



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

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

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

Y. H. Kim, S. Banta\*

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

A. Bonet, C. Pubill-Ulldemolins, C. Bo,\* H. Gulyás,\* E. Fernández\*

**Transition-Metal-Free Diboration by the Activation of Diboron Compounds with Simple Lewis Bases**

W. Liu, V. Khedkar, B. Baskar, M. Schürmann, K. Kumar\*

**Branching Cascades: A Concise Synthetic Strategy Targeting Diverse and Complex Molecular Frameworks**

M. Nakanishi, D. Katayev, C. Besnard, E. P. Kündig\*

**Synthesis of Fused Indolines by Palladium-Catalyzed Asymmetric C–C Coupling Involving an Unactivated Methylene Group**

A. S. P. Frey, F. G. N. Cloke,\* M. P. Coles, L. Maron, T. Davin

**Facile Conversion of CO/H<sub>2</sub> into Methoxide at a Uranium(III) Center**

A. W. Fay, M. A. Blank, C. C. Lee, Y. Hu,\* K. O. Hodgson,\* B. Hedman,\* M. W. Ribbe\*

**Spectroscopic Characterization of a Precursor Isolated from NifEN of an Iron–Molybdenum Cofactor**

V. Zinth, T. Dellmann, H.-H. Klauss, D. Johrendt\*

**Recovery of a Parentlike State in Ba<sub>1-x</sub>K<sub>x</sub>Fe<sub>1.86</sub>Co<sub>0.14</sub>As<sub>2</sub>**



*“I enjoy the wee hours spent bouncing e-mails back and forth with my many good colleagues all over the world. The most important thing I learned is to hire students, postdocs, and young colleagues who are smarter than me ...”*

This and more about Flemming Besenbacher can be found on page 6204.

## Author Profile

Flemming Besenbacher \_\_\_\_\_ 6204



F. H. Arnold



C. P. R.  
Hackenberger



K. C. Nicolaou



G. A. Somorjai



H. Waldmann

## News

Charles Stark Draper Prize:

F. H. Arnold \_\_\_\_\_ 6205

Heinz Maier-Leibnitz Prize:

C. P. R. Hackenberger \_\_\_\_\_ 6205

Franklin Institute Award:

K. C. Nicolaou \_\_\_\_\_ 6205

Frontiers of Knowledge Award:

G. A. Somorjai \_\_\_\_\_ 6205

Wilhelm Manchot Prize:

H. Waldmann \_\_\_\_\_ 6206

## Books

Organocatalytic Enantioselective  
Conjugate Addition Reactions

Jose L. Vicario, Dolores Badía, Luisa  
Carillo, Efraim Reyes

reviewed by C. Palomo Nicolau \_\_\_\_\_ 6207

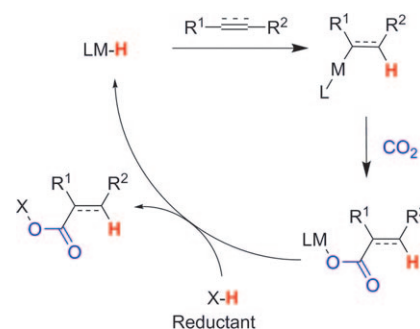
## Highlights

### Carboxylic Acid Synthesis

Y. G. Zhang,\* S. N. Riduan – 6210–6212

Catalytic Hydrocarboxylation of Alkenes and Alkynes with CO<sub>2</sub>

**Taming the enemy:** Great possibilities for the use of carbon dioxide as a renewable and environmentally friendly source of carbon in organic synthesis have been demonstrated through the hydrocarboxylation of simple alkenes and alkynes with CO<sub>2</sub> (see scheme). Several versatile methods for carboxylic acid synthesis have been developed on this basis.

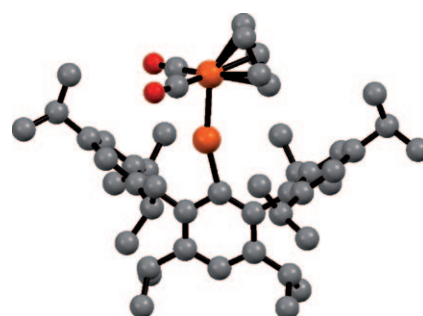


### Low-Coordinate Complexes

P. L. Holland\* – 6213–6214

Two-Coordinate Transition-Metal Centers With Metal–Metal Bonds

**M–M bonds meet two-coordination:** Systems with metal–metal bonds are of great interest in inorganic chemistry. A recent report describes the first example of a metal–metal bond to a two-coordinate transition-metal center (see structure, Fe orange, O red, C gray). The metal–metal bond in this “xenophilic complex” is best described as a dative bond.

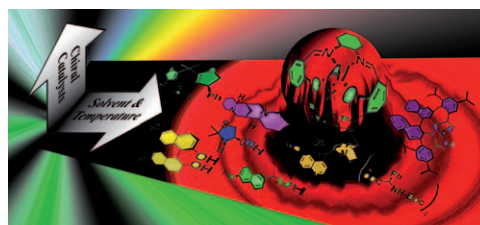


## Minireviews

### Asymmetric Catalysis

S. Piovesana, D. M. Scarpino Schietroma, M. Bella\* – 6216–6232

Multiple Catalysis with Two Chiral Units: An Additional Dimension for Asymmetric Synthesis



**Divide et Impera:** A newly emerging aspect of catalysis that involves the use of two chiral catalysts simultaneously is described (see picture). This Minireview

highlights the features of the two-catalyst reactions and the synthetic applications of the methods.

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

postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. Annual subscription price for institutions: US\$ 9442/8583 (valid for print and electronic / print or electronic delivery); for

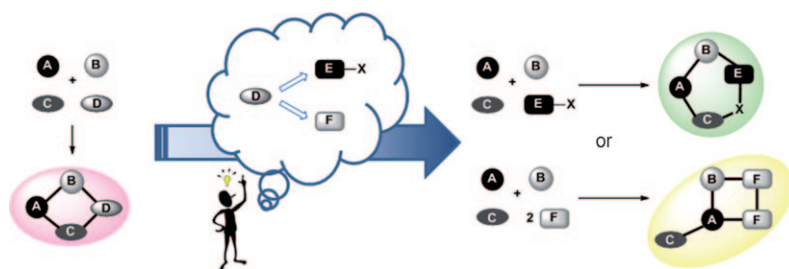
individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

## Reviews

### Multicomponent Reactions

E. Ruijter, R. Scheffelaar,  
R. V. A. Orru\* \_\_\_\_\_ 6234–6246

Multicomponent Reaction Design in the  
Quest for Molecular Complexity and  
Diversity



**MCRs à la carte:** Multicomponent reactions have become essential tools for the rapid generation of molecular complexity and diversity in chemical biology and drug discovery. These reactions are often dis-

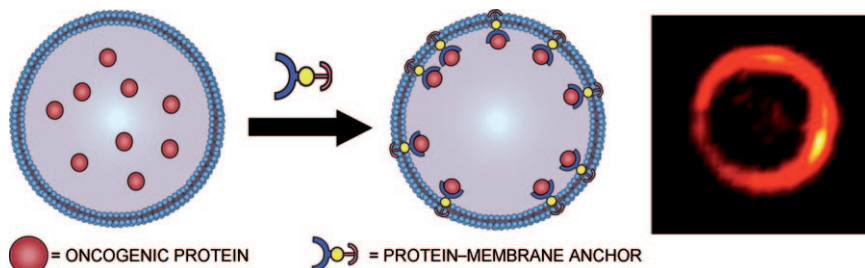
covered by serendipity, but rational design strategies are now playing an increasing role. Several such strategies are discussed in this Review.

## Communications

### Anticancer Agents

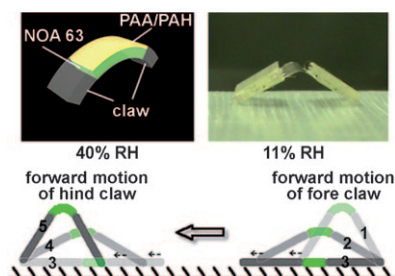
M. Avadisian, S. Fletcher, B. Liu, W. Zhao,  
P. Yue, D. Badali, W. Xu, A. D. Schimmer,  
J. Turkson, C. C. Gradinaru,\*  
P. T. Gunning\* \_\_\_\_\_ 6248–6253

Artificially Induced Protein–Membrane  
Anchorage with Cholesterol-Based  
Recognition Agents as a New Therapeutic  
Concept



**Keeping harm at bay:** In an in vitro strategy to prevent the cellular motility of oncogenic STAT3 protein, protein–membrane anchorage was induced by the use of a rationally designed cholesterol-based

protein–membrane anchor in breast-tumor cells. (The fluorescence image shows the localization of the protein to the liposome boundary of a multilamellar vesicle.)



**Fast and powerful:** A polyelectrolyte multilayer film was used to fabricate a humidity-responsive actuator that can drive a walking device carrying a load 120 times heavier than the actuator to walk steadily on a ratchet substrate under periodic alternation of the relative humidity (RH) between 11 and 40% (see picture). NOA 63: Norland Optical Adhesive 63, PAA: poly(acrylic acid), PAH: poly(allylamine hydrochloride).

### Smart Materials

Y. Ma, Y. Zhang, B. Wu, W. Sun, Z. Li,  
J. Sun\* \_\_\_\_\_ 6254–6257

Polyelectrolyte Multilayer Films for  
Building Energetic Walking Devices



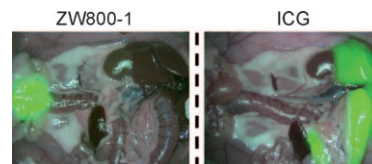
## Fluorescent Probes

H. S. Choi, K. Nasr, S. Alyabyev, D. Feith, J. H. Lee, S. H. Kim, Y. Ashitate, H. Hyun, G. Patonay, L. Strekowski, M. Henary,\* J. V. Frangioni\* — **6258 – 6263**



Synthesis and In Vivo Fate of Zwitterionic Near-Infrared Fluorophores

To address two fundamental and unsolved problems in optical imaging (nonspecific uptake of near-infrared fluorophores by normal tissues and organs and incomplete elimination of unbound targeted fluorophores from the body), novel zwitterionic near-infrared fluorophores (e.g., ZW800-1) were synthesized and their performance compared in vivo to conventional molecules (e.g., ICG) as a function of charge, charge distribution, and hydrophobicity (see picture).

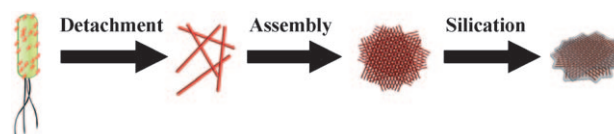


## Biomolecule Self-Assembly

B. Cao, H. Xu, C. Mao\* — **6264 – 6268**



Controlled Self-Assembly of Rodlike Bacterial Pili Particles into Ordered Lattices



**Pili pickup sticks:** Rodlike type 1 bacterial pili particles (see picture, red) self-assemble into highly ordered nanostructures through molecular recognition in the presence of suitable inducers. 1D bundles, 2D double-layer lattices, and 3D

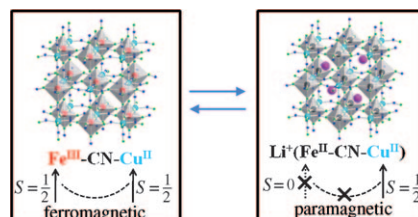
multilayer lattices were produced by varying the nature and concentration of the inducers. The self-assembled pili serve as templates for nucleating and organizing inorganic nanomaterials such as silica.

## Magnetic Materials

M. Okubo,\* D. Asakura, Y. Mizuno, T. Kudo, H. S. Zhou,\* A. Okazawa, N. Kojima, K. Ikeda, T. Mizokawa, I. Honma\* — **6269 – 6273**



Ion-Induced Transformation of Magnetism in a Bimetallic CuFe Prussian Blue Analogue



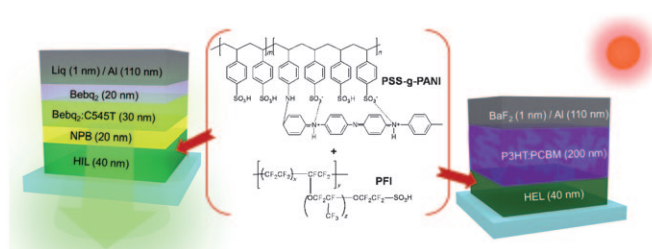
**Li ions for degaussing:** A Prussian blue analogue with Fe<sup>III</sup> and Cu<sup>II</sup> ions bridged by CN ligands underwent a ferromagnetic transition induced by ferromagnetic interactions between the Fe and Cu ions (see picture). Li ions penetrating into this ferromagnetic framework eliminated the ferromagnetic interaction and effected the formation of a paramagnetic framework. The ferromagnetism was recovered by extracting the Li ions.

## Organic Electronics

M.-R. Choi, T.-H. Han, K.-G. Lim, S.-H. Woo, D. H. Huh, T.-W. Lee\* — **6274 – 6277**



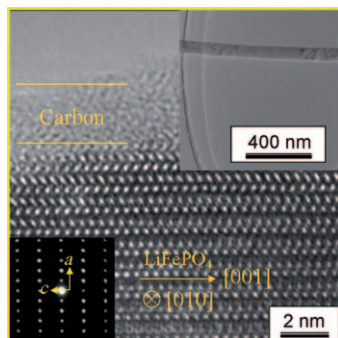
Soluble Self-Doped Conducting Polymer Compositions with Tunable Work Function as Hole Injection/Extraction Layers in Organic Optoelectronics



**Making light work:** Polymer-based compositions with a perfluorinated ionomer (PFI) as hole injection/extraction layers are introduced for organic LEDs and organic photovoltaic cells. The work functions of the layers formed by single

spin-coating could be tuned to improve device efficiency and device lifetime. The effects of the PFI surface layers on charge injection/extraction and device lifetime were investigated.



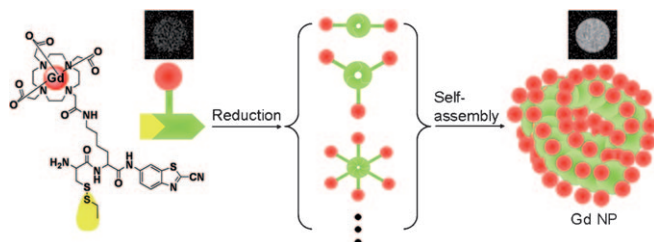


**From the spinning room:**  $\text{LiFePO}_4$  is a promising cathode material for lithium batteries, but it suffers from slow mass and charge transport. Electrospinning is able to produce single-crystalline  $\text{LiFePO}_4$  nanowires coated with amorphous carbon (see TEM images and small-angle electron diffraction pattern). Networks of these wires show very short diffusion lengths, thus leading to high rate performance and cycling capability.

### Cathode Materials

C. Zhu, Y. Yu,\* L. Gu,\* K. Weichert, J. Maier\* **6278 – 6282**

Electrospinning of Highly Electroactive Carbon-Coated Single-Crystalline  $\text{LiFePO}_4$  Nanowires



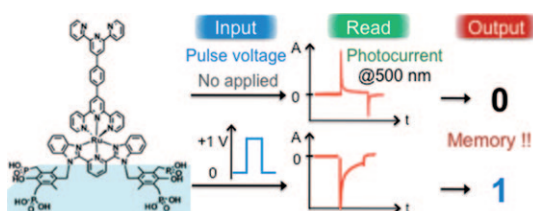
**Gd smart:** MRI contrast agents are presented that are based on a biocompatible condensation reaction. Upon reduction, a gadolinium-containing cell-permeable small-molecule probe condenses into

cyclic oligomers that subsequently self-assemble into nanoparticles (NPs) with enhanced relaxivity (by 110% at 1.5 T and 35°C, and 104% in live cells at 0.5 T).

### Contrast Agents

G. Liang, J. Ronald, Y. Chen, D. Ye, P. Pandit, M. L. Ma, B. Rutt, J. Rao\* **6283 – 6286**

Controlled Self-Assembling of Gadolinium Nanoparticles as Smart Molecular Magnetic Resonance Imaging Contrast Agents



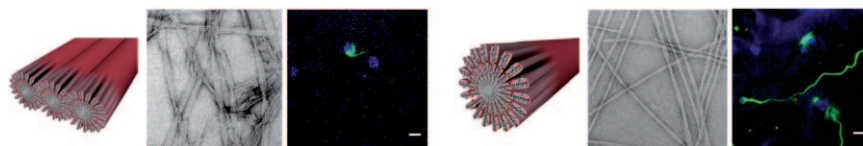
**Forget me not:** When an oxidizing voltage pulse was applied, ruthenium complexes immobilized on an ITO electrode showed

a memory effect, and the original anodic photoresponse (see picture, above) changed to a cathodic one (below).

### Molecular Devices

K. Terada, K. Kanaizuka, V. M. Iyer, M. Sannodo, S. Saito, K. Kobayashi, M. Haga\* **6287 – 6291**

Memory Effects in Molecular Films of Free-Standing Rod-Shaped Ruthenium Complexes on an Electrode



**The power of independence:** When exhibited on the surface of self-assembling peptide-amphiphile nanofibers, the hydrophobic laminin-derived IKVAV epitope induced nanofiber bundling through interdigitation with neighboring fibers and

thus decreased the bioactivity of the resulting materials. The inclusion of charged amino acids in the peptide amphiphiles disrupted the tendency to bundle and led to significantly enhanced neurite outgrowth (see picture).

### Supramolecular Biomaterials

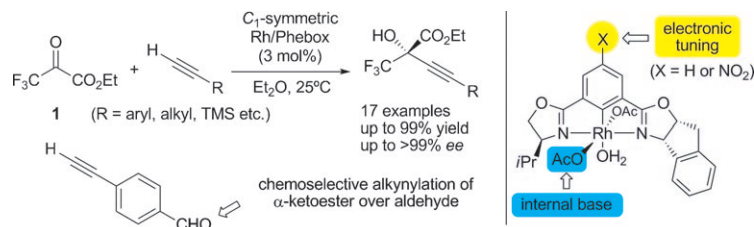
J. E. Goldberger, E. J. Berns, R. Bitton, C. J. Newcomb, S. I. Stupp\* **6292 – 6295**

Electrostatic Control of Bioactivity



## Asymmetric Catalysis

T. Ohshima,\* T. Kawabata, Y. Takeuchi,  
T. Kakinuma, T. Iwasaki, T. Yonezawa,  
H. Murakami, H. Nishiyama,  
K. Mashima\* ————— **6296–6300**



$C_1$ -Symmetric Rh/Phebox-Catalyzed  
Asymmetric Alkylation of  $\alpha$ -Ketoesters

**Thinking outside the box:** A newly developed  $C_1$ -symmetric Rh/Phebox complex efficiently catalyzed the asymmetric alkylation of  $\alpha$ -ketoester **1** with various aryl

and alkyl substituted terminal alkynes to provide the corresponding chiral tertiary propargylic alcohols with up to 99% ee (see scheme; TMS = trimethylsilyl).

## Distillable Salts

A. W. T. King,\* J. Asikkala, I. Mutikainen,  
P. Järvi, I. Kilpeläinen\* ——— **6301–6305**



Distillable Acid–Base Conjugate Ionic  
Liquids for Cellulose Dissolution and  
Processing

**Heating up:** Improved recyclability is necessary for ionic liquids destined for wood-based bioprocessing platforms. New “distillable” molten acid–base conjugates efficiently dissolve cellulose at temperatures of  $100^\circ C$ . Increased temperature induces a shift of the acid–base equilibrium toward the neutral species (see picture,  $TMG$  = 1,1,3,3-tetramethylguanidine), thus affording a vapor pressure and allowing for distillation of the mixture.

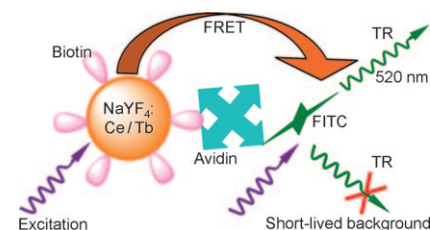
## Biosensors

D. T. Tu, L. Q. Liu, Q. Ju, Y. S. Liu,  
H. M. Zhu, R. F. Li,  
X. Y. Chen\* ————— **6306–6310**



Time-Resolved FRET Biosensor Based on  
Amine-Functionalized Lanthanide-Doped  
 $NaYF_4$  Nanocrystals

**Background elimination** and improved sensitivity were achieved by time-resolved (TR) detection with a FRET biosensor for traces of biomolecules such as avidin at concentrations down to 4.8 nM. As shown in the picture, UV excitation of biotinylated  $NaYF_4:Ce/Tb$  nanocrystals triggers energy transfer to fluorescein isothiocyanate (FITC), whose long-lived emission due to FRET can be distinguished from the short-lived background from direct excitation.

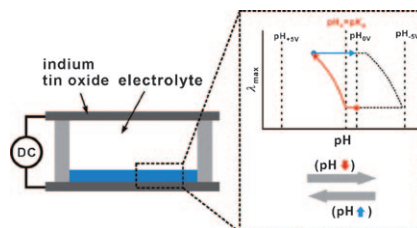


## Optoelectronics

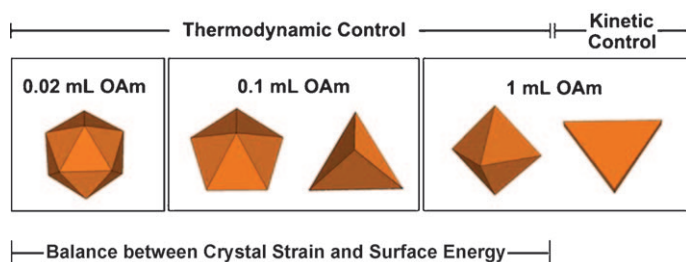
K. Hwang, D. Kwak, C. Kang, D. Kim,  
Y. Ahn, Y. Kang\* ————— **6311–6314**



Electrically Tunable Hysteretic Photonic  
Gels for Nonvolatile Display Pixels



**Plastic pixels:** Electrically tunable photonic pixels exhibiting nonvolatile photonic colors are demonstrated by coupling the hysteretic optical properties of PS-*b*-P2VP block copolymer photonic gels with an electrochemically induced pH gradient. The optical volatility of photonic pixels was tuned by controlling the hysteresis strength and the conversion pH value, which were both highly dependent on the species of anions pairing with pyridinium groups.



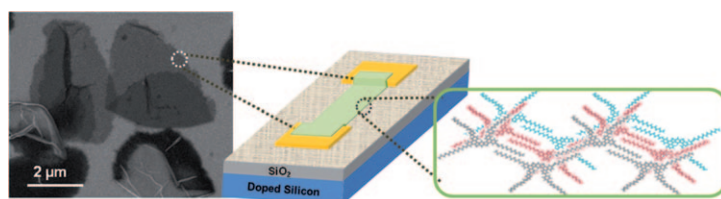
**Shape control:** Uniform Pd nanocrystals in the shape of icosahedron, decahedron, octahedron, and triangular plate were prepared in a hydrophobic system in which oleylamine (OAm) plays a crucial

role in shape evolution by mediating the counterbalance between crystal strain and surface energy (see picture). The as-obtained Pd nanocrystals are catalytically active in the oxidation of formic acid.

## Metal Nanocrystals

Z. Niu, Q. Peng, M. Gong, H. Rong,  
Y. Li\* 6315–6319

Oleylamine-Mediated Shape Evolution of Palladium Nanocrystals



**Butterflies in the stomach:** Organic field-effect transistors containing a free-standing film self-assembled from an amphiphilic butterfly-shaped benzodithiophene derivative as the active layer (see picture)

were fabricated by a solution transfer process. The direct self-assembly of the film from solution means that a substrate is not required for the film formation.

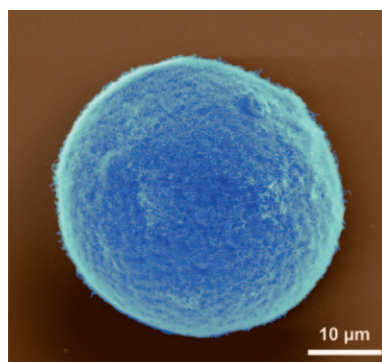
## Molecular Electronics

J. Yin, Y. Zhou, T. Lei, J. Pei\* 6320–6323

A Butterfly-Shaped Amphiphilic Molecule: Solution-Transferable and Free-Standing Bilayer Films for Organic Transistors



**Spray-on:** Peptide amphiphiles (PAs) and oppositely charged polymers can self-assemble into highly organized membranes (see picture) at the interface between two aqueous solutions. Nebulization was employed to spray the biopolymer into a solution of the peptide amphiphile and to template the formation of microcapsules that are loaded with a biopolymer solution and have surfaces that are decorated with nanoscale filaments.



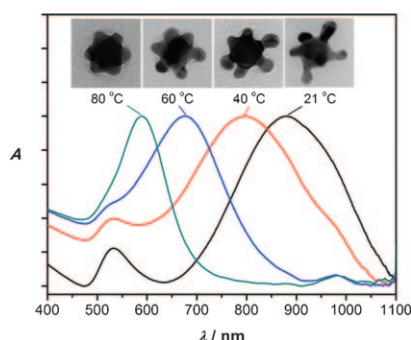
## Amphiphiles

D. I. Rożkiewicz, B. D. Myers,  
S. I. Stupp\* 6324–6327

Interfacial Self-Assembly of Cell-like Filamentous Microcapsules



**A star in the making:** Gold nano-hexapods with controlled arm lengths were synthesized by selective growth on the vertices of octahedral Au seeds. Depending on the arm length, their surface plasmon resonance peaks shifted from the visible to the near-infrared region (see picture), which could be readily controlled by varying the amount of HAuCl<sub>4</sub>, the reaction temperature, or both.



## Nanocrystals

D. Y. Kim, T. Yu, E. C. Cho, Y. Ma,  
O. O. Park, Y. Xia\* 6328–6331

Synthesis of Gold Nano-hexapods with Controllable Arm Lengths and Their Tunable Optical Properties



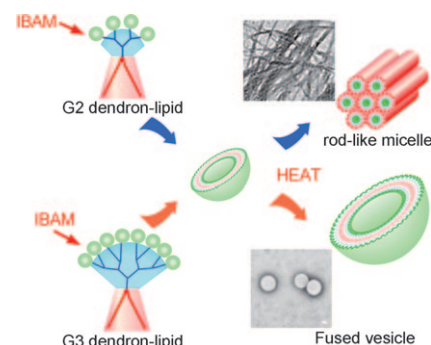
## Dendrimer-Based Vesicles

K. Kono,\* E. Murakami, Y. Hiranaka,  
E. Yuba, C. Kojima, A. Harada,  
K. Sakurai ————— **6332–6336**



Thermosensitive Molecular Assemblies  
from Poly(amidoamine) Dendron-Based  
Lipids

**The heat is on:** Vesicles formed from poly(amidoamine) dendron-based lipids with terminal isobutyramide (IBAM) groups undergo a temperature-dependent structural transition through a change in hydration of the vesicle surface. The vesicles are stable at low temperature, but form aggregates above a specific temperature and transform to inverted rodlike micelles or fused vesicles (see picture; G2/G3 = second/third generation).

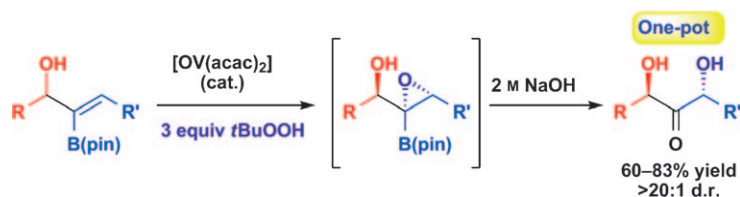


## Tandem Oxidations

M. M. Hussain, J. Hernández Toribio,  
P. J. Carroll, P. J. Walsh\* — **6337–6340**



Synthesis of 2-Keto-*anti*-1,3-diols by  
Chemoselective Tandem Oxidation of  
2-B(pin)-Substituted Allylic Alcohols



**A new role for vinyl boronates:** Vinyl boronate esters are well known as synthons for ketones and for their ability to participate in cross-coupling reactions. A tandem oxidation is introduced to convert

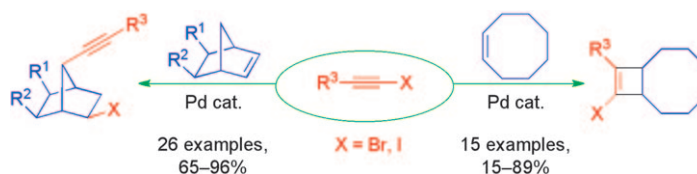
2-B(pin)-substituted allylic alcohols into 2-keto-*anti*-1,3-diols with high diastereoselectivity. Under these reaction conditions, the vinyl boronate ester is now a synthon for  $\alpha$ -hydroxy ketones.

## Synthetic Methods

Y. B. Li, X. H. Liu, H. F. Jiang,\* B. F. Liu,  
Z. W. Chen, P. Zhou ————— **6341–6345**



Palladium-Catalyzed Bromoalkynylation of  
C–C Double Bonds: Ring-Structure-  
Dependent Synthesis of 7-Alkynyl  
Norbornanes and Cyclobutenyl Halides



**Strain versus flexibility:** The palladium-catalyzed reaction of haloalkynes with norbornene derivatives leads to 7-alkynyl norbornane products (see scheme). Key to the success of this reaction is the formation of a “bridging” palladium spe-

cies, which can rearrange to result in a C-7 functionalization. The ring-structure-dependent [2+2] cycloaddition of haloalkynes with cyclooctene has been achieved in moderate to good yields under similar conditions.

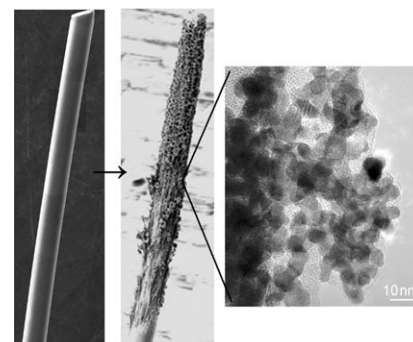
## Nanoparticle Synthesis

A. I. Yanson, P. Rodriguez,  
N. Garcia-Araez, R. V. Mom,  
F. D. Tichelaar,  
M. T. M. Koper\* ————— **6346–6350**



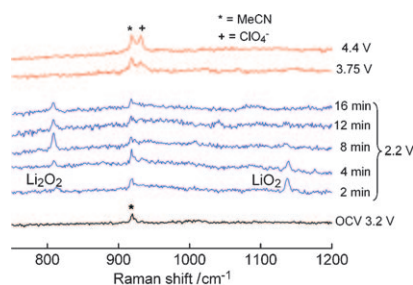
Cathodic Corrosion: A Quick, Clean, and  
Versatile Method for the Synthesis of  
Metallic Nanoparticles

**A simple and effective method** for the synthesis of nanoparticles is reported based on extreme cathodic polarization of a metal, formation of cation-stabilized metal anions, and their agglomeration (see picture). The improved catalytic activity of these nanoparticles in the oxidation of carbon monoxide as well as methanol is shown using platinum.





**Taking the shortcut:** Spectroscopic data (see picture) provide direct evidence that in non-aqueous  $\text{Li}^+$  electrolyte,  $\text{O}_2$  is reduced to  $\text{O}_2^-$ , which then forms  $\text{LiO}_2$  on the electrode surface which disproportionates to  $\text{Li}_2\text{O}_2$ . On charging,  $\text{Li}_2\text{O}_2$  decomposes directly, in a one-step reaction to evolve  $\text{O}_2$  and does not pass through  $\text{LiO}_2$  as an intermediate.



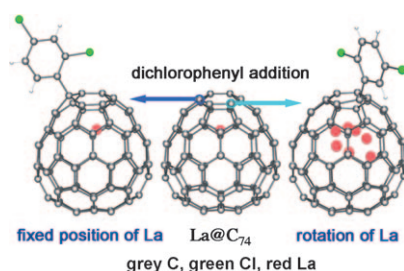
### Lithium–Oxygen Batteries

Z. Peng, S. A. Freunberger, L. J. Hardwick, Y. Chen, V. Giordani, F. Bardé, P. Novák, D. Graham, J.-M. Tarascon, P. G. Bruce\* — 6351–6355

Oxygen Reactions in a Non-Aqueous  $\text{Li}^+$  Electrolyte



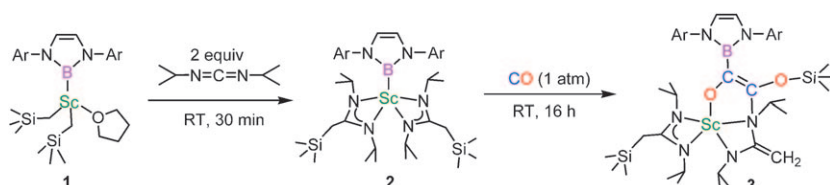
**Insoluble fullerenes solubilized:** Addition of dichlorophenyl radicals to insoluble  $\text{La@C}_{74}$  affords two series of regioisomers in which dichlorophenyl groups with different substitution patterns are singly bonded to one of two adjacent cage carbon atoms. X-ray diffraction studies reveal that the internal metal atom is responsible for such addition patterns, while addition to different sites modifies the motion of the metal atom (see picture).



### Endofullerenes

X. Lu, H. Nikawa, T. Kikuchi, N. Mizorogi, Z. Slanina, T. Tsuchiya, S. Nagase,\* T. Akasaka\* — 6356–6359

Radical Derivatives of Insoluble  $\text{La@C}_{74}$ : X-ray Structures, Metal Positions, and Isomerization



**Among the first of their kind:** Scandium boryl complex **1** and its Gd analogue were prepared by reaction of a boryl lithium compound with  $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_x][\text{BPh}_4]$  ( $\text{Ln} = \text{Sc}, \text{Gd}$ ). Reaction of **1** with  $N,N'$ -diisopropylcarbodiimide gave bis-

(amidinate) complex **2**, which affords **3** by double CO insertion into the  $\text{Sc}-\text{B}$  bond, nucleophilic addition of an amidinate, and migration of the  $\text{SiMe}_3$  to the resulting ketene moiety (see scheme).

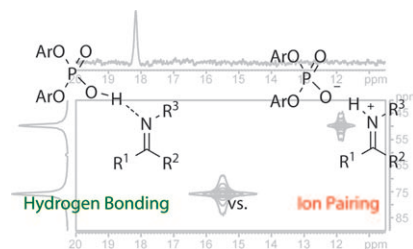
### Boryl Complexes

S. Li, J. Cheng, Y. Chen, M. Nishiura, Z. Hou\* — 6360–6363

Rare Earth Metal Boryl Complexes: Synthesis, Structure, and Insertion of a Carbodiimide and Carbon Monoxide



**Behind the scenes:** NMR spectroscopy was used to distinguish hydrogen bonding and ion pairing in the activation of imines by a phosphate catalyst (see structures). Hydrogen-bond strength and the amount of the hydrogen-bonded species present are decisive for the catalytic reaction and can be manipulated by introducing substituents with different electronic properties. This insight should guide the development of more efficient catalytic systems.



### Organocatalysis

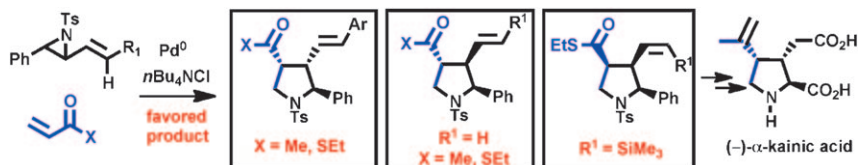
M. Fleischmann, D. Drettwan, E. Sugiono, M. Rueping,\* R. M. Gschwind\* — 6364–6369

Brønsted Acid Catalysis: Hydrogen Bonding versus Ion Pairing in Imine Activation



## Annulation Reactions

M. A. Lowe, M. Ostovar, S. Ferrini,  
C. C. Chen, P. G. Lawrence, F. Fontana,  
A. A. Calabrese,  
V. K. Aggarwal\* — 6370–6374



**Just add salt:** Vinyl aziridines have been treated with methyl vinyl ketone or ethyl thioacrylate in the presence of Pd<sup>0</sup> to give pyrrolidines with moderate to good diastereoselectivity. The presence of *n*Bu<sub>4</sub>NCl

was critical to successful annulation. The synthetic utility of the methodology has been demonstrated in a short (formal) synthesis of (–)-α-kainic acid.

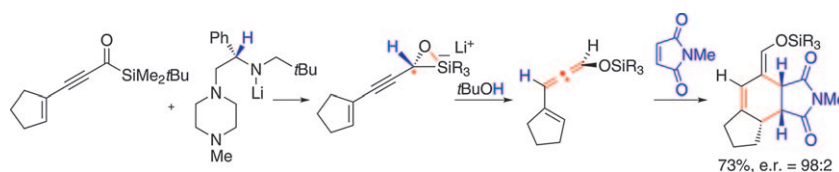


Palladium-Mediated Annulation of Vinyl Aziridines with Michael Acceptors: Stereocontrolled Synthesis of Substituted Pyrrolidines and Its Application in a Formal Synthesis of (–)-α-Kainic Acid



## Siloxyallenes

M. Sasaki, Y. Kondo, M. Kawahata,  
K. Yamaguchi, K. Takeda\* — 6375–6378



**Two flavors of selectivity:** An enantioselective Meerwein–Ponndorf–Verley-type reduction of alkynylsilanes by a chiral lithium amide followed by a Brook rearrangement and S<sub>E</sub>2' electrophilic substitution provides the title compounds in a

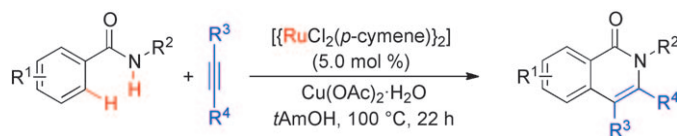
one-pot process. In the case of enynylsilanes, the generated vinylallenes undergo in situ [4+2] cycloaddition to afford highly functionalized polycyclic compounds with unusual facial selectivity.



Enantioselective Synthesis of Siloxyallenes from Alkynylsilanes by Reduction and a Brook Rearrangement and Their Subsequent Trapping in a [4+2] Cycloaddition

## C–H Bond Activation

L. Ackermann,\* A. V. Lygin,  
N. Hofmann — 6379–6382



**Bond activation in action:** Unprecedented ruthenium-catalyzed oxidative annulations of alkynes through cleavage of C–H bonds set the stage for an efficient 1(2*H*)-isoquinolone synthesis with ample scope

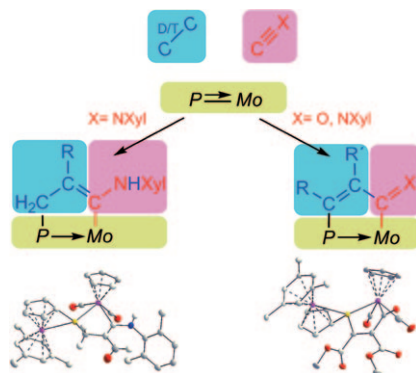
(see scheme; *t*Am = *tert*-amyl). Mechanistic studies provided strong evidence for a rate-limiting C–H bond metalation through carboxylate assistance.



Ruthenium-Catalyzed Oxidative Annulation by Cleavage of C–H/N–H Bonds

## Phosphinidenes

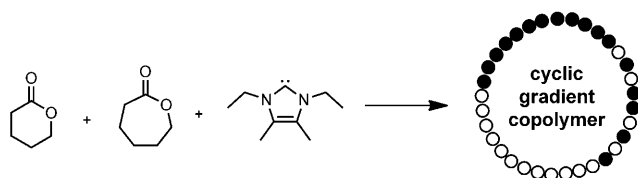
M. A. Alvarez, M. E. García,\* M. A. Ruiz,\*  
J. Suárez — 6383–6387



**A ligand makes a difference:** The reactivity of a dimolybdenum phosphinidene complex with alkenes and alkynes is substantially modified by the presence of two-electron donors such as CO or CNXyl (Xyl = xylyl). Under these multicomponent reaction conditions, rapid formation of phosphametallacyclopentene rings takes place at room temperature. These reactions proceed in all cases with very high chemo- and regioselectivity.



Enhanced Nucleophilic Behavior of a Dimolybdenum Phosphinidene Complex: Multicomponent Reactions with Activated Alkenes and Alkynes in the Presence of CO or CNXyl



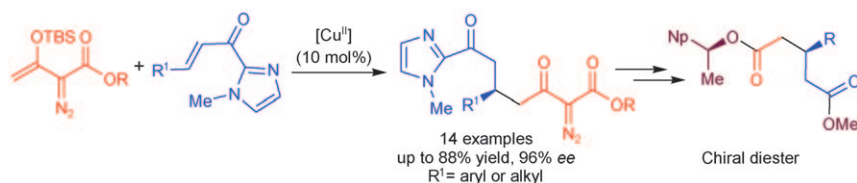
**How to get rich fast:** The zwitterionic copolymerization of  $\delta$ -valerolactone (VL) and  $\epsilon$ -caprolactone (CL) provides an expedient route to cyclic gradient copolymers. The faster ring-opening of VL relative to CL with N-heterocyclic car-

benes, coupled with sufficiently long lifetimes of the growing zwitterions leads to a polymer structure comprised of VL-rich sequences that transition to CL-rich sequences in a cyclic macromolecule (see scheme).

## Gradient Polymers

E. J. Shin, H. A. Brown, S. Gonzalez, W. Jeong, J. L. Hedrick, R. M. Waymouth\* — 6388 – 6391

Zwitterionic Copolymerization: Synthesis of Cyclic Gradient Copolymers



**In addition:** The Mukaiyama–Michael addition in the presence of a chiral copper(II) Lewis acid is a highly enantioselective and efficient method for the construction of a broad range of chiral  $\gamma$ -

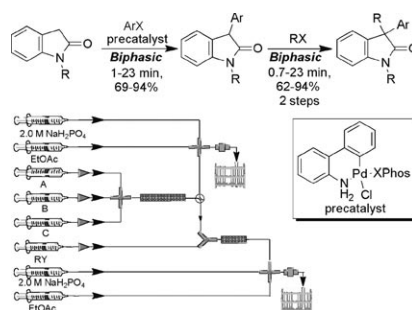
functionalized diazoacetates. These products can be conveniently transformed into useful enantiomer-enriched 1,5-di-esters (see scheme, Np = 1-naphthyl, TBS = *tert*-butyldimethylsilyl).

## Asymmetric Catalysis

X. Xu, W. Hu, M. P. Doyle\* — 6392 – 6395

Highly Enantioselective Catalytic Synthesis of Functionalized Chiral Diazoacetates

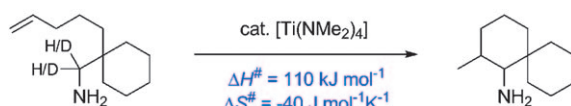
**Facilitating chemistry:** Key to the success of Pd-catalyzed  $\alpha$ -arylation of oxindoles in continuous flow involved a biphasic system, a precatalyst, and a packed-bed microreactor. Furthermore, this reaction was integrated into a two-step continuous-flow sequence for rapid, modular, and efficient syntheses of 3,3-disubstituted oxindoles.



## Continuous Synthesis

P. Li, S. L. Buchwald\* — 6396 – 6400

Continuous-Flow Synthesis of 3,3-Disubstituted Oxindoles by a Palladium-Catalyzed  $\alpha$ -Arylation/Alkylation Sequence



zero-order rate dependence on aminoalkene concentration  
kinetic isotope effect  $k_H/k_D = 7.3$

**Kinetic studies** on the intramolecular titanium-catalyzed hydroaminoalkylation of alkenes (see scheme) are consistent with theoretical results and lead to the conclusion that the rate-determining step

of the catalytic cycle is the C–H activation at the  $\alpha$  position to the nitrogen atom. The reaction has a high activation energy and involves a moderately ordered transition state.

## C–H Activation

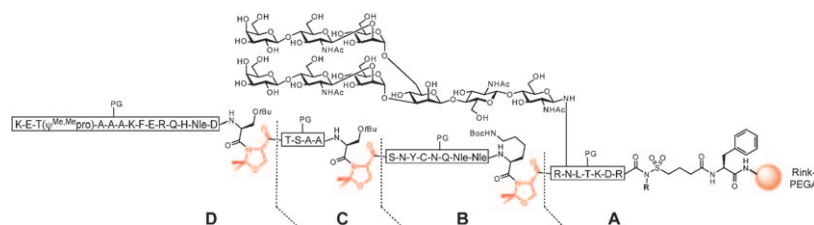
I. Prochnow, P. Zark, T. Müller,\* S. Doye\* — 6401 – 6405

The Mechanism of the Titanium-Catalyzed Hydroaminoalkylation of Alkenes

## Peptide Synthesis

C. Heinlein, D. Varón Silva, A. Tröster,  
J. Schmidt, A. Gross,  
C. Unverzagt\* ————— **6406–6410**

Fragment Condensation of C-Terminal  
Pseudoproline Peptides without  
Racemization on the Solid Phase



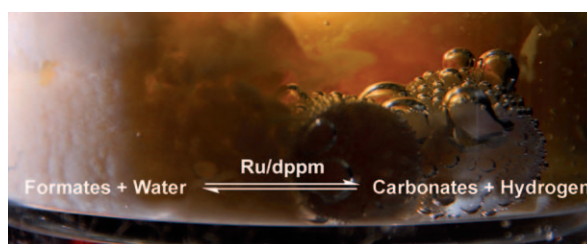
**Hot couplings without racemization:**  
Protected peptides featuring C-terminal  
pseudoprolines were synthesized on a  
solid support, and these versatile building  
blocks were used in convergent peptide-  
segment couplings, which proceeded

without racemization even under micro-  
wave conditions. The solubility-enhancing  
effect of pseudoproline residues facili-  
tated the synthesis of complex RNase 39-  
mer glycopeptide thioesters.

## Hydrogen Storage

A. Boddien, F. Gärtner, C. Federsel,  
P. Sponholz, D. Mellmann, R. Jackstell,  
H. Junge, M. Beller\* ————— **6411–6414**

CO<sub>2</sub>-“Neutral” Hydrogen Storage Based  
on Bicarbonates and Formates



**Let the circle be unbroken!** One ruthenium catalyst generated in situ facilitates the selective hydrogenation of bicarbonates and carbonates, as well as CO<sub>2</sub> and base, to give formates and also the

selective dehydrogenation of formates back to bicarbonates. The two reactions can be coupled, leading to a reversible hydrogen-storage system. dppm = 1,2-bis(diphenylphosphino)methane.

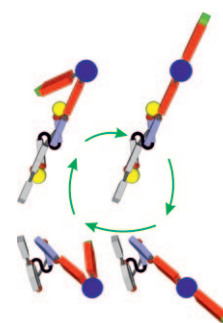
## Molecular Motor

G. Haberhauer\* ————— **6415–6418**



A Molecular Four-Stroke Motor

**Round and round it goes:** In the molecular four-stroke motor the forward and backward moving of the pushing blade of the motor is combined with the closing and opening of the blade in such a way that there is a net rotation about a virtual axis (see scheme). Thus, during one cycle, surrounding molecules should automatically be transported in a definite direction.



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



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



This article is available  
online free of charge  
(Open Access)

**The issues for June 2011 appeared online on the following dates**  
**Issue 24: June 1 • Issue 25: June 7 • Issue 26: June 15 • Issue 27: June 21**



# Sources

## Product and Company Directory

You can start the entry for your company in "Sources" in any issue of *Angewandte Chemie*.

If you would like more information, please do not hesitate to contact us.

Wiley-VCH Verlag – Advertising Department

Tel.: 0 62 01 - 60 65 65

Fax: 0 62 01 - 60 65 50

E-Mail: MSchulz@wiley-vch.de

## Service

Spotlight on Angewandte's  
Sister Journals \_\_\_\_\_ 6200–6202

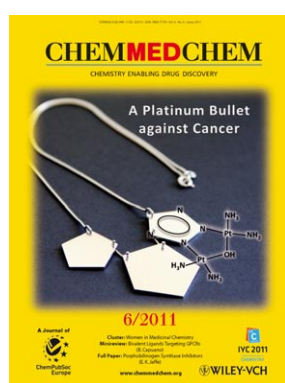
Sources \_\_\_\_\_ A39

Preview \_\_\_\_\_ 6419

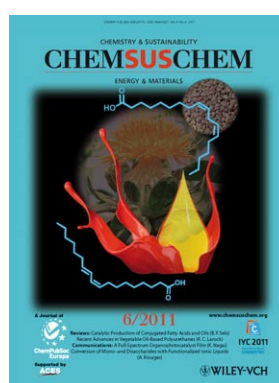
## Check out these journals:



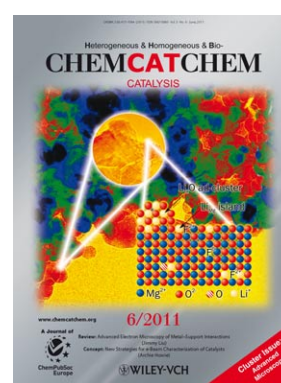
[www.chemasianj.org](http://www.chemasianj.org)



[www.chemmedchem.org](http://www.chemmedchem.org)



[www.chemsuschem.org](http://www.chemsuschem.org)



[www.chemcatchem.org](http://www.chemcatchem.org)