

## IN THIS ISSUE

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### Cover

See Alexander Steiner *et al.*, pp. 5152–5154.  
The cyclotriphosphazene  $P_3N_3Cl_6$  reacts with DMAP in superheated chloroform to form the hexacation  $[P_3N_3(DMAP)_6]^{6+}$  hosting five chloride ions in its cavities. Image reproduced by permission of Ramamoorthy Boomishankar, Joanne Ledger, Jean-Baptiste Guilbaud, Neil L. Campbell, John Bacsá, Richard Bonar-Law, Yaroslav Z. Khimyak and Alexander Steiner from *Chem. Commun.*, 2007, 5152.

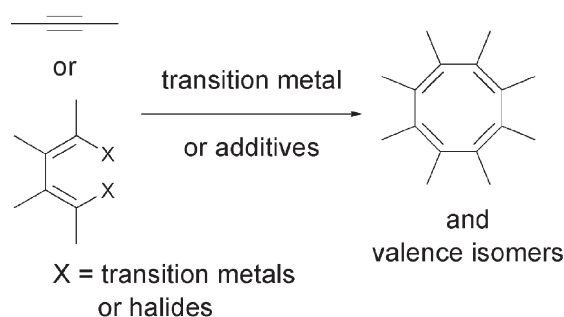
## FEATURE ARTICLES

5119

### Metal mediated synthesis of substituted cyclooctatetraenes

Chao Wang and Zhenfeng Xi\*

In this *Feature Article*, major achievements on transition metal mediated or catalyzed synthetic methods for substituted cyclooctatetraenes are described with focus on reaction patterns, mechanisms, and structural diversity of products.

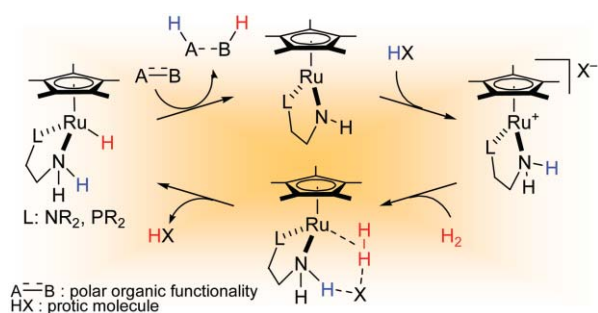


5134

### Catalytic hydrogenation of polar organic functionalities based on Ru-mediated heterolytic dihydrogen cleavage

Masato Ito and Takao Ikariya\*

This article highlights Ru-based molecular catalysts that promote hydrogenation of polar organic functionalities containing C–O bonds other than ketones or aldehydes, featuring our recent contributions to this area. The unique ability of Ru complexes to undergo heterolytic dihydrogen cleavage seems to play a key role in these catalyses.



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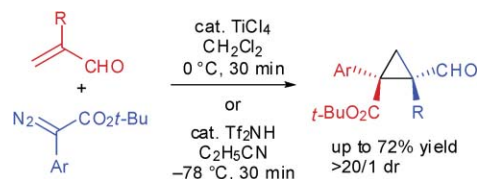
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### Construction of stereodefined 1,1,2,2-tetrasubstituted cyclopropanes by acid catalyzed reaction of aryldiazoacetates and $\alpha$ -substituted acroleins

Takuya Hashimoto, Yuki Naganawa, Taichi Kano and Keiji Maruoka\*

Michael-initiated ring closure of aryldiazoacetates and  $\alpha$ -substituted acroleins under acid catalysis offers a unique opportunity for the stereoselective formation of various tetrasubstituted cyclopropanes.

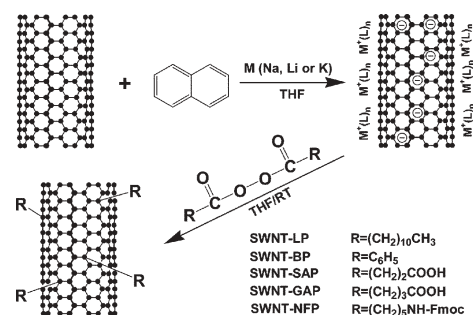


5146

### Rapid and controllable covalent functionalization of single-walled carbon nanotubes at room temperature

Yadienka Martínez-Rubí, Jingwen Guan, Shuqiong Lin, Christine Scriver, Ralph E. Sturgeon and Benoit Simard\*

We report a rapid and efficient procedure to functionalize SWNT where free radicals generated at room temperature by a redox reaction between reduced SWNT and diacyl peroxide derivatives were covalently attached to the SWNT wall.

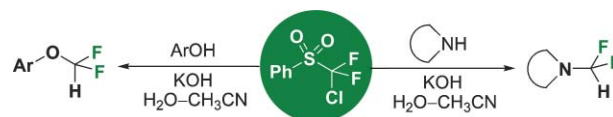


5149

### Chlorodifluoromethyl phenyl sulfone: a novel non-ozone-depleting substance-based difluorocarbene reagent for *O*- and *N*-difluoromethylations

Ji Zheng, Ya Li, Lajun Zhang, Jinbo Hu,\* Gerrit Joost Meuzelaar and Hans-Jürgen Federsel

Chlorodifluoromethyl phenyl sulfone, a previously unknown compound that can be readily prepared from non-ODS-based precursors, was found to act as a robust difluorocarbene reagent for *O*- and *N*-difluoromethylations.

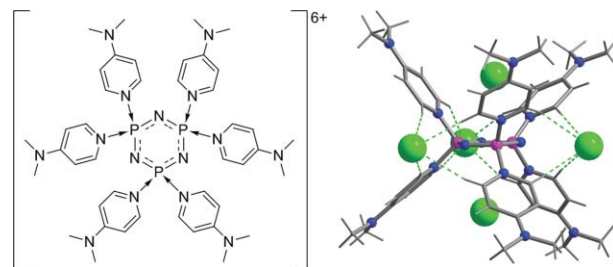


5152

### The *N*-donor stabilised cyclotriphosphazene hexacation $[P_3N_3(DMAP)_6]^{6+}$

Ramamoorthy Boomishankar, Joanne Ledger, Jean-Baptiste Guilbaud, Neil L. Campbell, John Bacsá, Richard Bonar-Law, Yaroslav Z. Khimiyak and Alexander Steiner\*

The cyclotriphosphazene  $P_3N_3Cl_6$  reacts with DMAP in superheated chloroform to form the hexacation  $[P_3N_3(DMAP)_6]^{6+}$  hosting five chloride ions in its cavities.







### Plenary Lectures

**A. Fürstner**, *Mülheim, Germany*

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*Pasadena, USA*

**T. Ikariya**, *Tokyo, Japan*

**J.-M. Lehn** (Nobel laureate)  
*Strasbourg, France*

**P. P. Power**, *Davis, USA*

### Honorary Guest

**Y. Chauvin** (Nobel laureate)

### Invited lectures

**M. Akita**, *Tokyo, Japan*

**P. Arnold**, *Edinburgh, UK*

**M. Beller**, *Rostock, Germany*

**C. Bianchini**, *Florence, Italy*

**N. Branda**, *Burnaby, Canada*

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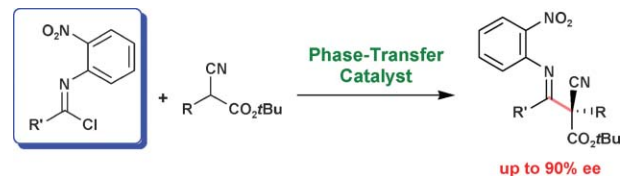


5155

### Enantioselective organocatalytic substitution of $\alpha$ -cyanoacetates on imidoyl chlorides – synthesis of optically active ketimines

Stefano Santoro, Thomas B. Poulsen and Karl Anker Jørgensen\*

Enantioselective substitution of  $\alpha$ -cyanoacetates on imidoyl chlorides under phase-transfer catalytic conditions, using a simple quinidine-derived catalyst, gives access to highly substituted ketimines in generally good yields and up to 90% ee.

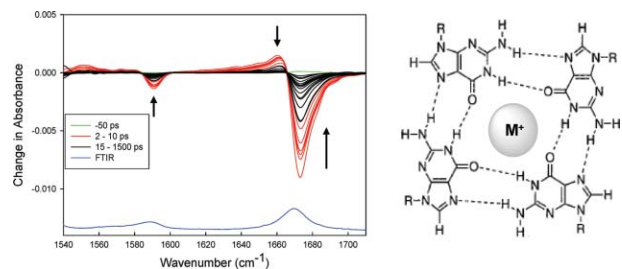


5158

### Picosecond infrared probing of the vibrational spectra of transients formed upon UV excitation of stacked G-tetrad structures

David A. McGovern, Susan Quinn,\* Gerard W. Doorley, Aine M. Whelan, Kate L. Ronayne, Michael Towrie, Anthony W. Parker\* and John M. Kelly\*

Ps-TRIR transient difference spectra of concentrated 5'-guanosine monophosphate (5'-GMP), polyguanylic acid (poly(G)) and the G-rich telomeric oligodeoxynucleotide sequence are compared to those of monomeric 5'-GMP.

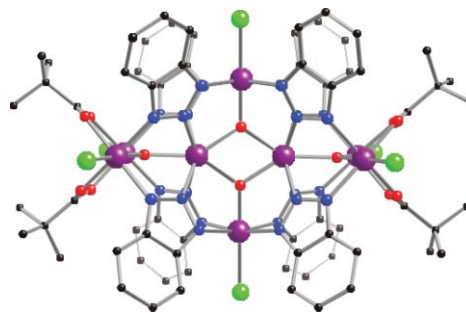


5161

### Large spin, magnetically anisotropic, octametallic vanadium(III) clusters with strong ferromagnetic coupling

Rachel Shaw, Floriana Tuna, Wolfgang Wernsdorfer, Anne-Laure Barra, David Collison\* and Eric J. L. McInnes\*

The dianionic [V<sup>III</sup><sub>8</sub>O<sub>4</sub>(bta)<sub>8</sub>(O<sub>2</sub>CR)<sub>4</sub>Cl<sub>6</sub>]<sup>2-</sup> clusters are reported in which strong ( $2J > +200 \text{ cm}^{-1}$ ) ferromagnetic exchange interactions stabilise an  $S = 4$ , magnetically anisotropic ground state.

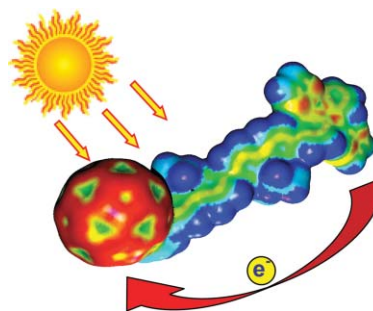


5164

### Determination of the attenuation factor in fluorene-based molecular wires

Carmen Atienza-Castellanos, Mateusz Wielopolski, Dirk M. Guldi,\* Cornelia van der Pol, Martin R. Bryce,\* Salvatore Filippone and Nazario Martín\*

Oligofluorene bridges behave as efficient molecular wires with a very low attenuation factor ( $\beta = 0.09 \text{ \AA}^{-1}$ ) in C<sub>60</sub>-exTTF donor-acceptor systems.



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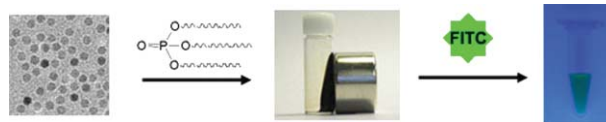


5167

### Versatile PEG-derivatized phosphine oxide ligands for water-dispersible metal oxide nanocrystals

Hyon Bin Na, In Su Lee, Heonjin Seo, Yong Il Park, Jung Hee Lee, Sang-Wook Kim\* and Taeghwan Hyeon\*

We report the simple synthesis of poly(ethylene glycol) (PEG)-derivatized phosphine oxide ligands. The synthetic procedure is readily applicable to the large-scale production of uniformly-sized water-dispersible oxide nanocrystals from the ligand exchange reaction of the corresponding organic dispersible nanocrystals.

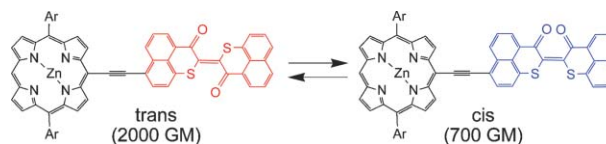


5170

### A photochromic porphyrin–perinaphthothioindigo conjugate and its two-photon absorption properties

Joanne T. Dy, Rena Maeda, Yasunori Nagatsuka, Kazuya Ogawa,\* Kenji Kamada, Koji Ohta and Yoshiaki Kobuke\*

A porphyrin–perinaphthothioindigo conjugate, having two-photon absorption cross-sections of  $\sim 2000$  GM and  $\sim 700$  GM for *trans*- and *cis*-isomers, respectively, was synthesized and exhibited photochromic behavior upon one- and two-photon excitation.

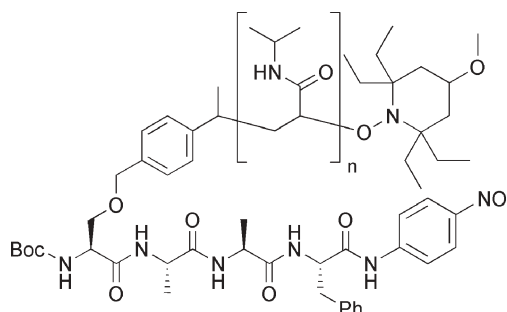


5173

### Reversible switching of substrate activity of poly-*N*-isopropylacrylamide peptide conjugates

Kian Molawi and Armido Studer\*

The activity of smart polymer peptide conjugates towards chymotrypsin catalyzed hydrolysis can be reversibly switched on and off using temperature as the trigger. At 22 °C hydrolysis is occurring, whereas at 37 °C the enzymatic reaction is completely stopped.

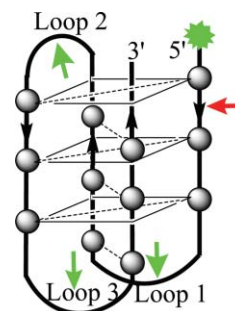


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### Single-walled carbon nanotubes binding to human telomeric i-motif DNA: significant acceleration of S1 nuclease cleavage rate

Yinghua Peng, Xi Li, Jinsong Ren and Xiaogang Qu\*

Single-walled carbon nanotubes (SWNTs) binding to human telomeric i-motif DNA can significantly accelerate S1 nuclease cleavage rate by increasing the enzyme turnover number.



# 42<sup>nd</sup> EUCHEM Conference on Stereochemistry



Known widely as the 'Bürgenstock Conference', this annual meeting has become famous as an outstanding international chemistry conference because of its high scientific quality, an optimal setting for intense interdisciplinary discussion, and a magnificent location above the lake of Lucerne in Switzerland.

**Stereochemistry** is the underlying principle by which we understand the processes of life and the properties of matter at the molecular level. It is a key element not only in all chemical disciplines, but also in modern molecular biology, molecular medicine, biophysics, and material design. Accordingly, the 'Bürgenstock Conference' has grown over the years into a multidisciplinary conference where frontier science is being discussed. Lectures at the conference cover many areas of chemistry and relevant highlights from neighbouring disciplines. For accounts of the 2006-conference see: a) R. S. Grainger, A. J. Wil-

son, *Chem. Commun.*, **2006**, 3269. c) R. S. Grainger, M. D. Toscano, *Chimia* **2006**, *60*, 330. See also: M. Rouhi, *Chem. Eng. News*, issue April 11, 2005.

## The 42<sup>nd</sup> EUCHEM Conference on Stereochemistry (Bürgenstock-Conference 2007)

will be held under the presidency of **Prof. Samir Z. Zard**, École Polytechnique, Palaiseau, France

**from Saturday 14<sup>th</sup> to Friday 20<sup>th</sup> April 2007 at Fürigen on the Bürgenstock, Switzerland**

Attendance will be limited to ca.120 participants. The organisers (the President: Samir Zard and the Members of the Organising Committee: François Diederich, Peter Kündig, Klaus Müller, Philippe Renaud, and Jay Siegel) will aim at a good balance of younger and more experienced participants from academic and industrial laboratories. According to its long tradition the detailed program (names of speakers and lecture titles) is not announced prior to the conference.

**Lectures will cover organic and metal-organic chemistry: new reactions, new reagents, novel synthetic strategies; asymmetric catalysis, advances in enantioselective control, chemistry of spin-unpaired reactive intermediates, new free radical-based synthetic methods, complex natural product synthesis. Frontier chemistry at the interfaces to biology and material science: novel molecular, structural, and mechanistic insights into chemical catalysis, enzyme function, and cell biology; molecular recognition, spontaneous and directed molecular assembly; molecular design towards novel analytical tools in the study of cellular surface interactions in biology; supramolecular chemistry for designed functional materials.**

The program consists of 14 plenary lectures with ample time for discussions so that each topic can be presented fully and be examined from different angles and perspectives. Lectures and discussions are held in the mornings and the evenings. The afternoons are free for recreation, informal discussions, and poster sessions.

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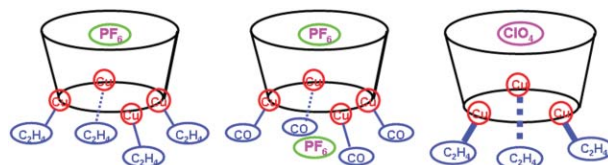


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### Bowl-shaped Cu(I) metallamacrocyclic ethylene and carbonyl adducts as structural analogues of organic calixarenes

Masahiko Maekawa,\* Hisashi Konaka, Toshie Minematsu, Takayoshi Kuroda-Sowa, Megumu Munakata and Susumu Kitagawa\*

Three novel Cu(I) metallacalixarenes with C<sub>2</sub>H<sub>4</sub> and CO legs, in which an anion is accommodated in the inside cavity, were self-assembled by anion templation and have been structurally characterized.

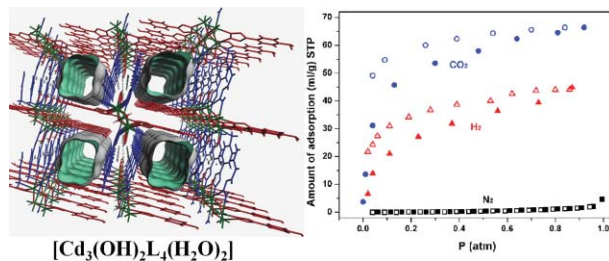


5182

### Selective gas sorption property of an interdigitated 3-D metal–organic framework with 1-D channels

Yang Zou, Seunghee Hong, Mira Park, Hyungphil Chun and Myoung Soo Lah\*

An interdigitated 3-D metal–organic framework with 1-D channels shows selective gas sorption behavior, which is based on the different nature of the interaction between the gas and the framework rather than on the size of the micropore.

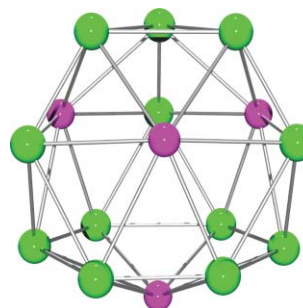


5185

### A series of nickel phosphonate–carboxylate cages

Barbara A. Breeze, Muralidharan Shanmugam, Floriana Tuna and Richard E. P. Winpenny\*

Three new polymetallic Ni cages are reported, including a dodecanuclear cage where the Ni(II) centres lie on the vertices of a truncated tetrahedron.

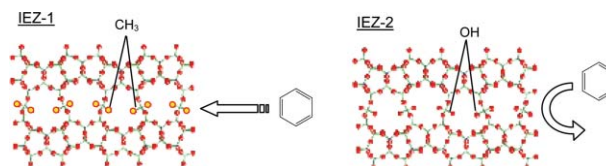


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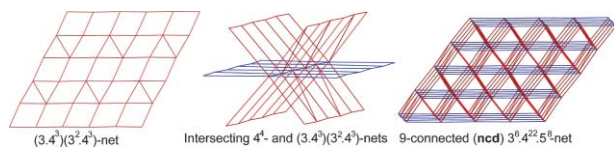
### Unique adsorption properties of organic–inorganic hybrid zeolite IEZ-1 with dimethylsilylene moieties

Satoshi Inagaki, Toshiyuki Yokoi, Yoshihiro Kubota and Takashi Tatsumi\*

The interlayer silylation of pure silica PLS-1 with dichlorodimethylsilane gave a novel organic–inorganic hybrid zeolite IEZ-1, of which the micropores adsorb benzene molecules, in contrast to its purely inorganic analogue IEZ-2.



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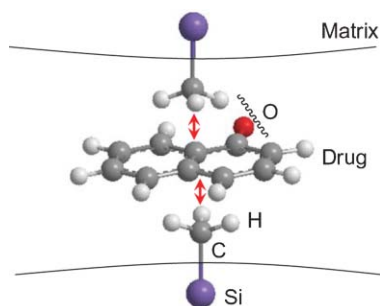


### High-connectivity networks: characterization of the first uninodal 9-connected net and two topologically novel 7-connected nets

J. Jacob Morris, Bruce C. Noll and Kenneth W. Henderson\*

Ring or cage complexes containing the large alkali metals potassium and rubidium provide multiple points for polymer extension using divergent Lewis bases. This strategy provides access to the formation of novel highly-connected networks.

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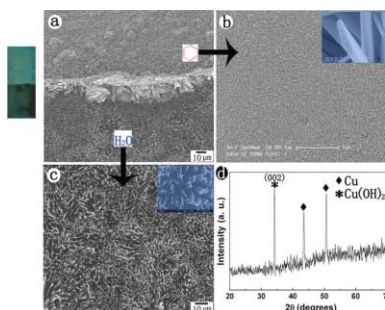


### Non-covalent interactions of a drug molecule encapsulated in a hybrid silica gel

Geo Paul, Stefan Steuernagel and Hubert Koller\*

The drug molecule Propranolol has been encapsulated by a sol-gel process in an organic-inorganic hybrid matrix by *in-situ* self-assembly; the 2D HETCOR solid state NMR spectroscopy provides direct proof of the intimate spatial relationship between the host matrix and guest drug molecules in the hybrid gel.

5197

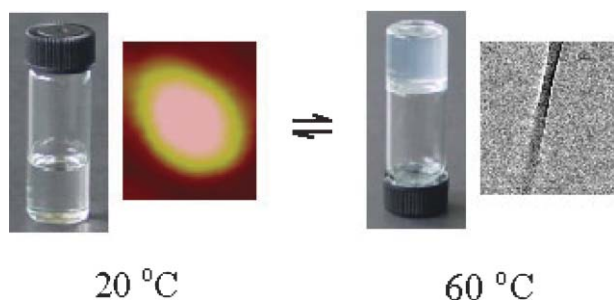


### A facile solution-chemistry method for Cu(OH)<sub>2</sub> nanoribbon arrays with noticeable electrochemical hydrogen storage ability at room temperature

Peng Gao,\* Milin Zhang, Zhongyi Niu and Quanping Xiao

Cu(OH)<sub>2</sub> nanoribbon arrays with noticeable hydrogen storage capacity were synthesized by a simple room-temperature solution reaction.

5200



### Heat-set gels and egg-like vesicles using two component gel system based on chiral calix[4]arenes

Jin-Lan Zhou, Xian-Jie Chen and Yan-Song Zheng\*

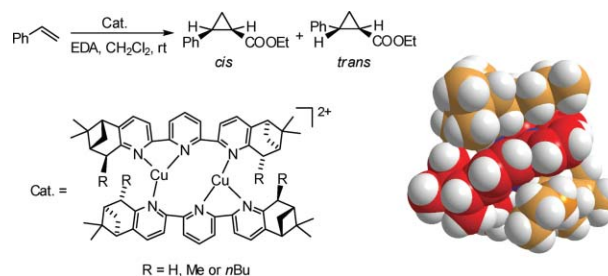
Chiral calix[4]arenes bearing long tertiary alkyl groups at the upper rim and *S*-1-phenylethylamine groups at the lower rim can form heat-set gels and egg-like vesicles enantioselectively with *D*-2,3-dibenzoyltartaric acid in cyclohexane.

5203

### Supramolecular double helical Cu(I) complexes for asymmetric cyclopropanation

Chi-Tung Yeung, Ho-Lun Yeung, Chui-Shan Tsang, Wai-Yeung Wong and Hoi-Lun Kwong\*

Chiral double-stranded helicites, formed between Cu(I) ion and  $C_2$ -symmetric oligopyridines, were used for the catalytic asymmetric cyclopropanation of alkenes.

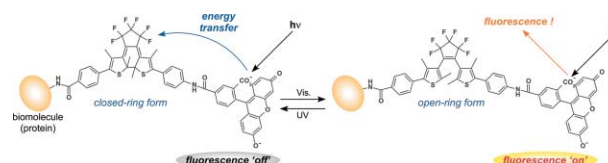


5206

### A fluorescent photochromic compound for labeling biomolecules

Nobuaki Soh, Kenji Yoshida, Hizuru Nakajima, Koji Nakano, Toshihiko Imato,\* Tuyoshi Fukaminato and Masahiro Irie\*

A fluorescent photochromic compound, composed of diarylethene, fluorescein and succinimidyl ester units, was developed for the controllable fluorescent labeling of biomolecules based on a small probing molecule.

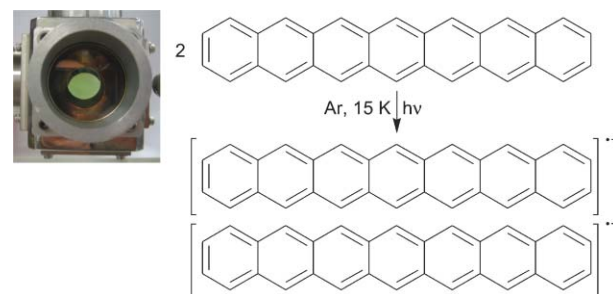


5209

### Stable photoinduced charge separation in heptacene

Holger F. Bettinger,\* Rajib Mondal and Douglas C. Neckers

Heptacene, a green hydrocarbon, undergoes intermolecular charge transfer upon UV photoexcitation in an argon matrix.

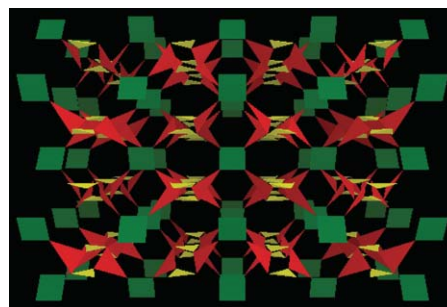


5212

### A novel metal–organic ternary topology constructed from triangular, square and tetrahedral molecular building blocks

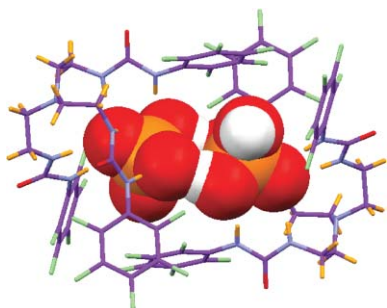
Gregory J. McManus, Zhenqiang Wang, Derek A. Beauchamp and Michael J. Zaworotko\*

$[\text{Cu}_4(5\text{-NH}_2\text{-1,3-bdc})_4(\text{pyridine})_2(\text{H}_2\text{O})_2]_n$  exhibits a novel topology for metal–organic networks, USF-5, which is constructed from vertex-linked triangular (red), square (green) and tetrahedral (yellow) molecular building blocks (MBBs).





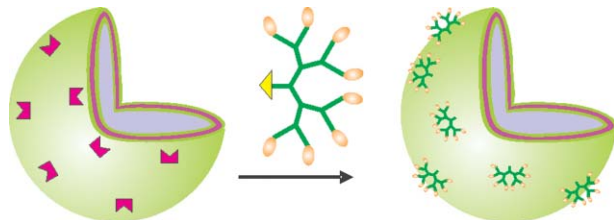
5214

**Trapped inorganic phosphate dimer**

P. S. Lakshminarayanan, I. Ravikumar, E. Suresh and Pradyut Ghosh\*

Two units of  $C_{3v}$  symmetric neutral receptor encapsulates a dimer of dihydrogen phosphate as a guest inside the cavity *via* sixteen hydrogen bonding interactions with the urea moieties and solvent molecules along with two anion $\cdots\pi$  interactions.

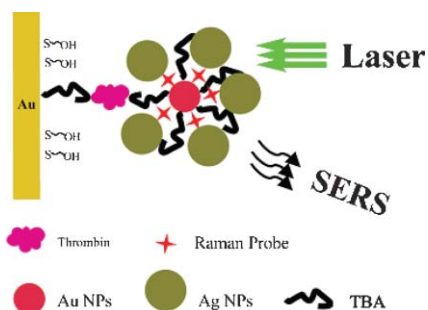
5217

**Multivalent polymer vesicles *via* surface functionalization**

Bo Li, Amanda L. Martin and Elizabeth R. Gillies\*

A new method was developed for the conjugation of multivalent dendritic groups to polymer vesicle surfaces.

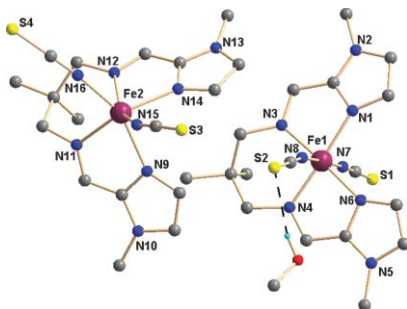
5220

**SERS opens a new way in aptasensor for protein recognition with high sensitivity and selectivity**

Yuling Wang, Hui Wei, Bingling Li, Wen Ren, Shaojun Guo, Shaojun Dong\* and Erkang Wang

SERS aptasensors for protein recognition based on Au nanoparticles labeled with aptamers and Raman reporters have been developed, which opens a new way for protein recognition of high sensitivity and selectivity.

5223

**An unprecedented co-crystal including a *cis*-high-spin and a *trans*-low-spin Fe<sup>II</sup> complex molecule**

Nicolas Bréfuel, Carine Duhayon, Sergiu Shova and Jean-Pierre Tuchagues\*

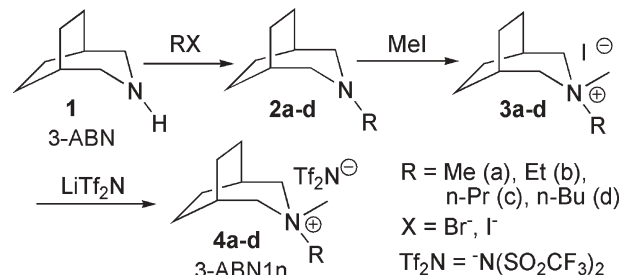
A *cis*-high-spin and a *trans*-low-spin molecule, simultaneously geometric and magnetic isomers, constitute the unit cell of an unprecedented iron(II) co-crystal:  $\{cis-[FeL^{B5}(NCS)_2] \cdot trans-[FeL^{B5}(NCS)_2]\} \cdot CH_3OH$ .

5226

**A new family of ionic liquids based on *N,N*-dialkyl-3-azabicyclo[3.2.2]nonanium cations: organic plastic crystal behaviour and highly reversible lithium metal electrodeposition**

Thomas R  ther,\* Junhua Huang and Anthony F. Hollenkamp

Novel ionic liquids based on *N,N*-dialkyl-3-azabicyclo[3.2.2]nonanium cations are described which, due to their properties, are attractive complements to well-known *N*-heterocyclic ionic liquids.

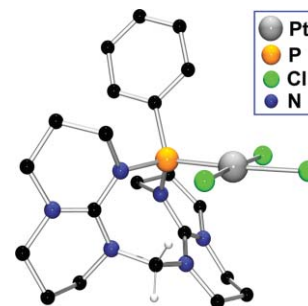


5229

**A Lewis-basic, dionio-substituted phosphane**

Martyn P. Coles\* and Peter B. Hitchcock

The methylene-linked bis{guanidine},  $H_2C\{hpp\}_2$  [where  $hppH = 1,3,4,6,7,8$ -hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine], reacts with  $PPhCl_2$  *via* chloride displacement to generate the dionio-substituted phosphane,  $[H_2C\{hpp\}_2PPh]^{2+}[Cl]^{-}_2$ . Despite a formally dicationic phosphorus centre, this compound displays Lewis-basic properties and will coordinate to platinum both in the solution- and solid-states.

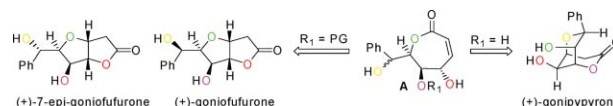


5232

**Total syntheses of (+)-7-epi-goniofufurone, (+)-gonioppyrone and (+)-goniofufurone from a common precursor**

Veejendra K. Yadav\* and Divya Agrawal

Total syntheses of (+)-7-epi-goniofufurone, (+)-gonioppyrone and (+)-goniofufurone have been achieved from an advanced common precursor formed from *D*-(+)-mannitol by changing the sequence of carbinol protection to allow the formation of either a  $\gamma$ - or  $\delta$ -lactone, selectively.

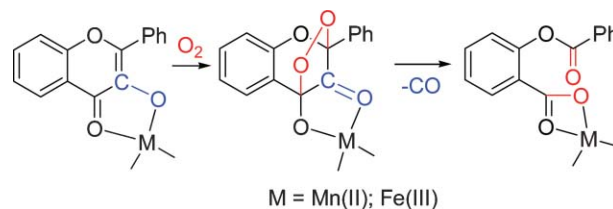


5235

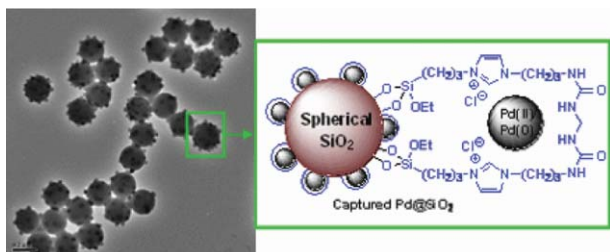
**Manganese and iron flavonolates as flavonol 2,4-dioxygenase mimics**

J  zsef Kaizer, G  bor Bar  th, J  zsef Pap, G  bor Speier,\* Michel Giorgi and Marius R  glie  r

Manganese(II) and iron(III) flavonolates were synthesized and their oxygenation reactions described.



5238

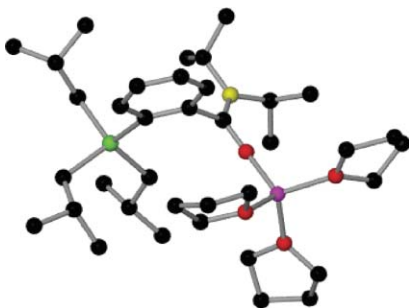


### Palladium nanoparticles captured onto spherical silica particles using a urea cross-linked imidazolium molecular band

Ju Yeon Shin, Bang Sook Lee, Yeongri Jung, Sung Jin Kim and Sang-gi Lee\*

Palladium nanoparticles were captured onto spherical silica particles using a urea cross-linked imidazolium molecular band to form raspberry-like Pd@SiO<sub>2</sub> composites, which can be recovered and reused without any loss of catalytic activity in Suzuki–Miyaura coupling.

5241

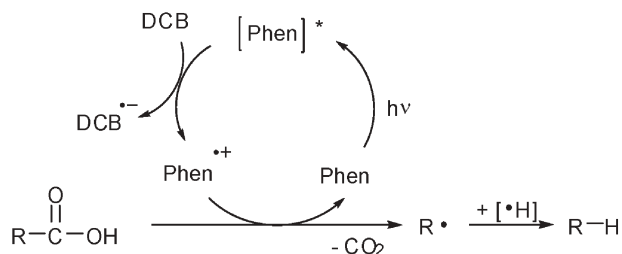


### Isolation and structural elucidation of a key aluminoaromatic intermediate and evidence for dismutation phenomena in TMP-alumination chemistry

Ben Conway, Eva Hevia, Joaquín García-Álvarez,\* David V. Graham, Alan R. Kennedy and Robert E. Mulvey\*

The first successful isolation and characterisation of an aluminoaromatic intermediate from a direct TMP-alumination reaction performed in THF solution is revealed.

5244



### Decarboxylative reduction of free aliphatic carboxylic acids by photogenerated cation radical

Yasuharu Yoshimi,\* Tatsuya Itou and Minoru Hatanaka\*

The decarboxylation of free aliphatic carboxylic acids was effected by a photogenerated cation radical of phenanthrene to yield the reduction product in the presence of a thiol.



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