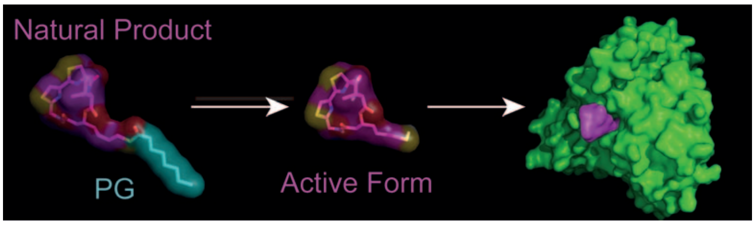
# CONTENTS

## CONCEPTS



**Natural prodrugs**: Bioactive natural products (see figure) often work through novel and sometimes surprising mechanisms of action and, therefore, they serve as inspiration to synthetic and medicinal chemists, in terms of both structure and mechanism.

**Natural Products**

*J. C. Kwan, H. Luesch** . . 13020 – 13029

**Weapons in Disguise—Activating Mechanisms and Protecting Group Chemistry in Nature**

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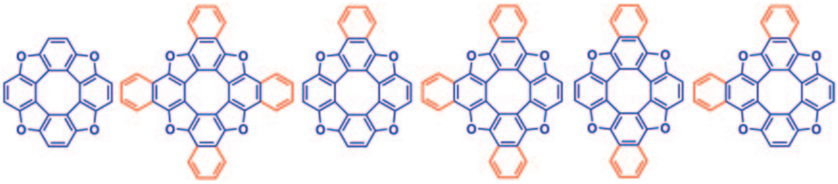
## COMMUNICATIONS



**Acid-mediated condensation** of a 2,3-dialkyl-1,4-benzoquinone with 1,4-naphthoquinone produces a series of alkane-soluble π-extended tetraoxa[8]circulenes; these structures (shown here) were successfully incorporated in organic light-emitting diodes.

**Blue OLEDs**

*C. B. Nielsen, T. Brock-Nannestad, T. K. Reenberg, P. Hammershøj, J. B. Christensen, J. W. Stouwdam, M. Pittelkow** . . . . . . . . . . . . . 13030 – 13034

**Organic Light-Emitting Diodes from Symmetrical and Unsymmetrical π-Extended Tetraoxa[8]circulenes**

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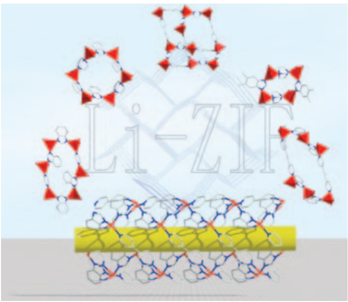
**Lightest tetrahedral node**: While silica-type tetrahedral frameworks can be readily emulated with divalent metal compounds (e.g., zinc imidazolate frameworks), it is more difficult with $Li^+$. Here, a new series of Li-based zeolitic imidazolate frameworks (Li-ZIFS) has been synthesized by using a strategy based on charge-complementary ligands designed to prevent excessively negative charge surrounding Li sites. Among them, some exhibit a high $CO_2$ adsorption capacity (e.g., 49 $cm^3 g^{-1}$ at 273 K and 1 atm).



**Metal–Organic Frameworks**

*S.-T. Zheng, Y. Li, T. Wu, R. A. Nieto, P. Feng,* X. Bu** . . . . . . . . . 13035 – 13040

VIP

**Porous Lithium Imidazolate Frameworks Constructed with Charge-Complementary Ligands**

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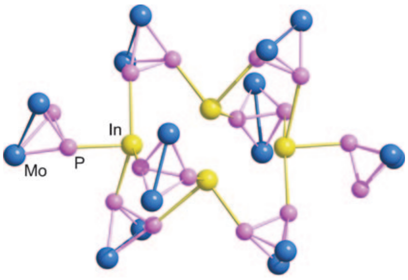
**A new soluble $In^+$ source** containing the very weakly coordinating anion $[Al\{OC(CF_3)_3\}_4]^-$ was developed. In reaction with a $P_2$ ligand complex an unprecedented tetracationic aggregate is formed featuring a short In···In distance (see picture). Polymeric strands arising from a reaction with a *cyclo*-$P_3$ ligand complex exhibit a novel coordination mode for $P_3$ units.



**Main Group Chemistry**

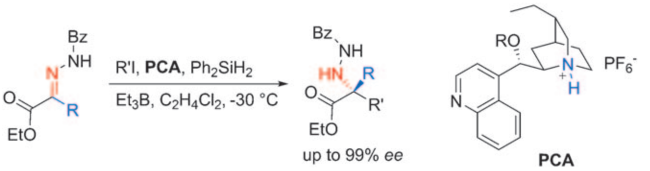
*S. Welsch, M. Bodensteiner, M. Dušek, M. Sierka, M. Scheer** . . . 13041 – 13045

**A Novel Soluble $In^I$ Precursor for $P_n$ Ligand Coordination Chemistry**

## Radical Addition

*S. Y. Kim, S. J. Kim, D. O. Jang** ................ 13046 – 13048

### Enantioselective Radical Addition to Ketimines: A Synthetic Route Towards α,α-Disubstituted α-Amino Acids



**A radical attack**: In the presence of a protonated cinchonine derivative, radical addition reactions proceeded efficiently, providing a general approach to the synthesis of a diverse range of enantioenriched α,α-disubstituted α-amino acids.

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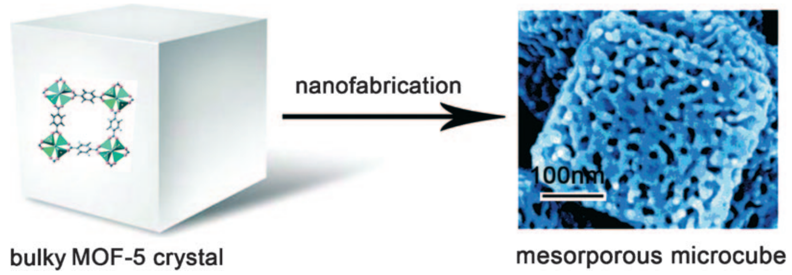
## Metal–Organic Frameworks

*Z. Xin, J. Bai,* Y. Pan, M. J. Zaworotko* .......... 13049 – 13052

### Synthesis and Enhanced $H_2$ Adsorption Properties of a Mesoporous Nanocrystal of MOF-5: Controlling Nano-/Mesostructures of MOFs To Improve Their $H_2$ Heat of Adsorption



**Controlled improvement**: For the first time, a novel mesoporous cube of MOF-5 (MNMOF-5) was prepared for which it was shown that controlling the nano-/mesostructures can improve the $H_2$ adsorption properties and facilitate the future applications of MOFs.

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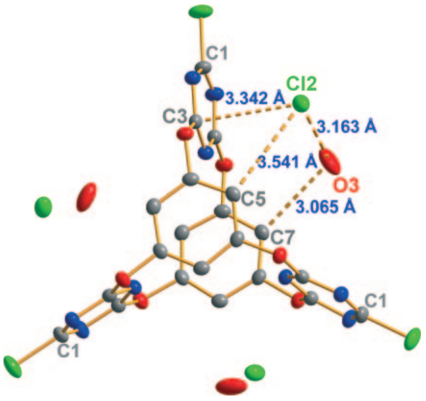
## Host–Guest Chemistry

*D.-X. Wang,* Q.-Q. Wang, Y. Han, Y. Wang,* Z.-T. Huang, M.-X. Wang** ............. 13053 – 13057

### Versatile Anion–π Interactions between Halides and a Conformationally Rigid Bis(tetraoxacalix[2]arene[2]triazine) Cage and Their Directing Effect on Molecular Assembly



**Interactive halides**: Bis(tetraoxacalix[2]arene[2]triazine), a conformationally rigid cage molecule of three V-shaped electron-deficient clefts, forms 1:1 complexes with fluoride (361 $\mathrm{M}^{-1}$), chloride (146 $\mathrm{M}^{-1}$) and bromide (95 $\mathrm{M}^{-1}$) in acetonitrile. Different anion–π interactions along with multiple hydrogen bonding, halogen bonding and lone-pair-electrons–π interactions directed the formation of different molecular assemblies (an example is shown here).

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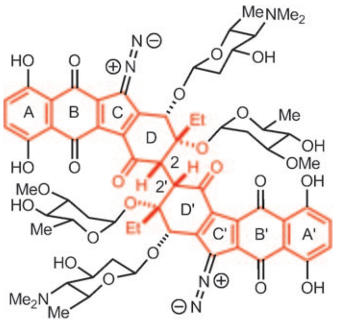
## Natural Product Synthesis

*H. G. Lee, J. Y. Ahn, A. S. Lee, M. D. Shair** ............... 13058 – 13062

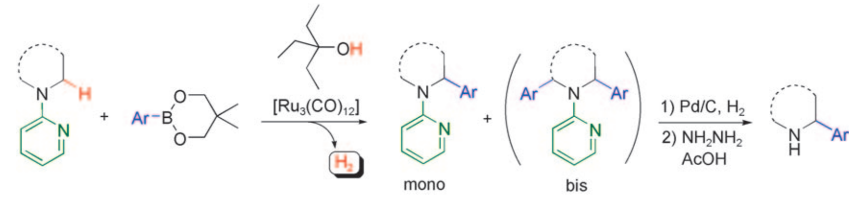
### Enantioselective Synthesis of the Lomaiviticin Aglycon Full Carbon Skeleton Reveals Remarkable Remote Substituent Effects during the Dimerization Event



lomaiviticin A

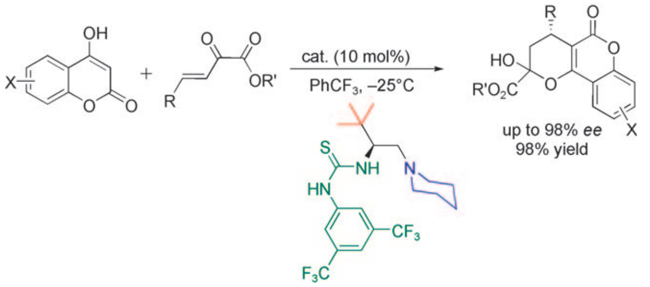
**A full carbon skeleton** of the natural product lomaiviticin has been synthesized. The approach features anionic annulation reactions to deliver A and B rings of the natural product, and stereoselective oxidative enolate coupling to form the central C2–C2′ σ bond. In the course of the investigation, a remarkable substituent effect at C11 position was observed.

## Homogeneous Catalysis



**All you need is an open vial!** The direct α arylation of cyclic alkylamines (see scheme) requires an open vial, as the hydrogen atom involved in the $C(sp^3)$–H-activation process is ultimately released as hydrogen gas. Reports on the formation of hydrogen gas in direct transition-metal-catalyzed functionalizations are still rare. Open-vial reactions proved crucial to this direct arylation procedure as, upon sealing, catalyst deactivation occurs.

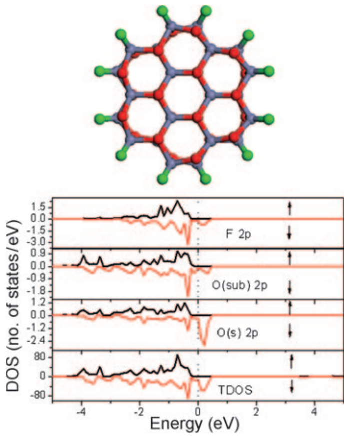
## Asymmetric Synthesis



**Efficient excess**: An efficient and facile enantioselective Michael addition reaction through hydrogen-bonding catalysis for the synthesis of coumarin complexes has been developed (see scheme). A simple bifunctional amine–thiourea small molecule has been discovered to catalyze this process with high yields and high to excellent enantiomeric excesses.

## Ferromagnetism

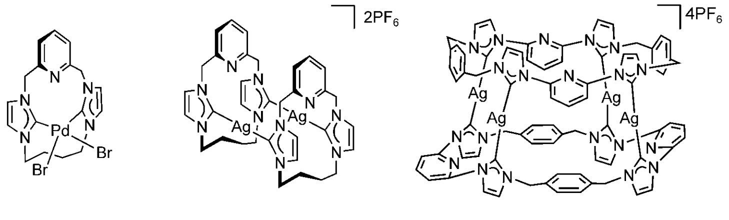
**Partial surface passivation** of surface zinc bonds is an alternative approach to conventional volume doping to induce ferromagnetism in ZnO nanowires. Nanowires with partial F passivation exhibit half-metallic ground-state properties. The ferromagnetic stability is improved when the dimensionality of ZnO decreases from two (surfaces) to one (nanowires). The surface passivation approach may be applicable to modulating the magnetic properties of general nanomaterials.



### Coordination Chemistry

*C. Radloff, H.-Y. Gong, C. Schulte to Brinke, T. Pape, V. M. Lynch, J. L. Sessler,* F. E. Hahn** ................ 13077 – 13081

**Metal-Dependent Coordination Modes Displayed by Macrocyclic Polycarbene Ligands**



[PdBr$_2$(**1**)]   *syn*-[Ag$_2$(**1**)$_2$](PF$_6$)$_2$   [Ag$_4$(**2**)$_2$](PF$_6$)$_4$

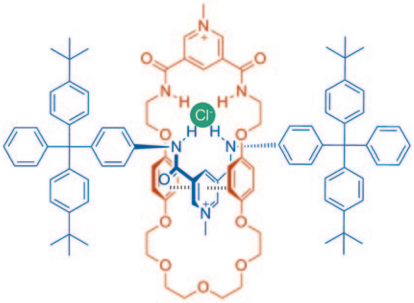
**Carbene–metal molecular box**: Two imidazolium macrocycles, H$_2$-**1**(X)$_2$ and H$_4$-**2**(PF$_6$)$_4$, act as precursors for the formation of poly(NHC) ligands. The carbene ligands display metal-dependent conformations in forming organometallic complexes. In particular, they are capable of stabilizing box-like structures such as *syn*-[Ag$_2$(**1**)$_2$]$^{2+}$ and [Ag$_4$(**2**)$_2$]$^{4+}$ when exposed to linearly coordinated silver cations. In contrast, a monomeric species featuring a C-Pd-C angle of about 90° is formed between **1** and Pd$^{II}$.

# FULL PAPERS

### Anion Recognition

*L. M. Hancock, L. C. Gilday, S. Carvalho, P. J. Costa, V. Félix, C. J. Serpell, N. L. Kilah, P. D. Beer** ................. 13082 – 13094

**Rotaxanes Capable of Recognising Chloride in Aqueous Media**

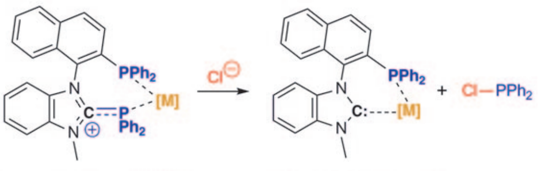


**Chloride wins**: A new, versatile chloride-anion-templating synthetic pathway is exploited in the preparation of a series of eight new [2]rotaxane host molecules (see image), including the first sulfonamide interlocked system. $^1$H NMR spectroscopic titration investigations demonstrate the rotaxanes' capability to recognise chloride anions in competitive aqueous solvent media, including a dicationic rotaxane that binds chloride in 35 % water.

### Palladium

*I. Abdellah, C. Lepetit, Y. Canac,* C. Duhayon, R. Chauvin** ............... 13095 – 13108

**Imidazoliophosphines are True N-Heterocyclic Carbene (NHC)–Phosphenium Adducts**



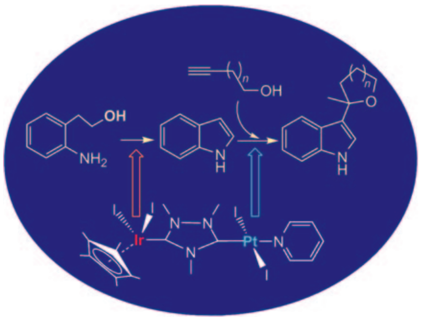
free or coordinated BIMIONAP   trapped NHC-phosphine

**Addition of anionic nucleophiles (Cl$^-$, *n*Bu$^-$)** to free BIMIONAP and BIMIONAP-containing palladium complexes results in selective cleavage of the N$_2$C–P bond, from which the released N-heterocyclic carbene (NHC) fragment can be trapped by protonation, hydrolysis, sulfurization, or coordination to Pd$^{II}$ centers (see scheme).

### Domino Reactions

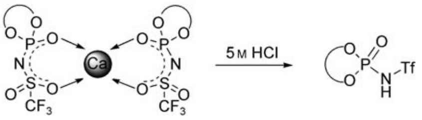
*A. Zanardi, J. A. Mata, E. Peris** .................... 13109 – 13115

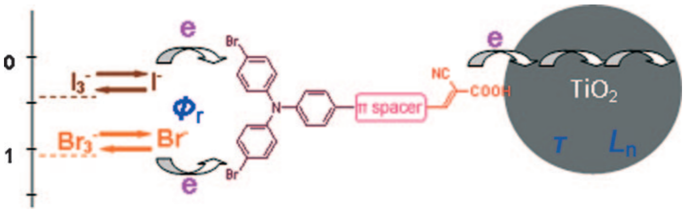
**An Ir–Pt Catalyst for the Multistep Preparation of Functionalized Indoles from the Reaction of Amino Alcohols and Alkynyl Alcohols**



**Three in one**: A heterodimetallic complex of Ir–Pt (see graphic) with a triazolyldiylidene linker has been obtained and fully characterized. The complex brings together some of the catalytic properties typically shown by Ir and Pt catalysts. A multistep reaction employing the Ir-mediated oxidative cyclization of 2-(*ortho*-aminophenyl)ethanol and the Pt-catalyzed cyclization–addition of alkynyl alcohols to indoles is reported.

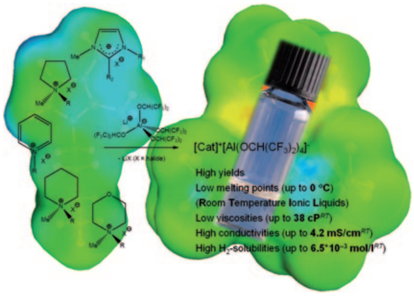
**Freedom!** The synthesis and structure determination of various 1,1′-bi-2-naphthol (BINOL)-based *N*-triflylphosphoramides and their corresponding calcium salts is presented. A simple acidic treatment of the calcium salts provides the metal-free Brønsted acids (see scheme; Tf = trifluoromethanesulfonyl).



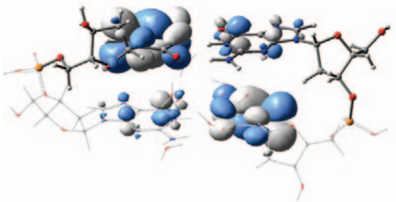


**A new middleman**: The $Br^-/Br_3^-$ redox mediator was proved to be a promising alternative to $I^-/I_3^-$ for application in dye-sensitized solar cells (see graphic). Studies show that the energy gap between the HOMO level of the dye and the potential of the $Br^-/Br_3^-$ redox mediator influences their charge-transfer processes and solar-energy conversion efficiency.

**New RTILs**: A series of ionic liquids (ILs) based on the weakly coordinating anion $[Al(hfip)_4]^-$ (see figure) has been synthesized and thoroughly characterized. The ILs were found to have widely interesting properties that suggest potential for these ILs in many applications (hfip = hexafluoroisopropoxy).



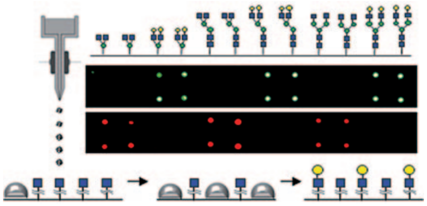
**DNA electron captors**: The minimal essential skeletal section of DNA helices, $[dGpdC]_2$, has been constructed, fully optimized, and analyzed by a quantum mechanical approach at a reliable level of theory (see image), showing that DNA double strands are capable of capturing low-energy electrons and forming electronically stable radical anions. The structural features of the optimized radical anion $[dGpdC]_2^{\bullet -}$ also suggest the possibility of interstrand proton transfer.



### Microarrays

*S. Serna, J. Etxebarria, N. Ruiz,
M. Martin-Lomas,
N.-C. Reichardt** .......... 13163 – 13175

#### Construction of *N*-Glycan Microarrays by Using Modular Synthesis and On-Chip Nanoscale Enzymatic Glycosylation

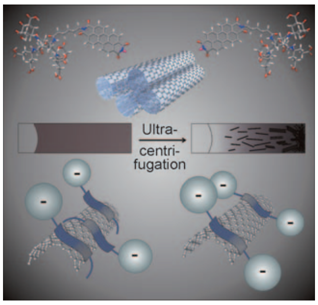


**Go nano!** Arrays of immobilised carbohydrates can be enzymatically processed with the help of glycosyl transferases in nanodroplets placed on top of individual spots. This methodology opens the way for the stereospecific on-chip construction of glycan arrays with very high ligand densities by using immobilised synthetic glycan scaffolds and minute amounts of recombinant glycosyltransferases (see figure).

### Carbon Nanotubes

*C. Backes, E. Karabudak,
C. D. Schmidt, F. Hauke, A. Hirsch,
W. Wohlleben** ............ 13176 – 13184

#### Determination of the Surfactant Density on SWCNTs by Analytical Ultracentrifugation

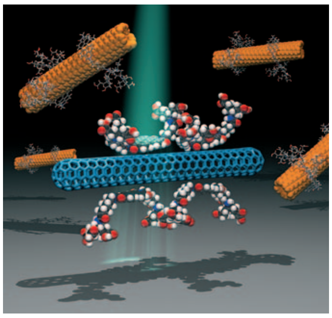


**Nanotube detergents**: Deep insights into the arrangement of various surfactants noncovalently bound to the sidewall of single-walled carbon nanotubes (SWCNTs, see figure) have been obtained by analysis of the sedimentation coefficients with analytical ultracentrifugation. The investigation included classical detergents, as well as synthesized perylene-based surfactants.

### Carbon Nanotubes

*C. Backes, U. Mundloch,
C. D. Schmidt, J. N. Coleman,
W. Wohlleben, F. Hauke,
A. Hirsch** ................. 13185 – 13192

#### Enhanced Adsorption Affinity of Anionic Perylene-Based Surfactants towards Smaller-Diameter SWCNTs

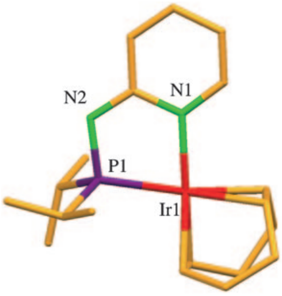


**Nanotube surfactant design**: The interactions of synthesized perylene-based surfactants with single-walled carbon nanotubes (SWCNTs) of various diameters have been investigated. The surfactants exhibit an enhanced adsorption affinity towards smaller-diameter SWCNTs (see figure), which could be of great importance for future nanotube separation by selective dispersion.

### Amine Alkylation

*S. Michlik, R. Kempe** . . . 13193 – 13198

#### New Iridium Catalysts for the Efficient Alkylation of Anilines by Alcohols under Mild Conditions

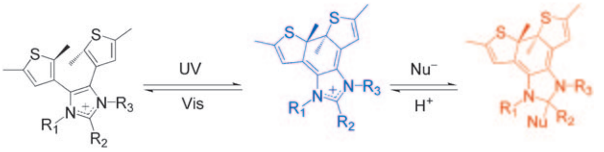


**Selective amine alkylation**: The synthesis of eight new iridium complexes containing anionic P,N ligands (see image) is described. These new complexes were used as highly active catalysts for the selective monoalkylation of anilines with primary alcohols, and gave nearly quantitative conversion under mild reaction conditions.

### Nucleophilic Addition

*G. Duan, N. Zhu,
V. W.-W. Yam** ............ 13199 – 13209

#### Syntheses and Photochromic Studies of Dithienylethene-Containing Imidazolium Derivatives and Their Reactivity towards Nucleophiles

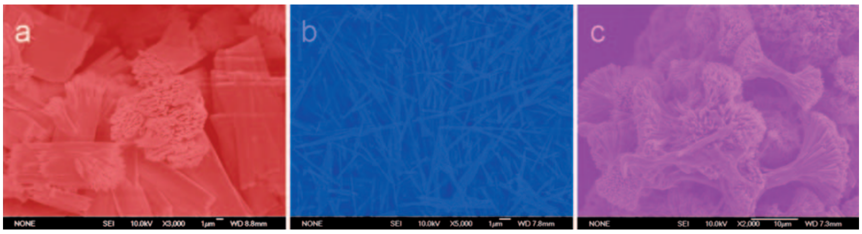


**An open-and-shut case**: A series of photochromic dithienylethene-containing imidazolium salts has been synthesized. The reactivities of these imidazolium derivatives towards nucleophiles show significant differences between their open and closed forms (see scheme).

## Crystal Growth

*J. Ma, X. Duan, J. Lian, T. Kim, P. Peng, X. Liu, Z. Liu, H. Li, W. Zheng** ................. 13210–13217

**$Sb_2S_3$ with Various Nanostructures: Controllable Synthesis, Formation Mechanism, and Electrochemical Performance toward Lithium Storage**

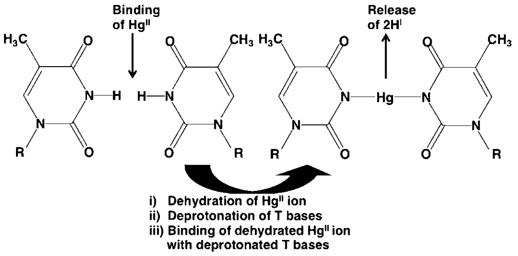


**How do your crystals grow?** Morphology control of $Sb_2S_3$ crystals (see figure) could be realized by using a solution-phase route, through manipulating the interaction between the solvent, additive, and nanostructures. In addition, the as-synthesized $Sb_2S_3$ nanomaterials are also shown to be improved electrode materials for lithium ion batteries.

## Nucleic Acids

*H. Torigoe,* A. Ono, T. Kozasa* .................. 13218–13225

**$Hg^{II}$ Ion Specifically Binds with T:T Mismatched Base Pair in Duplex DNA**



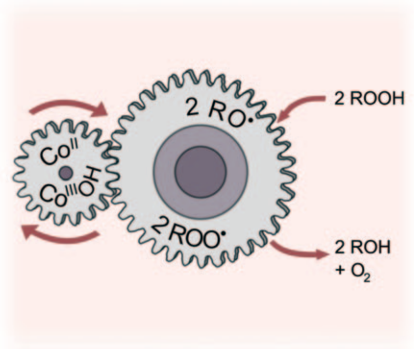
**Mercury rising**: We have investigated the binding mode between $Hg^{II}$ ions and the T:T mismatched base pair. $Hg^{II}$ ions surrounded by structured water molecules can be dehydrated, and the two protons at the N3 positions of T:T can then be released, as shown in the scheme. Dehydrated $Hg^{II}$ ions can then bind with the deprotonated thymine bases to form N3-Hg-N3.

## Radical Reactions

*N. Turrà, U. Neuenschwander, A. Baiker, J. Peeters, I. Hermans** ................ 13226–13235

**Mechanism of the Catalytic Deperoxidation of *tert*-Butylhydroperoxide with Cobalt(II) Acetylacetonate**

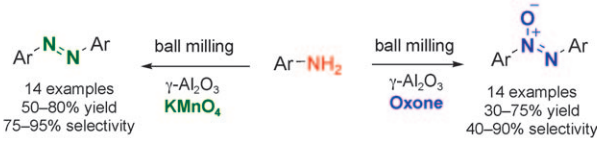
**Autoinhibition**: $Co^{II}$ ions initiate a radical-chain deperoxidation of *tert*-butylhydroperoxide propagated by peroxyl and alkoxyl radicals (see picture). The $Co^{II}$ ion is thereby converted into a $Co^{III}$–OH species, which can either induce initiation upon reaction with ROOH or termination upon the mutual association reaction of two $Co^{III}$–OH species. This behavior results in maximum deperoxidation activity as a function of the total cobalt concentration.



## Solvent-Free Oxidation

*R. Thorwirth, F. Bernhardt, A. Stolle,* B. Ondruschka, J. Asghari* .................. 13236–13242

**Switchable Selectivity during Oxidation of Anilines in a Ball Mill**

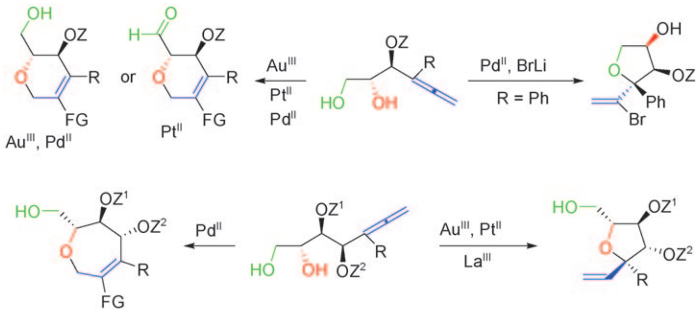


**Grinding reactions**: Highly efficient oxidative homocoupling of aromatic amines was performed under solvent-free conditions in a planetary ball mill (see scheme). The choice of solid oxidants and grinding auxiliaries allowed selective generation of the oxidized products. Other methods of energy input are compared with respect to reaction time and energy consumption.

## Synthetic Methods

*B. Alcaide,* P. Almendros,**
*R. Carrascosa,*
*T. Martínez del Campo* . . 13243 – 13252

### Metal-Catalyzed Cycloetherification Reactions of β,γ- and γ,δ-Allendiols: Chemo-, Regio-, and Stereocontrol in the Synthesis of Oxacycles

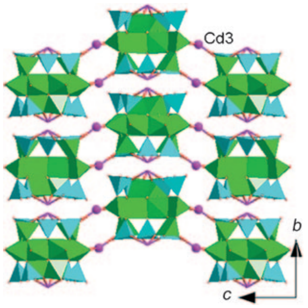


**Diversely functionalized enantiopure** tetrahydrofurans, dihydropyrans, and tetrahydrooxepines are prepared by using a chemo-, regio-, and stereoselective methodology. This approach involves controlled Pd-, Pt-, Au-, or La-catalyzed oxycyclization reactions of β,γ- and γ,δ-allenic diols (see scheme; FG = functional group, Z = protecting group).

## Polyoxometalates

*J. Zhou, J. Zhang, W.-H. Fang,*
*G.-Y. Yang** ................ 13253 – 13261

### A Series of Vanadogermanates from 1D Chain to 3D Framework Built by Ge–V–O Clusters and Transition-Metal-Complex Bridges

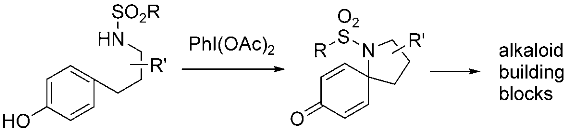


**Extended vanadogermanates** (VGOs) with 1-, 2- and 3D structures have been made under hydro(solvo)thermal conditions. The 1D chain is the first dicadmium-substituted VGO built from $\{Cd_2Ge_8V_{12}O_{40}(OH)_8(H_2O)\}$ clusters and transition-metal-complex (TMC) bridges (pictured), and the layer and framework are the first 2D/3D VGOs made of TMC linkers and $\{Ge_6V_{15}O_{48}(H_2O)\}/\{Ge_4V_{16}O_{42}(OH)_4(H_2O)\}$ clusters.

## Natural Products

*H. Liang,*
*M. A. Ciufolini** ........... 13262 – 13270

### Oxidative Spirocyclization of Phenolic Sulfonamides: Scope and Applications



**Making building blocks**: The oxidative dearomatization of *para-* and *ortho*-phenolic sulfonamides provides building blocks for spirocyclic alkaloids (see scheme). The chemistry of the products of this reaction and a concise total synthesis of putative lepadiformine is given.

## Hydrogen Bonds

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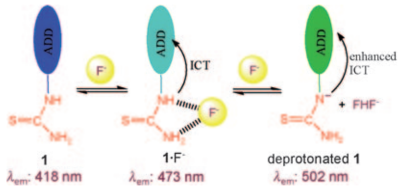
*P. Ramamurthy** .......... 13271 – 13277

### Fluorescence Spectroscopic Evidence for Hydrogen Bonding and Deprotonation Equilibrium between Fluoride and a Thiourea Derivative



**Anion-receptor dynamics**: Anion-receptor H-bonding and deprotonation equilibrium was studied by fluorescence spectroscopic techniques. Three different emission maxima are observed, which correspond to the free receptor, H-bonded complex and deprotonated species (see figure). Existence of these three species and their equilibrium were confirmed by time-resolved emission spectroscopic studies.

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