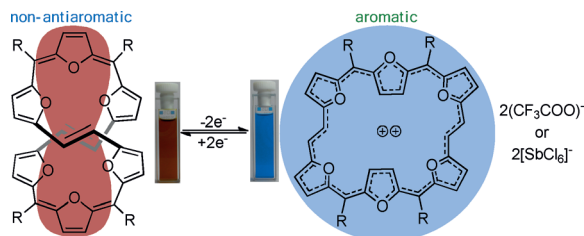


## Antiaromaticity

T. Y. Gopalakrishna,  
V. G. Anand\* 6678–6682



Reversible Redox Reaction Between  
Antiaromatic and Aromatic States of  
32 $\pi$ -Expanded Isophlorins



**Pi redox:** Expanded isophlorins can undergo reversible two-electron redox reactions to interconvert between 32 $\pi$ -antiaromatic and 30 $\pi$ -aromatic states. trifluoroacetic acid, Et<sub>3</sub>O<sup>+</sup>SbCl<sub>6</sub><sup>−</sup>, or NOBF<sub>4</sub> and triethylamine, zinc, or FeCl<sub>2</sub>

can be employed as oxidizing and reducing agents, respectively. This reversible redox process can also regulate the topology between a figure-eight and planar conformation.

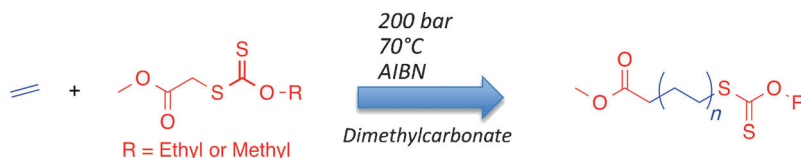


## Polymerization

C. Dommanget, F. D'Agosto,\*  
V. Monteil\* 6683–6686



Polymerization of Ethylene through  
Reversible Addition–Fragmentation Chain  
Transfer (RAFT)



**Controlled growth:** Xanthates were employed as controlling agents in the radical polymerization of ethylene (see scheme). The reversible addition–frag-

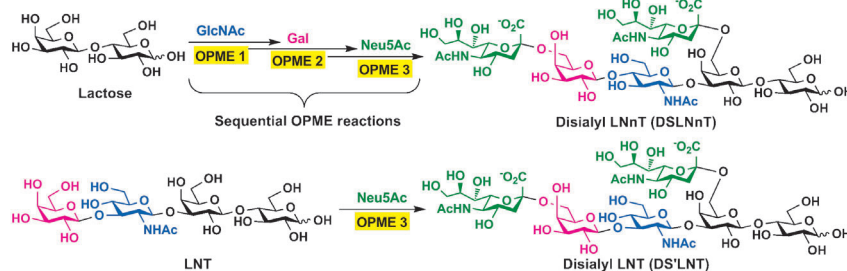
mentation chain-transfer technique proceeds under relatively mild reaction conditions ( $T = 70^\circ\text{C}$ ,  $P = 200\text{ bar}$ ). AIBN = 2,2'-azobisisobutyronitrile.

## Enzymatic Synthesis

H. Yu, K. Lau, V. Thon, C. A. Autran,  
E. Jantscher-Krenn, M. Xue, Y. Li,  
G. Sugiarto, J. Qu, S. Mu, L. Ding, L. Bode,  
X. Chen\* 6687–6691



Synthetic Disialyl Hexasaccharides  
Protect Neonatal Rats from Necrotizing  
Enterocolitis



**Sweet protection:** Two novel synthetic disialyl hexaoses obtained by highly efficient one-pot multienzyme (OPME) reactions were shown to protect neonatal rats from necrotizing enterocolitis (see

scheme; GlcNAc: *N*-acetylglucosamine; Gal: galactose; Neu5Ac: *N*-acetylneuraminic acid; DSLNT: disialyllacto-*N*-neotetraose; LNT: lacto-*N*-tetraose; DS'LNT:  $\alpha$ 2–6-linked disialyllacto-*N*-tetraose).

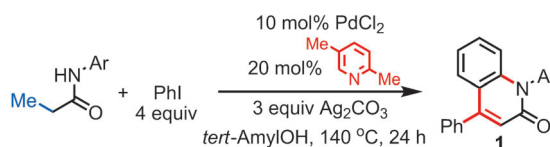


## Cascade C–H Activation

Y. Deng, W. Gong, J. He,  
J.-Q. Yu\* 6692–6695

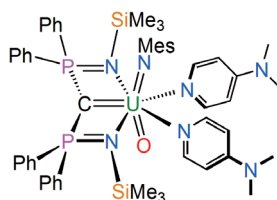


Ligand-Enabled Triple C–H Activation  
Reactions: One-Pot Synthesis of Diverse  
4-Aryl-2-quinolinones from  
Propionamides



**Building complexity:** Diverse 4-aryl-2-quinolinones such as **1** are prepared from propionamides in one pot by pyridine ligand-promoted triple sequential C–H activation reactions and a stereospecific

Heck reaction. In these cascade reactions, three new C–C bonds and one C–N bond are formed to rapidly build molecular complexity from propionic acid.

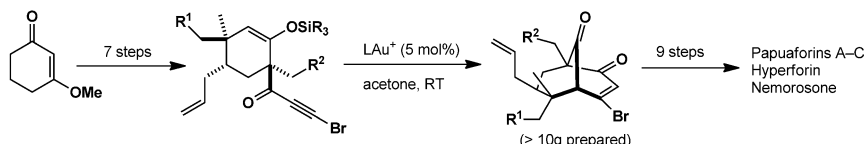


**Three not of a kind:** An unprecedented arrangement of three formal multiply bonded ligands to one metal center, where the coordinated heteroatoms derive from different element groups, is found in the uranium(VI) carbene imido oxo complex  $[U(BIPM^{TMS})(NMe_5)(O)(DMAP)_2]$  (Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>).

### Metal–Ligand Multiple Bonds

E. Lu, O. J. Cooper, J. McMaster, F. Tuna, E. J. L. McInnes, W. Lewis, A. J. Blake, S. T. Liddle\* ————— **6696–6700**

Synthesis, Characterization, and Reactivity of a Uranium(VI) Carbene Imido Oxo Complex



**Five gold rings:** The concise total syntheses of the polyprenylated polycyclic acylphloroglucinols (PPAPs) hyperforin and papuaforins A–C, and the formal synthesis of nemorosone have been realized in 17 steps. Key to the realization of these

syntheses is the short and scalable assembly of densely substituted PPAP scaffolds through a gold(I)-catalyzed 6-endo-dig carbocyclization of cyclic silyl-enol ethers.

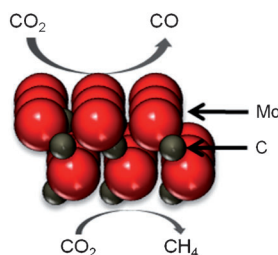
### Total Synthesis

G. Bellavance, L. Barriault\* ————— **6701–6704**

Total Syntheses of Hyperforin and Papuaforins A–C, and Formal Synthesis of Nemorosone through a Gold(I)-Catalyzed Carbocyclization



**Active, selective, and cheap:** Mo<sub>2</sub>C and cobalt-modified Mo<sub>2</sub>C were both shown to be effective catalysts for CO<sub>2</sub> conversion by hydrogen in flow reactor experiments over powder catalysts. In-situ XANES measurements verified that Mo<sub>2</sub>C can undergo an oxidation-carburization cycle. Modifying Mo<sub>2</sub>C with small amounts of cobalt further improved catalytic performance.



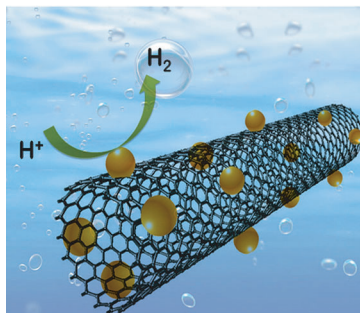
### Heterogeneous Catalysis

M. D. Porosoff, X. Yang, J. A. Boscoboinik, J. G. Chen\* ————— **6705–6709**

Molybdenum Carbide as Alternative Catalysts to Precious Metals for Highly Selective Reduction of CO<sub>2</sub> to CO



**A nanohybrid** that consists of carbon nanotubes decorated with CoP nanocrystals (CoP/CNT) was prepared by the low-temperature phosphidation of a Co<sub>3</sub>O<sub>4</sub>/CNT precursor. As a novel non-noble-metal hydrogen-evolution electrocatalyst that operates in acidic media, this nanohybrid exhibits an onset overpotential of only 40 mV and maintained its catalytic activity for at least 18 hours.



### Hydrogen-Evolution Catalysts

Q. Liu, J. Tian, W. Cui, P. Jiang, N. Cheng, A. M. Asiri, X. Sun\* ————— **6710–6714**

Carbon Nanotubes Decorated with CoP Nanocrystals: A Highly Active Non-Noble-Metal Nanohybrid Electrocatalyst for Hydrogen Evolution





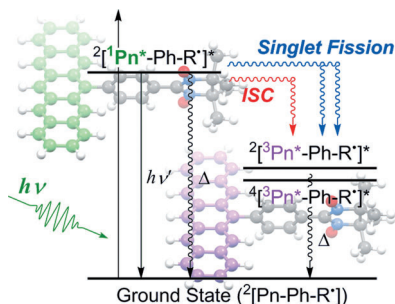
## Photophysics

A. Ito, A. Shimizu, N. Kishida,  
Y. Kawanaka, D. Kosumi, H. Hashimoto,  
Y. Teki\* 6715–6719



Excited-State Dynamics of Pentacene  
Derivatives with Stable Radical  
Substituents

**The state of play:** Enhanced intersystem crossing (ISC) and singlet fission have been shown to occur in pentacene (Pn) derivatives with stable radical substituents. These effects result in the ultrafast formation of a triplet excited state in the pentacene moiety from a photoexcited singlet state, even in dilute solution. The excited-state dynamics of the derivatives were evaluated in detail through transient absorption measurements.

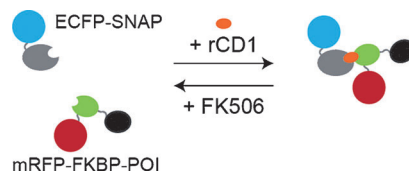


## Inside Back Cover



## Molecular Switches

S. Feng, V. Laketa, F. Stein, A. Rutkowska,  
A. MacNamara, S. Depner, U. Klingmüller,  
J. Saez-Rodriguez,  
C. Schultz\* 6720–6723



**Little helper:** Chemical dimerizers are powerful tools for manipulation of enzyme activities in intact cells. The first rapidly reversible chemical dimerization system is introduced, which permits to determine kinetics of lipid metabolizing enzymes in living cells. This new method was applied to induce and stop phosphatidylinositol 3-kinase activity, allowing to quantitatively measure 3,4,5-trisphosphate turnover.



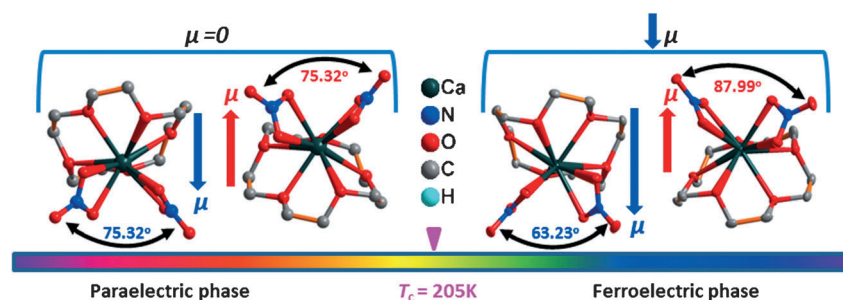
A Rapidly Reversible Chemical Dimerizer  
System to Study Lipid Signaling in Living  
Cells

## Coordination Distortion

H.-Y. Ye, Y. Zhang, D.-W. Fu,  
R.-G. Xiong\* 6724–6729



A Displacive-Type Metal Crown Ether  
Ferroelectric Compound:  
 $\text{Ca}(\text{NO}_3)_2(15\text{-crown-5})$



**Following the Curie** symmetry principle and Aizu rule, it was discovered there is a paraelectric-to-ferroelectric phase transition in  $\text{Ca}(\text{NO}_3)_2(15\text{-crown-5})$  at  $T_c = 205\text{ K}$ , which was confirmed by calorim-

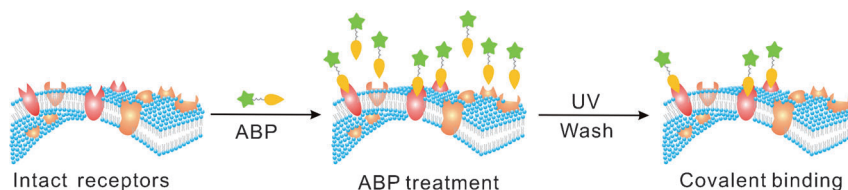
etry and second harmonic generation measurements. The ferroelectric mechanism is attributable to distortion of the coordination of the central Ca atom.

## Single-Cell Proteomics

F. Xu, H. Zhao, X. Feng, L. Chen, D. Chen,  
Y. Zhang, F. Nan,\* J. Liu,\*  
B.-F. Liu\* 6730–6733

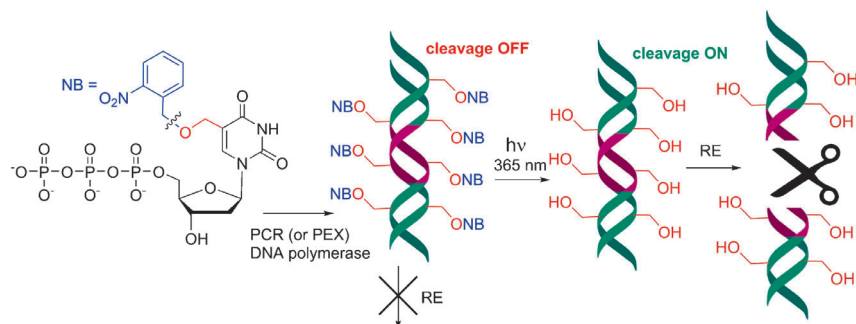


Single-Cell Chemical Proteomics with an  
Activity-Based Probe: Identification of  
Low-Copy Membrane Proteins on Primary  
Neurons



**Singles only:** A single-cell chemical proteomics strategy with an activity-based probe (ABP) enables observation of low-abundance membrane receptors at the single-cell level by discriminating them

from the whole proteome. The strategy avoids problems associated with cytometry-based techniques, and could be used to identify low-copy receptors on the primary neurons of animals.



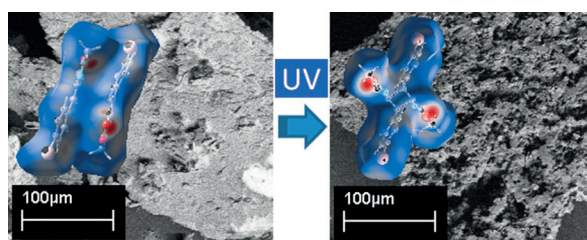
**Stability:** A modified nucleoside triphosphate is incorporated into DNA sequences using polymerase. The resulting photocaged DNA is resistant against cleavage

by restriction endonucleases (REs) and fully replicable by polymerase chain reaction (PCR) or primer extension (PEX).

## Photocaged DNA

Z. Vaníková, M. Hocek\* — 6734–6737

Polymerase Synthesis of Photocaged DNA Resistant against Cleavage by Restriction Endonucleases



**Changing phases:** In the course of solid-state photoreactions, the single crystal of a reactant can be transformed into a single crystal of the product or it can become amorphous. Between these sce-

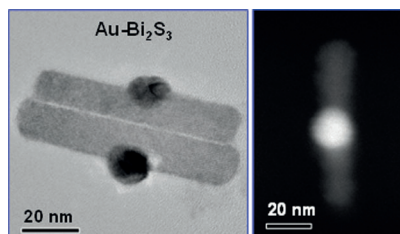
narios exist the reconstructive phase transformations, where the single crystal becomes a powder. A detailed description of the latter is given.

## Photoreconstructions

T. Runčevski,\* M. Blanco-Lomas, M. Marazzi, M. Cejuela, D. Sampedro,\* R. E. Dinnebier — 6738–6742

Following a Photoinduced Reconstructive Phase Transformation and its Influence on the Crystal Integrity: Powder Diffraction and Theoretical Study

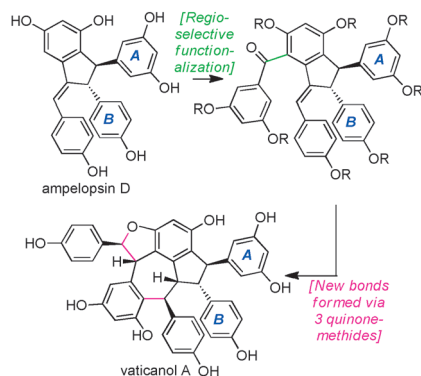
**Promising returns of gold on the side:** In a designed Au–Bi<sub>2</sub>S<sub>3</sub> heteronanostructure photocatalyst, Au nanoparticles were located at the center of the semiconductor nanorods (see picture), rather than at the tip, as usually reported. These nanostructures were found to be efficient visible-light photocatalysts and to have excellent photocurrent and photoresponse properties.



## Nanostructures

G. Manna, R. Bose, N. Pradhan\* — 6743–6746

Photocatalytic Au–Bi<sub>2</sub>S<sub>3</sub> Heteronanostructures



**Three's Company:** The resveratrol trimer vaticanol A, along with a number of diastereomeric congeners, has been synthesized for the first time through an effective strategy utilizing three reactive quinone methide intermediates to forge three critical bonds (highlighted in pink). These events, one of which succeeded only under very specific conditions, expediently generated its [7,5]-carbocyclic core and afforded a unique sequence for dihydrobenzofuran formation.

## Natural Product Synthesis

T. H. Jepsen, S. B. Thomas, Y. Lin, C. I. Stathakis, I. de Miguel, S. A. Snyder\* — 6747–6751

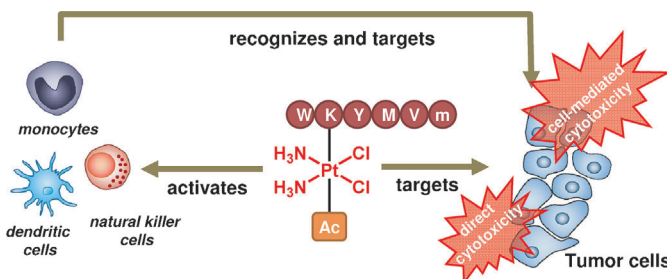
Harnessing Quinone Methides: Total Synthesis of (±)-Vaticanol A

## Anticancer Drugs

D. Y. Q. Wong, C. H. F. Yeo,  
W. H. Ang\* 6752–6756



Immuno-Chemotherapeutic Platinum(IV)  
Prodrugs of Cisplatin as Multimodal  
Anticancer Agents



**Two-pronged attack:** A cisplatin prodrug was developed with the ability to induce cancer cell death through two distinct pathways, targeted direct cytotoxicity and activation of innate immune cells for cell-

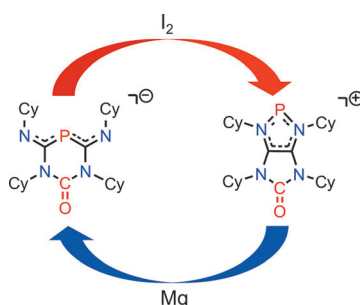
mediated cytotoxicity, to realize the concept of a multimodal immuno-chemo-therapeutic approach (see figure; m: D-Met).

## Phosphorus Heterocycles

D. Heift, Z. Benkő,\*  
H. Grützmacher\* 6757–6761



Redox-Triggered Reversible  
Interconversion of a Monocyclic and  
a Bicyclic Phosphorus Heterocycle



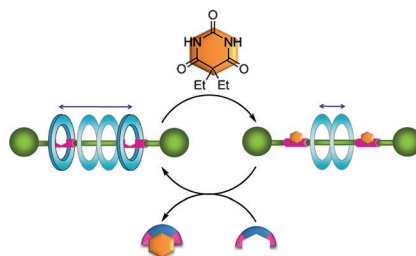
**Turning a negative into a positive:** The fully reversible conversion between an anionic six-membered phosphorus–nitrogen heterocycle and a bicyclic diazaphospholenium cation as stable redox states leads to an “umpolung” of the electronic properties which is of interest for smart materials.

## Rotaxanes

A. Martinez-Cuezva, J. Berna,\*  
R.-A. Orenes, A. Pastor,  
M. Alajarin 6762–6767



Small-Molecule Recognition for  
Controlling Molecular Motion in  
Hydrogen-Bond-Assembled Rotaxanes



**A “narcotic” effect** of barbitol on the Brownian motion of novel [2]rotaxanes with two di(acetylamino)pyridine binding sites was observed: The establishment of hydrogen-bond arrays with barbitol caused dynamic restraint of the ring shuttling (see picture). The original translational motion was reestablished by a competitive recognition event with an external barbitol binder.

## DNA Replication

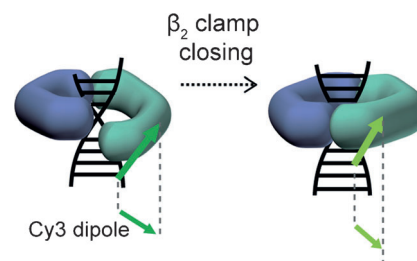


W.-K. Cho, S. Jergic, D. Kim, N. E. Dixon,  
J.-B. Lee\* 6768–6771



Loading Dynamics of a Sliding DNA  
Clamp

**When one clamp closes...** Single-molecule Förster resonance energy transfer and single-molecule fluorescence polarization were used to monitor the loading of a sliding DNA clamp onto double-stranded DNA by the clamp loader (see picture). Thus, the dynamic features of a DNA clamp in the DNA/DNA-clamp/clamp-loader ternary complex were revealed.





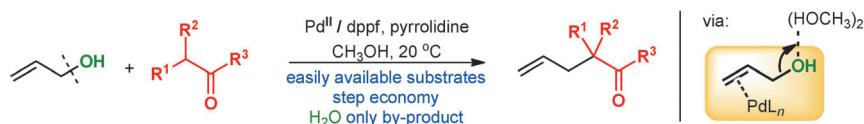
**Bull's eye!** An activatable photosensitizer capable of specifically inducing the death of  $\beta$ -galactosidase-expressing cells in response to light irradiation was developed. Reaction with the enzyme resulted

in a dynamic structural change to the phototoxic open form (see scheme), thus enabling the specific ablation of cells of interest in living tissues.

### Targeted Cell Ablation

Y. Ichikawa, M. Kamiya, F. Obata, M. Miura, T. Terai, T. Komatsu, T. Ueno, K. Hanaoka, T. Nagano, Y. Urano\* — 6772 – 6775

Selective Ablation of  $\beta$ -Galactosidase-Expressing Cells with a Rationally Designed Activatable Photosensitizer



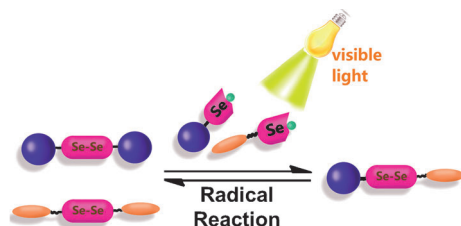
**Concerted action:** Allylic alcohols were directly used in the title reaction under mild conditions. The reaction smoothly proceeds by the concerted action of a Pd catalyst, a pyrrolidine co-catalyst, and a hydrogen-bonding solvent, and does not

require any additional reagents. A computational study suggested that methanol plays a crucial role in the formation of the  $\pi$ -allylpalladium complex by lowering the activation barrier.

### Homogeneous Catalysis

X. Huo, G. Yang, D. Liu, Y. Liu, I. D. Gridnev,\* W. Zhang\* — 6776 – 6780

Palladium-Catalyzed Allylic Alkylation of Simple Ketones with Allylic Alcohols and Its Mechanistic Study



**Diselenide bonds** are dynamic covalent bonds. Their metathesis can be induced by irradiation with visible light and likely proceeds through a radical mechanism, as the exchange reaction between two

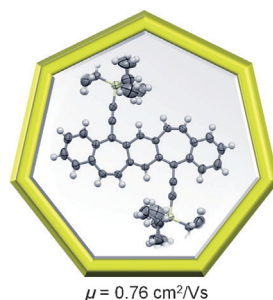
different diselenides was suppressed by the addition of the radical scavenger 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO).

### Dynamic Covalent Bonds

S. Ji, W. Cao, Y. Yu, H. Xu\* — 6781 – 6785

Dynamic Diselenide Bonds: Exchange Reaction Induced by Visible Light without Catalysis

**All sixes and sevens:** A new class of conjugated polycyclic molecules have a nearly flat  $\text{C}_6$ - $\text{C}_7$ - $\text{C}_6$ - $\text{C}_7$ - $\text{C}_6$  polycyclic framework with a *p*-quinodimethane core. With a field-effect mobility of up to  $0.76 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  as measured from solution-processed thin-film transistors, these molecules are alternatives to the pentacene analogues for application in organic electronic devices.



### Conjugated Polycycles

X. Yang, D. Liu, Q. Miao\* — 6786 – 6790

Heptagon-Embedded Pentacene: Synthesis, Structures, and Thin-Film Transistors of Dibenzo[*d,d'*]benzo[1,2-*a*:4,5-*a'*]dicycloheptenes

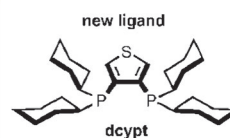


## C–O Activation

R. Takise, K. Muto, J. Yamaguchi,\*  
K. Itami\* 6791 – 6794



Nickel-Catalyzed  $\alpha$ -Arylation of Ketones  
with Phenol Derivatives



**The nickel-catalyzed  $\alpha$ -arylation** of ketones with readily available phenol derivatives (esters and carbamates) provides access to useful  $\alpha$ -arylated ketones. The use of 3,4-bis(dicyclohexylphosphino)thiophene

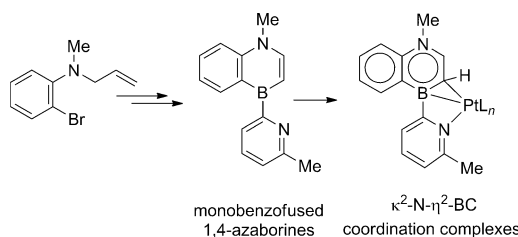
(dcypt) as an air-stable ligand enables this transformation. The intermediate of an assumed C–O oxidative addition was isolated and characterized by X-ray crystal-structure analysis.

## BN Heterocycles

S. Xu, F. Haefner, B. Li, L. N. Zakharov,  
S.-Y. Liu\* 6795 – 6799



Monobenzofused 1,4-Azaborines:  
Synthesis, Characterization, and  
Discovery of a Unique Coordination Mode



**Breaking N-BC News:** The first general synthesis of boron-substituted monobenzofused 1,4-azaborines has been devel-

oped. As part of the synthetic investigations, a unique  $\kappa^2$ -N- $\eta^2$ -BC coordination mode was discovered and investigated.

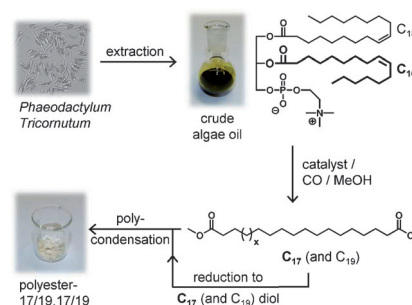
## Chemicals from Algae

P. Roesle, F. Stempfle, S. K. Hess,  
J. Zimmerer, C. Río Bártulos, B. Lepetit,  
A. Eckert, P. G. Kroth,\*  
S. Mecking\* 6800 – 6804



Synthetic Polyester from Algae Oil

**Algae as feedstock:** Crude algae oil from the strain *Phaeodactylum tricornutum* was transformed into polycondensation-grade purity monomers and thus utilized as feedstock for the production of an algae oil based polyester.

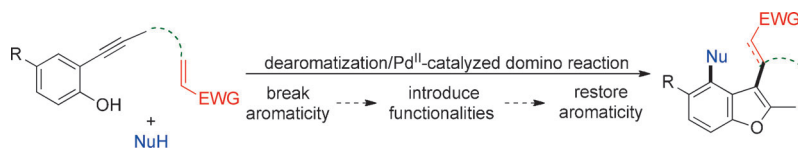


## Synthetic Methods

Z. Han, L. Zhang, Z. Li,\*  
R. Fan\* 6805 – 6809

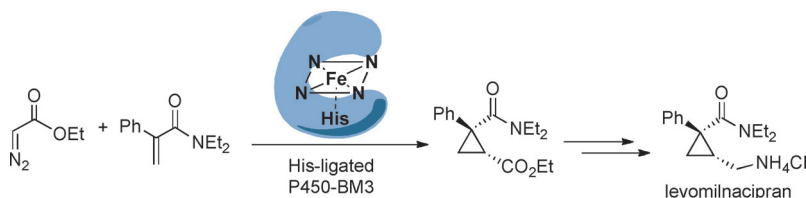


Direct Assembly of 3,4-Difunctionalized  
Benzofurans and Polycyclic Benzofurans  
by Phenol Dearomatization and  
Palladium-Catalyzed Domino Reaction



**Destruction and reconstruction:** The combination of a hypervalent-iodine-mediated oxidative dearomatization and palladium-catalyzed domino reaction

provides a practical approach to 3,4-difunctionalized benzofurans and polycyclic benzofurans from 2-alkynylphenols.



**Old cytochrome, new tricks:** Mutation of the proximal Cys residue in the cytochrome P450 enzyme from *Bacillus megaterium* (P450-BM3) leads to highly active, oxygen tolerant, and enantioselective cat-

alysts for the cyclopropanation of N,N-diethyl-2-phenylacrylamide. Directed evolution of a histidine-ligated P450-BM3 enabled the enantioselective formal synthesis of levomilnacipran.

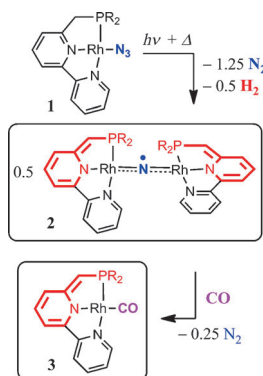
## Biocatalysis

Z. J. Wang, H. Renata, N. E. Peck, C. C. Farwell, P. S. Coelho, F. H. Arnold\* **6810–6813**

Improved Cyclopropanation Activity of Histidine-Ligated Cytochrome P450 Enables the Enantioselective Formal Synthesis of Levomilnacipran

Front Cover

**The first isolated nitridyl radical** ( $\cdot\text{N}^{2-}$ ) complex was obtained by photochemical activation of the rhodium–azide complex [(PNNH)Rh(N<sub>3</sub>)] (**1**), producing N<sub>2</sub>, H<sub>2</sub>, and the paramagnetic complex **2**. Complex **2** reacts selectively with CO to produce complex **3**, presumably by N,N-coupling of nitridyl radicals.

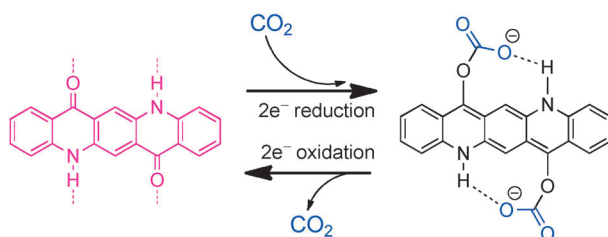


## Rhodium–Nitridyl Complex

Y. Gloaguen, C. Rebreyend, M. Lutz, P. Kumar, M. Huber, J. I. van der Lugt, S. Schneider,\* B. de Bruin\* **6814–6818**

An Isolated Nitridyl Radical-Bridged {Rh(N<sup>•</sup>)Rh} Complex

Inside Cover



**Capture and release:** The established industrial colorant quinacridone reacts with CO<sub>2</sub> following electrochemical reduction, with an uptake efficiency of

4.6 mmol CO<sub>2</sub>/g quinacridone at room temperature. The CO<sub>2</sub> can be released by electrochemical oxidation.

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

D. H. Apaydin,\* E. D. Głowacki, E. Portenkirchner, N. S. Sariciftci **6819–6822**

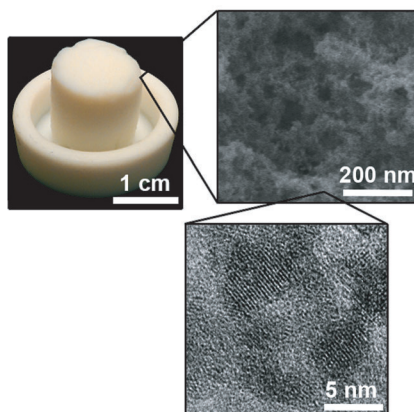
Direct Electrochemical Capture and Release of Carbon Dioxide Using an Industrial Organic Pigment: Quinacridone

**BaTiO<sub>3</sub> Aerogels**

F. Rechberger, F. J. Heiligt, M. J. Süess,  
M. Niederberger\* — 6823 – 6826



Assembly of BaTiO<sub>3</sub> Nanocrystals into  
Macroscopic Aerogel Monoliths with  
High Surface Area



**Bridging length scales:** A powerful strategy of assembling surface-functionalized nanocrystalline BaTiO<sub>3</sub> particles into a highly porous macroscopic framework is presented. After supercritical drying, the obtained structures show a large surface area and a low density. By starting off with functional building blocks on the nano-scale and ending with a body in the centimeter range, over seven orders of magnitude in length scales are addressed.



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



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picture (front or back cover, and inside  
or outside).



A video clip is available as Supporting  
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(see article for access details).



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



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have chosen on the basis of the referee  
reports to be of particular importance for  
an intensely studied area of research.