



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:

C. Parthier, S. Görlich, F. Jaenecke, C. Breithaupt, U. Bräuer, U. Fandrich, D. Clausnitzer, U. F. Wehmeier, C. Böttcher, D. Scheel, M. T. Stubbs\*

**The O-Carbamoyl Transferase TobZ Catalyzes an Ancient Enzymatic Reaction**

A. Patzer, M. Schütz, T. Möller, O. Dopfer\*

**IR Spectrum and Structure of the Adamantane Cation: Direct Evidence for Jahn–Teller Distortion**

D. Globisch, C. A. Lowery, K. C. McCague, K. D. Janda\*

**Uncharacterized DPD Molecules Shown by NMR Analysis: Implications for a Greater Signaling Diversity in Bacterial Species**

C. Lux, M. Wollenhaupt, T. Bolze, Q. Liang, J. Köhler, C. Sarpe, T. Baumert\*

**Circular Dichroism in the Photoelectron Angular Distributions of Camphor and Fenchone from Multiphoton Ionization with Femtosecond Laser Pulses**

C. Giese, F. Zosel, C. Puorger, R. Glockshuber\*

**The Most Stable Protein/Ligand Complex: Applications for One-Step Affinity Purification and Identification of Protein Assemblies**

X.-F. Xiong, Q. Zhou, J. Gu, L. Dong, T.-Y. Liu, Y.-C. Chen\*

**Trienamine Catalysis of 2,4-Dienones: Development and Application in Asymmetric Diels–Alder Reaction**

M. T. C. Walvoort, H. Van den Elst, O. J. Plante, L. Kröck, P. H. Seeberger, H. S. Overkleeft, G. A. van der Marel,\* J. D. Codée\*

**Automated Solid-Phase Synthesis of  $\beta$ -Mannuronic Acid Alginates**

P. G. Schiro, M. Zhao, J. S. Kuo, K. M. Koehler, D. E. Sabath, D. T. Chiu\*

**Sensitive and High-Throughput Isolation of Rare Cells from Peripheral Blood with Ensemble-Decision Aliquot Ranking**



*“The best stage in a scientist’s career is the first ten years of independent research.*

*The best advice I have ever been given is studying science instead of liberal arts ...”*

This and more about Qi-Lin Zhou can be found on page 3748.

## Author Profile

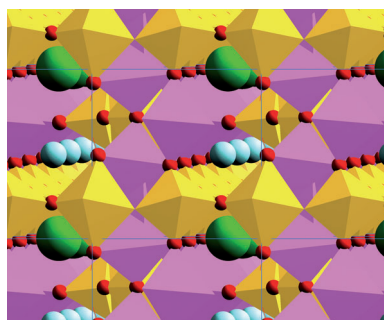
Qi-Lin Zhou \_\_\_\_\_ 3748

Antiviral Drug Strategies

Erik De Clercq

## Books

reviewed by T. W. Bell \_\_\_\_\_ 3749



**Structure prediction** of stable and metastable phases is put on equal footing for the first time, with a solid thermodynamical background. How to estimate the lifetime of metastable phases is demonstrated by recent groundbreaking work of Jansen, Pentin, and Schön. At the heart lies the exploration of the Gibbs free-energy landscapes and the extended phase diagrams for complex systems.

## Highlights

### Structure Prediction

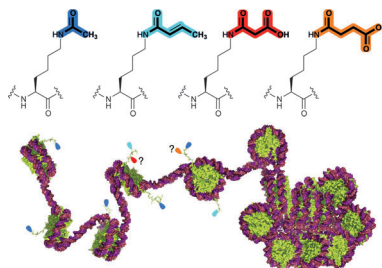
S. M. Woodley,\* A. A. Sokol . 3752–3754

From Ergodicity to Extended Phase Diagrams

**Protein Modifications**

C. A. Olsen\* 3755–3756

Expansion of the Lysine Acylation  
Landscape



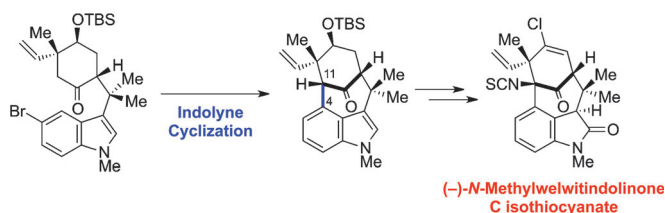
**Leaving marks:** The number of known posttranslational modifications for lysine has been expanded considerably. In addition to acetylation of side-chain amino functionalities of lysine residues in proteins, crotonylation, succinylation, and malonylation have now been identified as posttranslational modifications in histone and in non-histone proteins.

**Minireviews**

**Natural Product Synthesis**

A. D. Hutters, E. D. Styduhar,  
N. K. Garg\* 3758–3765

Total Syntheses of the Elusive  
Welwitindolinones with Bicyclo[4.3.1]  
Cores



**17 years in the making:** The welwitindolinones with bicyclo[4.3.1] cores are a class of natural products that have attracted tremendous interest from the synthetic community. Contemporary

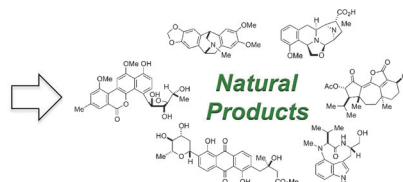
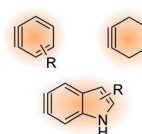
studies aimed at the total synthesis of these challenging targets are described, including two recently completed syntheses (see one example).

**Natural Product Synthesis**

C. M. Gampe,  
E. M. Carreira\* 3766–3778

Arynes and Cyclohexyne in Natural  
Product Synthesis

**Benzynes, Indolynes,  
and Cyclohexyne**



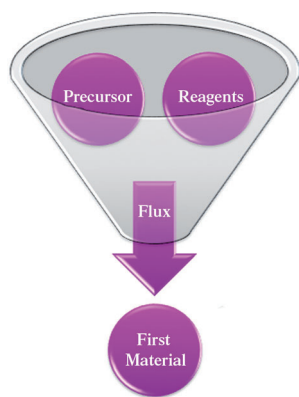
**Highly reactive!** The latest developments in the field of aryne and angle-strained cycloalkyne chemistry have led to recent applications of benzynes, indolynes, and cyclohexyne in natural product syntheses.

The inherent reactivity of these intermediates can be harnessed to rapidly increase molecular complexity. The syntheses presented are highly instructive for synthetic organic chemists.

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a national chemical society prices are available  
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sales tax.



**The flux of the matter:** The search for the “First Material”, the archetype in which a new phenomenon is first observed, has been a prime motivator for materials research. One method to discover such “First Materials” is crystal growth from high-temperature solutions using a flux as solvent (see scheme). This approach has been extremely successful in the discovery of new materials and is described using quaternary and higher oxides as examples.

## Reviews

### Crystal Growth

D. E. Bugaris,\*  
H.-C. zur Loye\* \_\_\_\_\_ 3780–3811

Materials Discovery by Flux Crystal Growth: Quaternary and Higher Order Oxides



## Communications

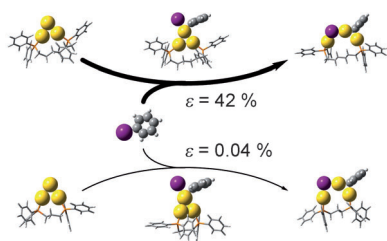
### Sonogashira Coupling

P. S. D. Robinson, G. N. Khairallah,\*  
G. da Silva, H. Lioe,  
R. A. J. O’Hair\* \_\_\_\_\_ 3812–3817

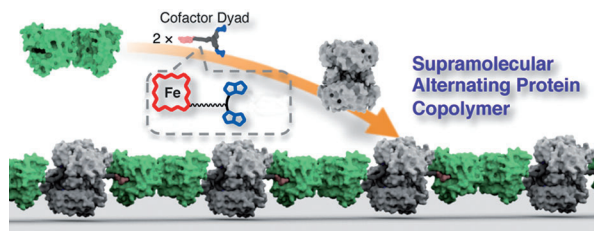
Gold-Mediated C–I Bond Activation of Iodobenzene



Frontispiece



**Controversy resolved!** A combination of gas-phase ion–molecule reactions and theoretical studies confirm bisligated mononuclear Au<sup>I</sup> complexes are unable to undergo oxidative addition of iodobenzene for Sonogashira coupling, but that the ligated gold clusters [Au<sub>3</sub>L]<sup>+</sup> (L=Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub>; n=3–6) activate the C–I bond. DFT calculations on the transition states show that the linker size *n* tunes the cluster reactivity.



**Alternating:** A cofactor dyad consisting of a heme group (red in picture) and a bis(biotin) unit (blue) was synthesized and shown to specifically bind to both apomyoglobin and streptavidin. In the pres-

ence of the dyad, the 1:1 association of a disulfide-bridged myoglobin dimer (green) with streptavidin (gray) afforded a submicrometer-sized fibrous alternating copolymer.

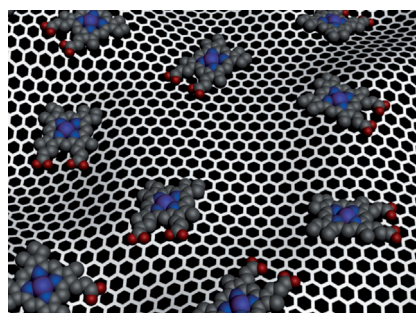
### Protein Assembly

K. Oohora, S. Burazerovic, A. Onoda,  
Y. M. Wilson, T. R. Ward,\*  
T. Hayashi\* \_\_\_\_\_ 3818–3821

Chemically Programmed Supramolecular Assembly of Hemoprotein and Streptavidin with Alternating Alignment



Front Cover



**Well supported:** Stable hemin–graphene conjugates (see picture) formed by immobilization of monomeric hemin on graphene, showed excellent catalytic activity, more than 10 times better than that of the recently developed hemin–hydrogel system and 100 times better than that of unsupported hemin. The catalysts also showed excellent binding affinities and catalytic efficiencies approaching that of natural enzymes.

### Biomimetic Catalysis

T. Xue, S. Jiang, Y. Qu, Q. Su, R. Cheng,  
S. Dubin, C.-Y. Chiu, R. Kaner, Y. Huang,\*  
X. Duan\* \_\_\_\_\_ 3822–3825

Graphene-Supported Hemin as a Highly Active Biomimetic Oxidation Catalyst



Inside Back Cover

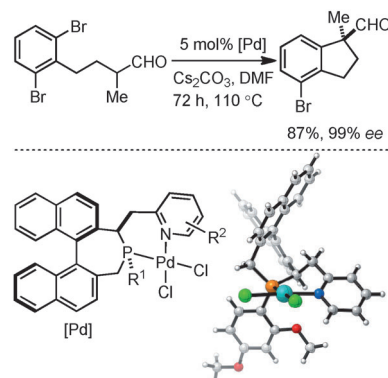
## Asymmetric Catalysis

P. Nareddy, L. Mantilli, L. Guénée,  
C. Mazet\* 3826–3831



Atropoisomeric (P,N) Ligands for the Highly Enantioselective Pd-Catalyzed Intramolecular Asymmetric  $\alpha$ -Arylation of  $\alpha$ -Branched Aldehydes

**Three-in-one:** A short synthetic route readily gives access to a new class of chiral (P,N) ligands characterized by three distinct elements of chirality. These ligands are highly enantioselective in the challenging Pd-catalyzed intramolecular asymmetric  $\alpha$ -arylation of  $\alpha$ -branched aldehydes (see picture).



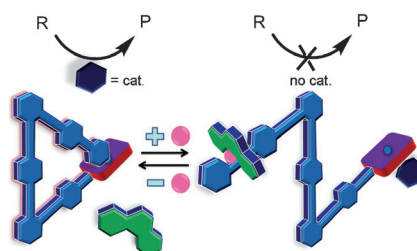
## Molecular Switch

M. Schmittl,\* S. De,  
S. Pramanik 3832–3836



Reversible ON/OFF Nanoswitch for Organocatalysis: Mimicking the Locking and Unlocking Operation of CaMKII

**Flip a switch:** A nanoswitch uses chemical inputs to turn an organocatalytic Knoevenagel reaction on and off (see scheme: R = reactant, P = product). To stop catalysis the chemical input (pink and green) wraps around the inhibitory segment of the nanoswitch to effect release or unlocking of the switch. The process can run reversibly over three cycles without loss of activity.

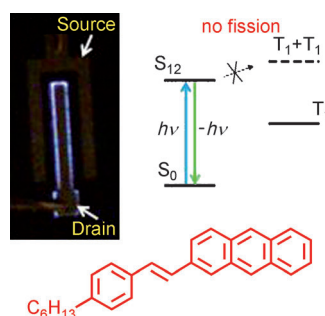


## Organic Electronics

A. Dadvand, A. G. Moiseev, K. Sawabe,  
W.-H. Sun, B. Djukic, I. Chung,  
T. Takenobu, F. Rosei,  
D. F. Perepichka\* 3837–3841



Maximizing Field-Effect Mobility and Solid-State Luminescence in Organic Semiconductors



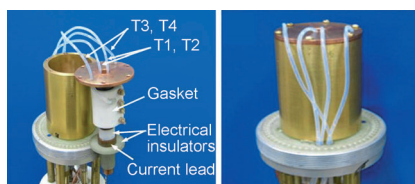
**Conductive and emissive:** Organic transistors made from a simple styrylanthracene derivative (see scheme) have high charge mobility and high luminescence quantum yields. These properties are attributed to the lack of singlet fission, and challenge the idea that the efficient  $\pi$  interactions required for high mobility always lead to quenching of emission. The transistors emit blue electroluminescence and are stable during operation and storage.

## Fuel Cells

O. H. Han,\* K. S. Han, C. W. Shin, J. Lee,  
S.-S. Kim, M. S. Um, H.-I. Joh, S.-K. Kim,  
H. Y. Ha 3842–3845

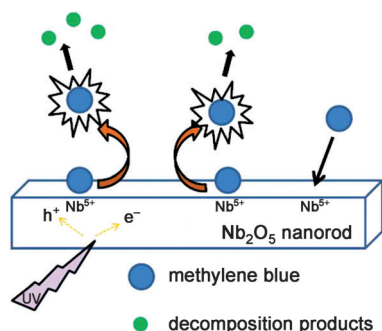


Observation of Methanol Behavior in Fuel Cells In Situ by NMR Spectroscopy



**The chemical conversion** of methanol in direct methanol fuel cells was followed in situ by NMR spectroscopy. Comparing data of the methanol oxidation on Pt and PtRu anode catalysts allowed the role of Ru in both Faradaic and non-Faradaic reactions to be investigated. The spatial distributions of chemicals could also be determined. (Picture: T1–T4 = inlet and outlet tubes.)



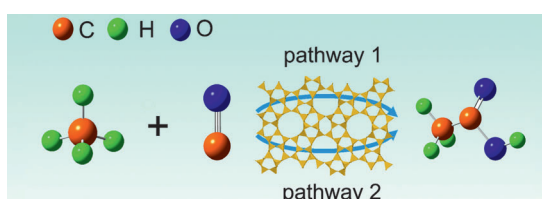


**Nb<sub>2</sub>O<sub>5</sub> nanorods** and nanospheres were synthesized, and their photocatalytic activity for methylene blue decomposition in water compared. Nb<sub>2</sub>O<sub>5</sub> nanorods clearly displayed higher activity, despite their comparable surface area. With a shape-dependent surface acidity, hydrothermal stability, and high photoactivity, these Nb<sub>2</sub>O<sub>5</sub> nanorods are a unique and exciting nanomaterial for non-classical photocatalytic mineralization of organic compounds in water.

### Shape-Dependent Photocatalysis

Y. Zhao, C. Eley, J. Hu, J. S. Foord, L. Ye, H. He, S. C. E. Tsang\* — 3846–3849

Shape-Dependent Acidity and Photocatalytic Activity of Nb<sub>2</sub>O<sub>5</sub> Nanocrystals with an Active TT (001) Surface



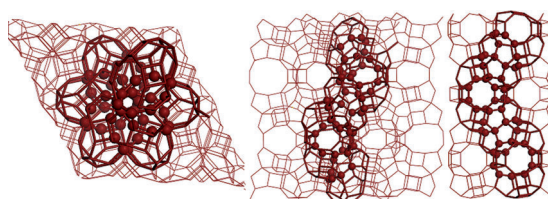
**Two ways:** A Zn-modified ZSM-5 zeolite catalyst was developed for the reaction of methane with carbon monoxide to directly produce acetic acid (see scheme) under mild conditions (573–623 K), and two

different intermediate-dependent reaction pathways were unambiguously identified for acetic acid formation by in situ solid-state NMR spectroscopy.

### Heterogeneous Catalysis

X. M. Wang, G. D. Qi, J. Xu,\* B. J. Li, C. Wang, F. Deng\* — 3850–3853

NMR-Spectroscopic Evidence of Intermediate-Dependent Pathways for Acetic Acid Formation from Methane and Carbon Monoxide over a ZnZSM-5 Zeolite Catalyst



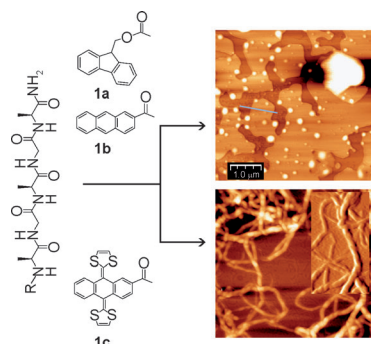
**A microporous polymorph** of SiO<sub>2</sub>, HPM-1, has a chiral structure and contains helical pores. The defect-free pure SiO<sub>2</sub> composition, which has been previously

considered unfeasible for this structure type, bestows a high thermal and hydrothermal stability upon this material.

### Chiral Zeolites

A. Rojas, M. A. Camblor\* — 3854–3856

A Pure Silica Chiral Polymorph with Helical Pores



**Chromophore–peptide systems:** A study on a series of pentapeptides covalently connected to planar  $\pi$  systems (**1a** and **1b**) or to a curved  $\pi$  system (**1c**) showed the influence of the concave shape on the efficient chiral transmission at nano- and mesoscales. Control over the hierarchical growth by H bonding,  $\pi$ – $\pi$ , and solvophobic interactions made possible the efficient generation of electroactive 3D helical fibers (see picture).

### Supramolecular Chemistry

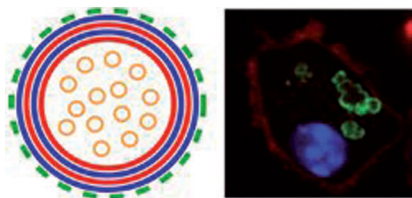
J. L. López, C. Atienza, A. Insuasty, J. López-Andarias, C. Romero-Nieto, D. M. Guldi,\* N. Martín\* — 3857–3861

Concave versus Planar Geometries for the Hierarchical Organization of Mesoscopic 3D Helical Fibers



## Vaccines

B. G. De Geest,\* M. A. Willart,  
B. N. Lambrecht, C. Pollard, C. Vervaeet,  
J. P. Remon, J. Grooten,  
S. De Koker ————— 3862–3866



**Immunizing:** To evoke highly potent immune responses against recombinant antigens, hollow capsules consisting of layers of dextran sulphate and poly-L-arginine that encapsulate the antigen ovalbumin (orange circles) were coated with immune-activating CpG-containing oligonucleotides (green). These capsules were readily internalized by dendritic cells (see picture) and showed activity in further immunization experiments.



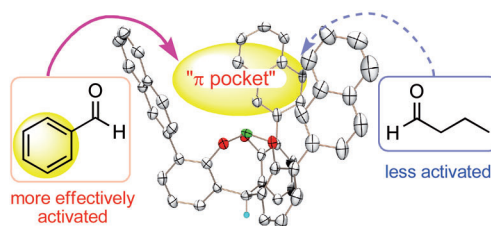
Surface-Engineered Polyelectrolyte Multilayer Capsules: Synthetic Vaccines Mimicking Microbial Structure and Function

## Molecular Recognition

H. Nakajima, M. Yasuda,\* R. Takeda,  
A. Baba\* ————— 3867–3870



Recognition of Aromatic Compounds by  $\pi$  Pocket within a Cage-Shaped Borate Catalyst



**Taking shape:** The ability of a Lewis acid catalyst to distinguish between aromatic and aliphatic hydrocarbon moieties was accomplished by using cage-shaped borate catalysts  $B(OC_6H_3Ar)_3CH$  (see

picture) having a  $\pi$  pocket derived from aryl substituents surrounding the boron center. The catalyst predominantly activated aromatic aldehydes over aliphatic ones for reaction.

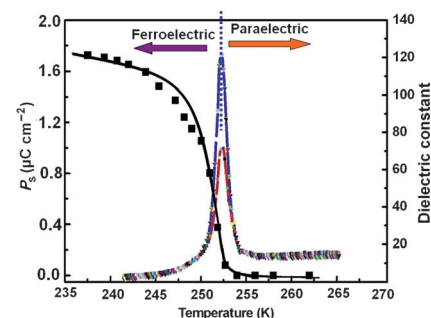
## Phase Transitions

Z. Sun, T. Chen, J. Luo,\*  
M. Hong ————— 3871–3876



Bis(imidazolium) L-Tartrate: A Hydrogen-Bonded Displacive-Type Molecular Ferroelectric Material

**A hydrogen-bonded ionic cocrystal** with imidazole as molecular rotator and L-tartaric acid as homochiral component is reported as a displacive-type ferroelectric material. It undergoes a paraelectric–ferroelectric phase transition (see picture) at 252 K with exceptional dielectric responses triggered by atomic displacements.



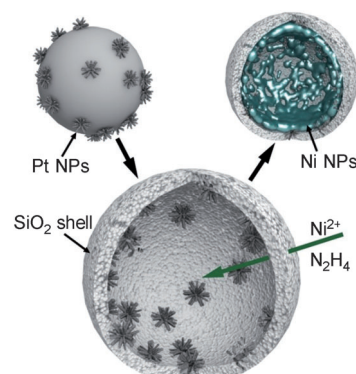
## Nanocapsules

M. Sanlés-Sobrido, M. Pérez-Lorenzo,  
B. Rodríguez-González, V. Salgueiriño,\*  
M. A. Correa-Duarte\* ——— 3877–3882

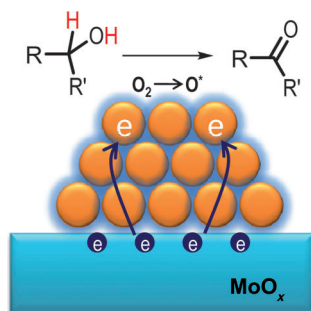


Highly Active Nanoreactors: Nanomaterial Encapsulation Based on Confined Catalysis

**It happens inside:** Highly active nano-reactors are prepared by encapsulating dendritic Pt nanoparticles (NPs) grown on a polystyrene template inside hollow porous silica capsules. The catalytic activity of these Pt NPs is preserved after encapsulation and template removal. Different metals, such as Ni, can thus be reduced inside the capsules, thereby leading to the formation of composites with tunable magnetic properties.



**Back Cover**

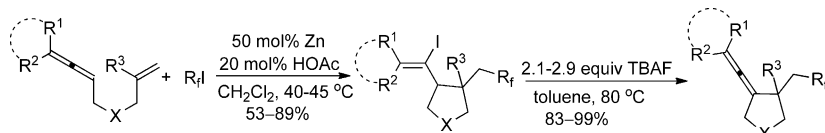


**The sensing of electrons** confined inside surface defect sites has been demonstrated. Tetracyanoethylene was employed as a single-electron acceptor to characterize the reduction of fully oxidized MoO<sub>3</sub>. Electron transfer deposits negative charge on closely contacted gold nanoparticles on the surface, which explains the high catalytic activity in the aerobic oxidation of alcohols.

## Heterogeneous Catalysis

F. Wang,\* W. Ueda, J. Xu\* — 3883–3887

Detection and Measurement of Surface Electron Transfer on Reduced Molybdenum Oxides (MoO<sub>x</sub>) and Catalytic Activities of Au/MoO<sub>x</sub>



**Something radical:** The first example of alkene-to-allene radical cyclization of allene-enes is reported. The highly chemoselective intermolecular radical addition reaction of the alkene and subsequent, exclusive *exo*-radical addition to the

allene was realized with perfluoroalkyl radicals (see scheme). A subsequent TBAF-promoted dehydroiodination of the cyclization products forms cyclopentanes and regenerates an allene moiety (TBAF = tetra-*n*-butylammonium fluoride).

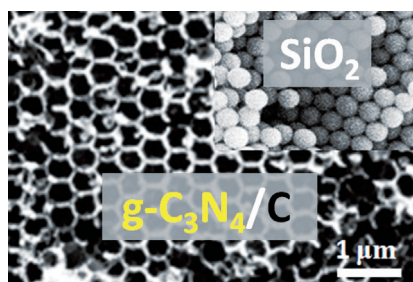
## Heterocycles

R. Zeng, C. Fu,\* S. Ma\* — 3888–3891

Formal Alkylation of Allenes through Highly Selective Radical Cyclizations of Allene-enes



**Honeycomb catalysis:** A facile oxygen reduction reaction has been observed on a graphitic C<sub>3</sub>N<sub>4</sub>/carbon catalyst with three-dimensional interconnected macropores (see picture with SiO<sub>2</sub> template). This material not only shows catalytic activity that is comparable to that of commercial Pt/C, but also has much higher organic-fuel tolerance and long-term stability.



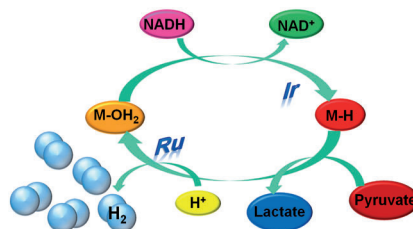
## Macroporous Catalysts

J. Liang, Y. Zheng, J. Chen, J. Liu, D. Hulicova-Jurcakova, M. Jaroniec, S. Z. Qiao\* — 3892–3896

Facile Oxygen Reduction on a Three-Dimensionally Ordered Macroporous Graphitic C<sub>3</sub>N<sub>4</sub>/Carbon Composite Electrocatalyst



**Artificial enzymes:** Half-sandwich arene ruthenium(II) and cyclopentadienyl iridium(III) complexes containing *N,N*-chelated ligands can use NADH as a source of hydride for the reduction of ketones (see picture). Moreover, cyclopentadienyl phenanthroline iridium(III) derivatives at micromolar concentrations are robust catalysts for the production of H<sub>2</sub> from NADH in water and can raise the NAD<sup>+</sup>/NADH ratio in cancer cells.



## Biomimetic Chemistry

S. Betanzos-Lara, Z. Liu, A. Habtemariam, A. M. Pizarro, B. Qamar, P. J. Sadler\* — 3897–3900

Organometallic Ruthenium and Iridium Transfer-Hydrogenation Catalysts Using Coenzyme NADH as a Cofactor

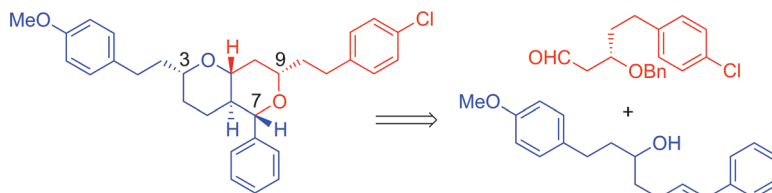


## Synthetic Methods

A. J. Bunt, C. D. Bailey, B. D. Cons,  
S. J. Edwards, J. D. Elsworth, T. Pheko,  
C. L. Willis\* — 3901–3904



Bicyclic Oxygen Heterocycles from  $\gamma,\delta$ -Unsaturated Alcohols: Synthetic Targets Inspired by Blepharocalyxin D



**trans-2,8-Dioxabicyclodecanes** were prepared in high yield with the creation of up to three stereocenters in a single pot by the acid-mediated reaction of  $\gamma,\delta$ -unsaturated alcohols with aldehydes (see

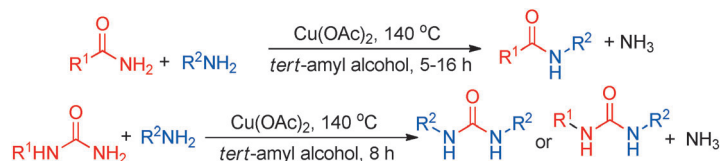
scheme, Bn = benzyl). This versatile reaction enables the stereoselective introduction of substituents at the C3, C4, C7, and C9 positions of the bicyclic framework.

## Synthetic Methods

M. Zhang, S. Imm, S. Bähn, L. Neubert,  
H. Neumann, M. Beller\* — 3905–3909



Efficient Copper(II)-Catalyzed Transamidation of Non-Activated Primary Carboxamides and Ureas with Amines



**Amid(e) them all:** Primary carboxamides and ureas react with aromatic and aliphatic amines in the presence of a copper

catalyst to give a wide range of functionalized amides (see scheme).

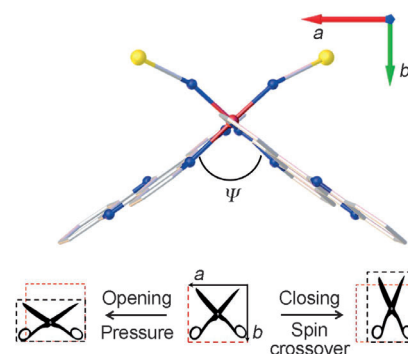
## Molecular Materials

H. J. Shepherd, T. Palamarciuc, P. Rosa,  
P. Guionneau,\* G. Molnár,\* J.-F. Létard,  
A. Bousseksou — 3910–3914



Antagonism between Extreme Negative Linear Compression and Spin Crossover in  $[\text{Fe}(\text{dpp})_2(\text{NCS})_2]\cdot\text{py}$

A scissor-like geometric mechanism is responsible for the strongest negative linear compression effect yet observed in a molecular material,  $[\text{Fe}(\text{dpp})_2(\text{NCS})_2]\cdot\text{py}$  (see picture; dpp = dipyrdo[3,2-*a*:2'3'-*c*]phenazine), C gray, N blue, S yellow, Fe red). The same mechanism is also responsible for suppressing the high-spin to low-spin transition under pressure.

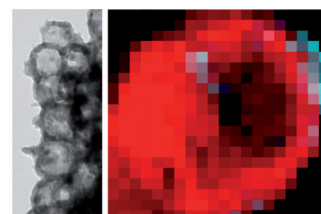
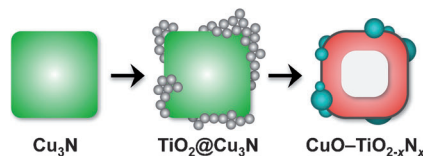


## Photocatalytic CO<sub>2</sub> Conversion

S. I. In, D. D. Vaughn II,  
R. E. Schaak\* — 3915–3918



Hybrid CuO-TiO<sub>2-x</sub>N<sub>x</sub> Hollow Nanocubes for Photocatalytic Conversion of CO<sub>2</sub> into Methane under Solar Irradiation

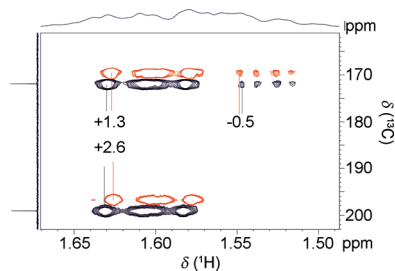


**Methane-producing hollow nanocubes:** Hybrid CuO-TiO<sub>2-x</sub>N<sub>x</sub> hollow nanocubes have been synthesized by first depositing TiO<sub>2</sub> onto Cu<sub>3</sub>N nanocube templates, then heating in air to oxidize the Cu<sub>3</sub>N to CuO

while concomitantly incorporating nitrogen into the TiO<sub>2</sub>. The nanostructured CuO-TiO<sub>2-x</sub>N<sub>x</sub> material photocatalytically converts CO<sub>2</sub> into methane under solar irradiation.



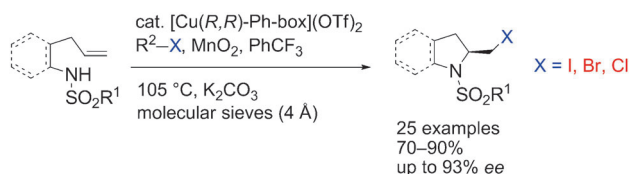
**Simply successful:** A proton-selective HSQMB-C-TOCSY experiment can be used to measure small proton-carbon ( $^nJ_{CH}$ ;  $n > 1$ ) coupling constants on both protonated and non-protonated carbon atoms (see spectrum). The method combines in a single pulse scheme all the benefits of the widely used HSQMB and HSQC-TOCSY experiments. The magnitude and the sign of  $^nJ_{CH}$  can be determined simply with excellent accuracy.



## NMR Spectroscopy

J. Saurí, J. F. Espinosa,  
T. Parella\* 3919–3922

A Definitive NMR Solution for a Simple and Accurate Measurement of the Magnitude and the Sign of Small Heteronuclear Coupling Constants on Protonated and Non-Protonated Carbon Atoms



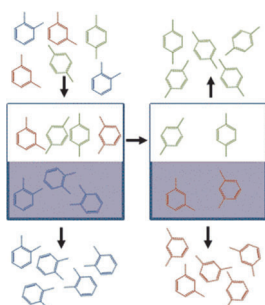
**Problem solved:** The title reaction was used for the synthesis of chiral 2-bromo, chloro, and iodoalkyl indolines and 2-iodoalkyl pyrrolidines (see scheme). Stereocenter formation is believed to occur by enantioselective *cis* aminocupra-

tion and C–X bond formation is believed to occur by atom transfer. The utility of the products as versatile synthetic intermediates was demonstrated, as was a radical cascade cyclization sequence.

## Enantioselective Aminohalogenation

M. T. Bovino,  
S. R. Chemler\* 3923–3927

Catalytic Enantioselective Alkene Aminohalogenation/Cyclization Involving Atom Transfer

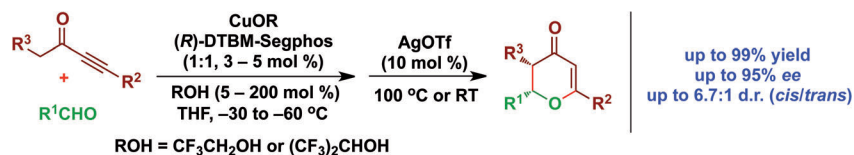


A **Werner complex** is highly selective for *o*-xylene in a vapor mixture containing all three isomers. However, in the absence of *o*-xylene, the substrate shows similar selectivity for *m*-xylene over *p*-xylene. Kinetic studies show a different trend whereby *m*-xylene is absorbed most rapidly, implying that thermodynamic factors must be responsible for the selectivity.

## Xylene Separation

M. Lusi, L. J. Barbour\* 3928–3931

Solid-Vapor Sorption of Xylenes: Prioritized Selectivity as a Means of Separating All Three Isomers Using a Single Substrate



**Ynones as diene surrogates:** The asymmetric synthesis of enantiomerically enriched substituted dihydropyranones is described. The products are obtained in two steps by a copper(I)-catalyzed direct aldol reaction of ynones followed by

a silver-catalyzed oxy-Michael reaction. This easy method is compatible with both aromatic and aliphatic substrates, and provides excellent chemoselectivity under mild reaction conditions.

## Asymmetric Synthesis

S.-L. Shi, M. Kanai,\*  
M. Shibasaki\* 3932–3935

Asymmetric Synthesis of Dihydropyranones from Ynones by Sequential Copper(I)-Catalyzed Direct Aldol and Silver(I)-Catalyzed Oxy-Michael Reactions

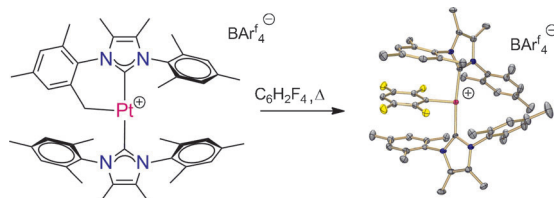


### Agostic Interactions

O. Rivada-Wheelaghan, M. A. Ortuño,  
J. Díez, A. Lledós,\*  
S. Conejero\* 3936–3939



Tuning N-Heterocyclic Carbenes in T-Shaped Pt<sup>II</sup> Complexes for Intermolecular C–H Bond Activation of Arenes



**Small change matters:** T-shaped Pt<sup>II</sup> complexes with less flexible substituents, than, for example, isopropyl or *tert*-butyl groups, on N-heterocyclic carbene (NHC) ligands allow for C–H bond activation reactions of aromatic compounds (see

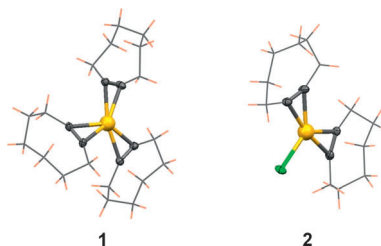
scheme; BAf<sub>4</sub><sup>−</sup> = tetrakis[3,5-trifluoromethyl]phenyl]borate; F yellow, Pt red). NHC substituents that are not highly branched prevent agostic interactions and reduce the barriers to achieve the C–H bond cleavage.

### Gold Complexes

A. Das, C. Dash, M. Yousufuddin,  
M. A. Celik, G. Frenking,\*  
H. V. R. Dias\* 3940–3943



Isolable Tris(alkyne) and Bis(alkyne) Complexes of Gold(I)



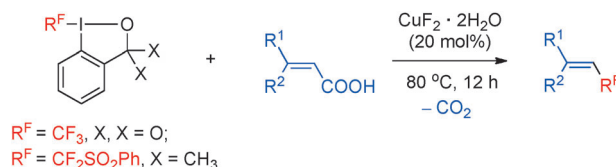
**Golden trefoils:** Tris(alkyne)gold complex [(cocyt)<sub>3</sub>Au][SbF<sub>6</sub>] (see picture; 1-SbF<sub>6</sub>) can be synthesized from cyclooctyne (cocyt) and AuSbF<sub>6</sub> generated in situ. Treatment of AuCl with cyclooctyne led to the bis(alkyne)gold complex [Au(cocyt)<sub>2</sub>Cl] (2). DFT analysis indicates that the cyclooctyne ligands are net electron donors in 1 but overall electron acceptors in 2. AuSbF<sub>6</sub> is shown to mediate [2+2+2] cycloaddition reactions of alkynes.

### Synthetic Methods

Z. He, T. Luo, M. Hu, Y. Cao,  
J. Hu\* 3944–3947



Copper-Catalyzed Di- and Trifluoromethylation of α,β-Unsaturated Carboxylic Acids: A Protocol for Vinylic Fluoroalkylations



**Dual action:** The Lewis acid CuF<sub>2</sub>·2 H<sub>2</sub>O efficiently catalyzes the reaction between electrophilic fluoroalkylating agents and α,β-unsaturated carboxylic acids by dually

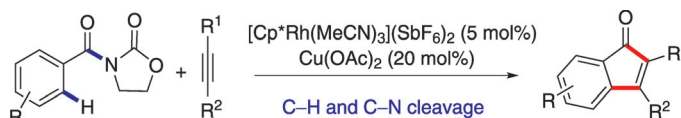
activating both reactants, thus affording di- and trifluoromethyl alkenes in high yields with excellent *E/Z* selectivity.

### C–H Activation

B.-J. Li, H.-Y. Wang, Q.-L. Zhu,  
Z.-J. Shi\* 3948–3952

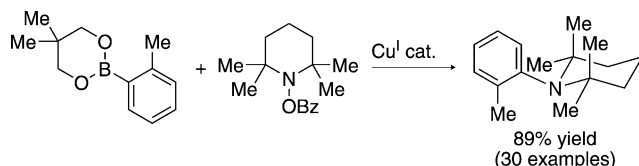


Rhodium/Copper-Catalyzed Annulation of Benzimides with Internal Alkynes: Indenone Synthesis through Sequential C–H and C–N Cleavage



**Doubled up:** A rhodium(III)/copper(II) system co-catalyzes the annulation of benzimides with internal alkynes for the synthesis of indenones (see scheme; Cp\* = C<sub>5</sub>Me<sub>5</sub>). The reaction involves an uncommon nucleophilic addition of

a transition-metal–carbon bond to an imide moiety. This novel reaction provides a facile route to synthesize indenones from readily available benzimides and internal alkynes.



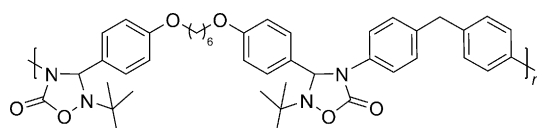
**No longer a hindrance:** Copper-catalyzed electrophilic amination of aryl boronic esters is accomplished under mild reaction conditions using 2.5–5.0 mol % of a catalyst derived from copper *tert*-but-

oxide and Xantphos ligand (see scheme). The reaction tolerates a wide range of functional groups and can be used to prepare some of the most hindered anilines made to date.

## Synthetic Methods

R. P. Rucker, A. M. Whittaker, H. Dang, G. Lalic\* — 3953–3956

Synthesis of Hindered Anilines: Copper-Catalyzed Electrophilic Amination of Aryl Boronic Esters



**A premier in polymer chemistry:** The cycloaddition of bisoxaziridines with 4,4'-methylene diphenyl diisocyanate yields novel linear poly(1,2,4-oxadiazolidin-5-one) derivatives (see scheme). The polymers are relatively stable (> 200 °C) and

model reactions show that the reaction rate strongly depends on the electronic properties of the oxaziridine unit; electron-donating substituents on the C atom of the heterocyclic ring promote the cycloaddition.

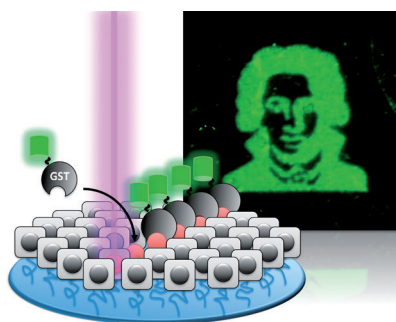
## Polycycloaddition

M. Dickmeis, H. Cinar, H. Ritter\* — 3957–3959

Poly(1,2,4-oxadiazolidin-5-one)s Synthesized by Polycycloaddition of Bisoxaziridines and Diisocyanate



**Light, GSH, action!** Glutathione (GSH) fulfills a universal role as redox factor, scavenger of reactive oxygen species, and as an essential substrate in the conjugation, detoxification, and reduction reactions catalyzed by glutathione S-transferase (GST). A photoactivatable glutathione allows the GSH-GST network to be triggered by light. GST fusion proteins can be assembled in situ at variable density and structures by laser-scanning activation.



## Chemical Biology

V. Gatterdam, T. Stoess, C. Menge, A. Heckel,\* R. Tampé\* — 3960–3963

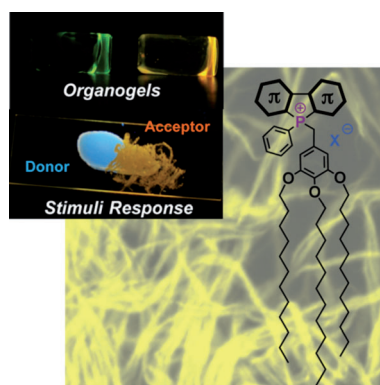
Caged Glutathione – Triggering Protein Interaction by Light



Inside Cover



**Sensitive gels:** The amphiphilic features of phosphole-lipids lead to intriguing self-assembly properties and the formation of highly fluorescent organogels. Moreover, the dynamic structural features of the system make it possible to amplify the mechanochromic emission shifts (100 nm) in a donor–acceptor system through thermally and mechanically responsive fluorescence resonance energy transfer (FRET).



## Phosphole-Lipids

Y. Ren, W. H. Kan, V. Thangadurai, T. Baumgartner\* — 3964–3968

Bio-Inspired Phosphole-Lipids: From Highly Fluorescent Organogels to Mechanically Responsive FRET



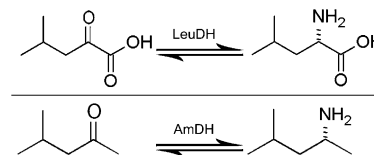
### Asymmetric Amine Synthesis

M. J. Abrahamson, E. Vázquez-Figueroa,  
N. B. Woodall, J. C. Moore,  
A. S. Bommarius\* \_\_\_\_\_ **3969–3972**



Development of an Amine  
Dehydrogenase for Synthesis of Chiral  
Amines

A **leucine dehydrogenase** has been successfully altered through several rounds of protein engineering to an enantioselective amine dehydrogenase. Instead of the wild-type  $\alpha$ -keto acid, the new amine dehydrogenase now accepts the analogous ketone, methyl isobutyl ketone (MIBK), which corresponds to exchange of the carboxy group by a methyl group to produce chiral (*R*)-1,3-dimethylbutylamine.



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## Angewandte Corrigendum

Nanoparticle-Stabilized Double  
Emulsions and Compressed Droplets

C. Miesch, I. Kosif, E. Lee, J.-K. Kim,  
T. P. Russell,\* R. C. Hayward,\*

T. Emrick\* \_\_\_\_\_ **145–149**

*Angew. Chem. Int. Ed.* **2012**, *51*

DOI: 10.1002/anie.201106665

The authors of this Communication wish to insert an additional citation in reference [25]. This is to note the report of Fletcher and co-workers on stabilizing both simple and multiple emulsions of ionic liquids with two different fumed silica particles, in which the particles have different wettability.

[25] a) B. P. Binks, J. Philip, J. A. Rodrigues, *Langmuir* **2005**, *21*, 3296; b) B. P. Binks, A. K. F. Dyab, P. D. I. Fletcher, *Chem. Commun.* **2003**, 2540.