

## IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (17) 2185-2292 (2005)



### Cover

See Toshifumi Dohi *et al.*, page 2205. A new recyclable hypervalent iodine(III) reagent has a beautiful, fine tetrahedral structure. Image reproduced by permission of Toshifumi Dohi, Akinobu Maruyama, Misaki Yoshimura, Koji Morimoto, Hirofumi Tohma, Motoo Shiro and Yasuyuki Kita from *Chem. Commun.*, 2005, 2205.



### Inside cover

See Dinesh G. Patel *et al.*, page 2208. Single crystal photoisomerization of spiro-oxazine leads to thermally irreversible, photochemically reversible process for optical data storage in the solid state. Image reproduced by permission of Dinesh G. Patel, Jason B. Benedict, Roni A. Kopelman and Natia L. Frank from *Chem. Commun.*, 2005, 2208.

## CHEMICAL SCIENCE

C33

Drawing together the research highlights and news from all RSC publications, *Chemical Science* provides a 'snapshot' of the latest developments across the chemical sciences showcasing newsworthy articles, as well as the most significant scientific advances.

## Chemical Science

May 2005/Volume 2/Issue 5

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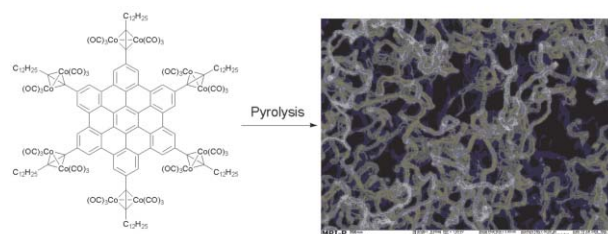
## FEATURE ARTICLE

2197

### New carbon-rich materials for electronics, lithium battery, and hydrogen storage applications

Andrew C. Grimsdale, Jishan Wu and Klaus Müllen\*

Methods for the preparation of novel carbon-rich materials for use in electronic devices, lithium batteries or possible hydrogen storage applications are presented.



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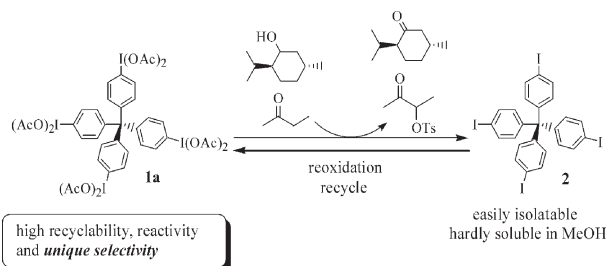
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2205

**A unique site-selective reaction of ketones with new recyclable hypervalent iodine(III) reagents based on a tetraphenylmethane structure**

Toshifumi Dohi, Akinobu Maruyama, Misaki Yoshimura, Koji Morimoto, Hirofumi Tohma, Motoo Shiro and Yasuyuki Kita\*

We have synthesized new recyclable reagents having a tetraphenylmethane backbone and used them in a unique site-selective  $\alpha$ -tosyloxylation of ketones.

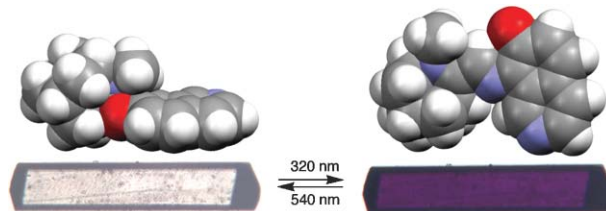


2208

**Photochromism of a spirooxazine in the single crystalline phase**

Dinesh G. Patel, Jason B. Benedict, Roni A. Kopelman and Natia L. Frank\*

A new spirooxazine, spiro[azahomoadamantane-isoquinolinoxazine], was synthesized and crystallized in the colorless closed form. Single crystals were found to undergo photocolouration that is photochemically reversible and thermally irreversible; a first for this class of photochromes.

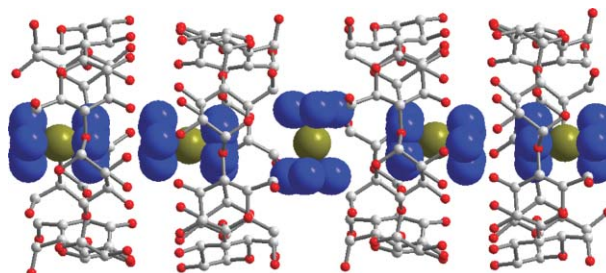


2211

**A unique tetramer of 4 : 5  $\beta$ -cyclodextrin–ferrocene in the solid state**

Yu Liu,\* Rui-Qin Zhong, Heng-Yi Zhang and Hai-Bin Song

Crystalline 4 : 5  $\beta$ -cyclodextrin–ferrocene was prepared by hydrothermal treatment, showing a unique tetramer with two distinct packing modes.

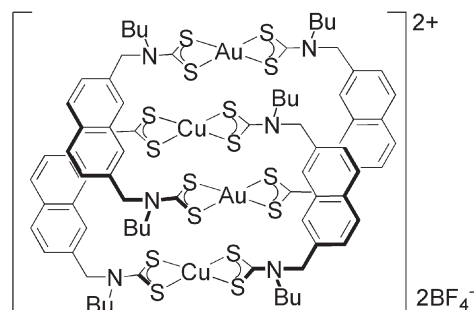


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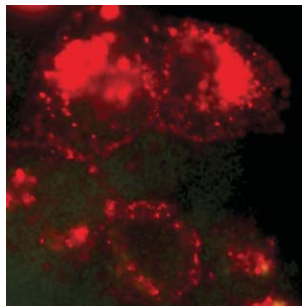
**Heteropolymetallic copper(II)–gold(III) dithiocarbamate [2]catenanes *via* magic ring synthesis**

Wallace W. H. Wong, James Cookson, Emma A. L. Evans, Eric J. L. McInnes, Joanna Wolowska, John P. Maher, Peter Bishop and Paul D. Beer\*

A rare class of mixed-metal [2]catenane has been assembled *via* magic ring synthesis of dinuclear copper(II) and gold(III) dithiocarbamate macrocycles.



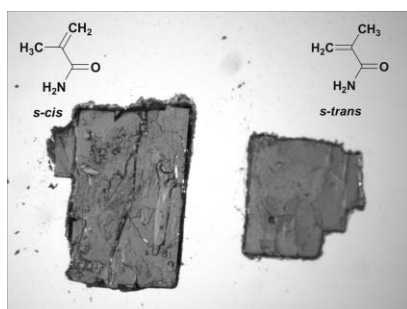
2217

**Cellular internalization and targeting of semiconductor quantum dots**

Sophie M. Rozenzhak, Madhavi P. Kadakia, Tina M. Caserta, Tiffany R. Westbrook, Morley O. Stone and Rajesh R. Naik

Peptide-mediated uptake of quantum dots into mammalian cells.

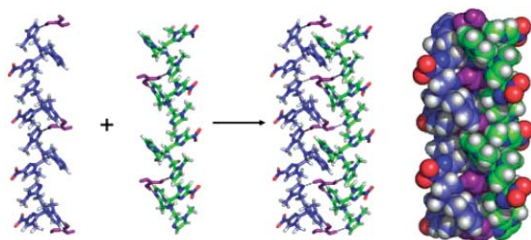
2220

**Conformational polymorphism of methacrylamide**

Chengyun Guo, Magali B. Hickey, Evan R. Guggenheim, Volker Enkelmann and Bruce M. Foxman\*

The industrially important compound methacrylamide crystallizes as concomitant conformational polymorphs; the monoclinic Form I contains only the *s-cis* conformer, while the orthorhombic Form II contains only the *s-trans* conformer.

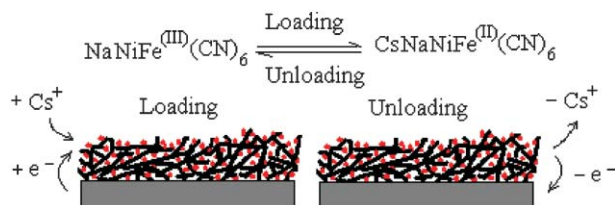
2223

**A supramolecular assembly of side-by-side polyimidazole tripod coils stabilized by  $\pi$ - $\pi$  stacking and unique boric acid templated hydrogen bonding interactions**

Lionel E. Cheruzel, Mark S. Mashuta and Robert M. Buchanan\*

This study describes the crystal structure of a supramolecular assembly composed of side-by-side antiparallel polyimidazole coils and boric acid filled 1D channels that mimic membrane assemblies involved in the transport of ions, water and other small molecules.

2226

**Novel hybrid materials with high stability for electrically switched ion exchange: carbon nanotube-polyaniline-nickel hexacyanoferrate nanocomposites**

Yuehe Lin\* and Xiaoli Cui

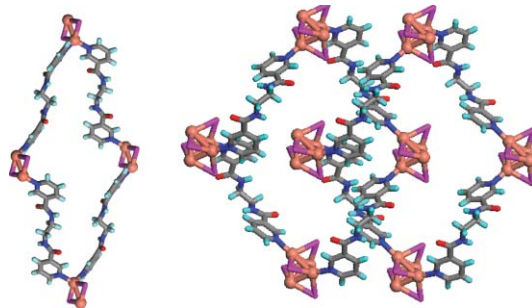
A novel and stable carbon nanotube-polyaniline-nickel hexacyanoferrate nanocomposite film has been synthesized by electrodeposition, and the feasibility for removing radioactive caesium through an electrically switched ion exchange process using the nanocomposite film has been evaluated in a mixture containing  $\text{NaNO}_3$  and  $\text{CsNO}_3$ .

2229

**$\beta$ -sheet recognition in the non-interpenetrated and interpenetrated two-dimensional coordination networks containing cavities**

Madhushree Sarkar and Kumar Biradha\*

Secondary building units of CuI ( $\text{Cu}_2\text{I}_2$  and  $\text{Cu}_4\text{I}_4$ ) were shown to generate 2D-coordination networks of (4,4)-topology with *exo*-bidentate ligands that contain diamide as spacer.  $\text{Cu}_2\text{I}_2$  and  $\text{Cu}_4\text{I}_4$  units generate non-interpenetrated and interpenetrated networks respectively. Both networks exhibit a  $\beta$ -sheet hydrogen bond pattern in their crystal structures.

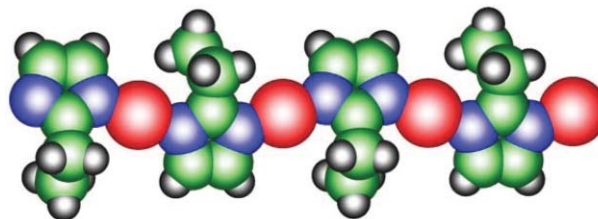


2232

**Triple-stranded helices and zigzag chains of copper(I) 2-ethylimidazolate: solvent polarity-induced supramolecular isomerism**

Xiao-Chun Huang, Jie-Peng Zhang, Yan-Yong Lin and Xiao-Ming Chen\*

The solvent effect of different polarities in hydro(solvo)thermal reaction of  $\text{Cu}^{\text{II}}$  and 2-ethylimidazole leads to the generation of two supramolecular isomers of triple-stranded helical and zigzag chain-like structures of  $\text{Cu}^{\text{I}}$  2-ethylimidazolate.

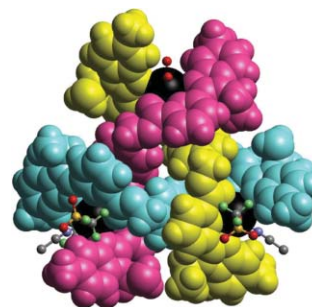


2235

**Isolation and characterization of the first circular single-stranded polymetallic lanthanide-containing helicate**

Jean-Michel Senegas, Sylvain Koeller, Gérald Bernardinelli and Claude Piguet\*

The assembly of the bimetallic triple-stranded helicate  $[\text{Eu}_2(\text{L}3)]^{6+}$  competes with the formation of the trimetallic circular single-stranded helicate  $[\text{Eu}_3(\text{L}3)]^{9+}$ , which can be isolated under specific external conditions.

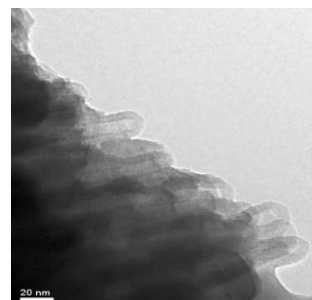


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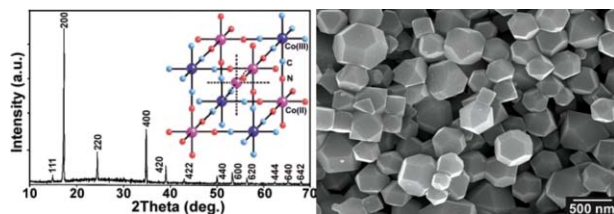
**Low temperature catalytic conversion of methane to methanol by barium sulfate nanotubes supporting sulfates:  $\text{Pt}(\text{SO}_4)_2$ ,  $\text{HgSO}_4$ ,  $\text{Ce}(\text{SO}_4)_2$  and  $\text{Pb}(\text{SO}_4)_2$**

Fengbo Li and Guoqing Yuan\*

Barium sulfate nanotubes perform excellently in supporting sulfates ( $\text{Pt}(\text{SO}_4)_2$ ,  $\text{HgSO}_4$ ,  $\text{Ce}(\text{SO}_4)_2$  and  $\text{Pb}(\text{SO}_4)_2$ ) for low temperature catalytic conversion of methane to methanol under strongly acidic conditions in a conventional gas-phase reactor.



2241

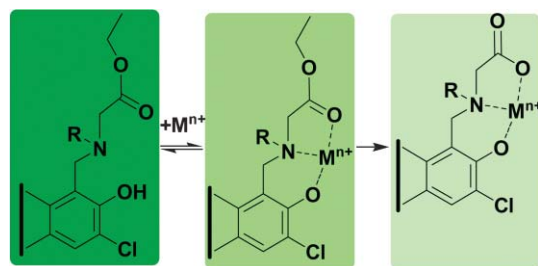


### Shape-controlled synthesis of Prussian blue analogue $\text{Co}_3[\text{Co}(\text{CN})_6]_2$ nanocrystals

Minhua Cao, Xinglong Wu, Xiaoyan He and Changwen Hu\*

Prussian blue analogue  $\text{Co}_3[\text{Co}(\text{CN})_6]_2$  nanocrystals with morphologies of truncated nanocubes (polyhedra), cubes and rods, were synthesized in large quantities by a direct dissociation of the single-source precursor  $\text{K}_3[\text{Co}(\text{CN})_6]$  in a microemulsion system.

2244

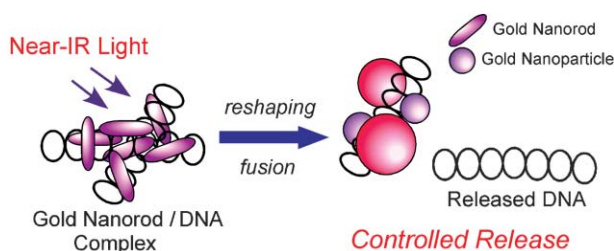


### Double discrimination by binding and reactivity in fluorescent metal ion detection

Andriy Mokhir\* and Roland Krämer

A fluorescent metal ion hybrid sensor containing reactive ester groups allows discrimination on the basis of the hydrolytic reactivities of metal ions, which display the same qualitative fluorescence response on binding only.

2247

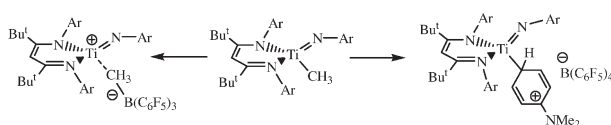


### Controlled release of plasmid DNA from gold nanorods induced by pulsed near-infrared light

Hironobu Takahashi, Yasuro Niidome\* and Sunao Yamada\*

Pulsed near-infrared laser irradiation induced release of plasmid DNA immobilized on gold nanorods without structural degradation, by selective excitation of longitudinal plasmon oscillation.

2250



### Latent low-coordinate titanium imides supported by a sterically encumbering $\beta$ -diketiminato ligand

Falguni Basuli, Rodney L. Clark, Brad C. Bailey, Doug Brown, John C. Huffman and Daniel J. Mindiola\*

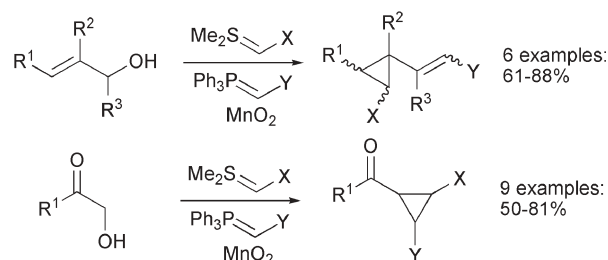
A family of cationic and low-coordinate titanium(IV) imide complexes supported by a sterically demanding  $\beta$ -diketiminato ligand  $\text{Nacnac}^-$  ( $\text{Nacnac}^- = [\text{ArNC}(t\text{Bu})_2]\text{CH}_2$ ,  $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ ) have been prepared, and shown to form discrete salts, zwitterions, or Meisenheimer-type products.

2253

### Tandem oxidation processes: a combined phosphorus- and sulfur-ylide approach to polysubstituted cyclopropanes

Magalie F. Oswald, Steven A. Raw and Richard J. K. Taylor\*

A new manganese dioxide-mediated tandem oxidation process (TOP) has been developed which, by suitable combination of stabilised phosphorus- and sulfur-ylides, allows the direct conversion of allylic alcohols or  $\alpha$ -hydroxyketones into polysubstituted cyclopropanes.

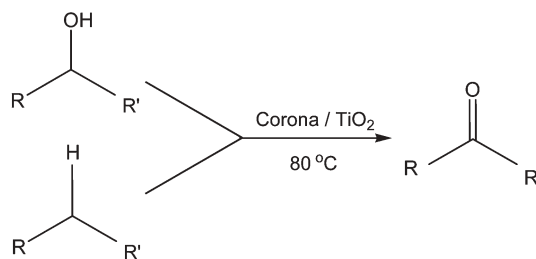


2256

### Corona-induced photooxidation of alcohols and hydrocarbons over TiO<sub>2</sub> in the absence of a UV light source – A novel and environmentally friendly method for oxidation

Unnikrishnan R. Pillai and Endalkachew Sahle-Demessie\*

Corona-induced photooxidation is a novel methodology for the oxidation of alcohols and hydrocarbons utilizing the advantage of the high oxidizing power of ozone formed in the reactor and the photooxidation capability of the UV light generated during the corona discharge.

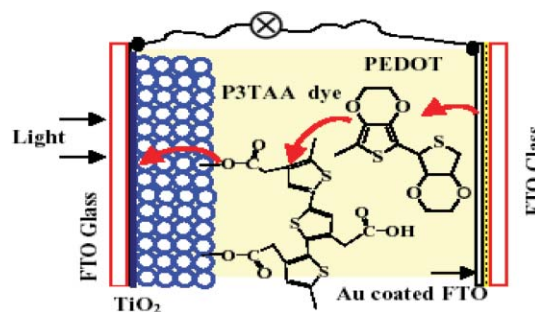


2259

### Volatile solvent-free solid-state polymer-sensitized TiO<sub>2</sub> solar cells with poly(3,4-ethylenedioxythiophene) as a hole-transporting medium

Rohan Senadeera,\* Norihiro Fukuri, Yasuteru Saito, Takayuki Kitamura, Yuji Wada and Shozo Yanagida\*

Novel, volatile solvent free, solar cells were fabricated using thiophene derivative polymer sensitized TiO<sub>2</sub> electrodes together with an electrochemically polymerized hole-conductor, poly(3,4-ethylenedioxythiophene) (PEDOT) with promising photoresponses.

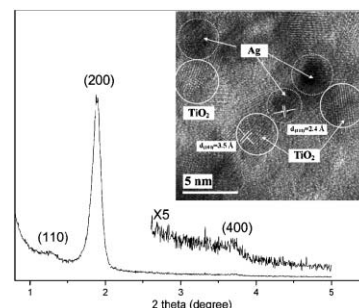


2262

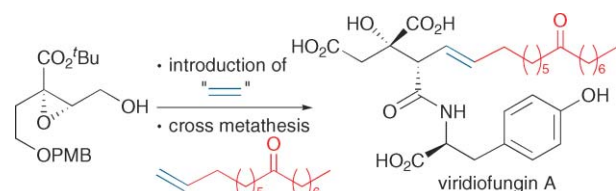
### A robust three-dimensional mesoporous Ag/TiO<sub>2</sub> nanohybrid film

Xinchen Wang, Jimmy C. Yu,\* Chunman Ho and Angelo C. Mak

A highly ordered mesoporous Ag/TiO<sub>2</sub> nanohybrid film was successfully fabricated.



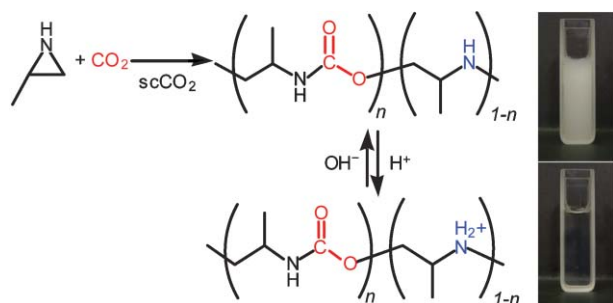
2265

**Total synthesis of viridifungin A**

Kenji Morokuma, Keisuke Takahashi, Jun Ishihara and Susumi Hatakeyama\*

Viridifungin A, an amino alkyl citrate antibiotic, was enantioselectively synthesized in naturally occurring form for the first time, employing regio- and stereoselective opening of the chiral glycidate with  $\text{CH}_2=\text{CHMgBr/CuI}$  and cross metathesis of the citric acid core and hexadec-15-en-8-one as key steps.

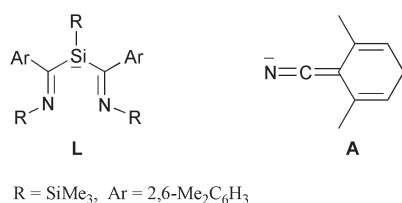
2268

**Double stimuli-responsive behavior of aliphatic poly(urethane-amine)s derived from supercritical carbon dioxide**

Osamu Ihata, Yoshihito Kayaki\* and Takao Ikariya\*

Copolymeric products from 2-methylaziridine and carbon dioxide showed sharp and rapid phase transitions in response to both temperature and pH. Thanks to the pressure- and temperature-tunable physical properties of supercritical carbon dioxide, the stimuli-responsive property was controllable in a wide temperature or pH range.

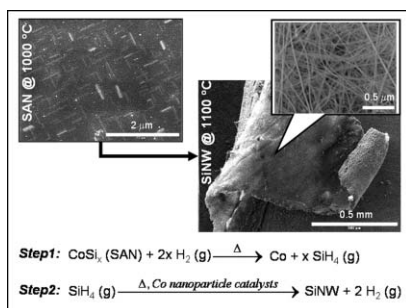
2271

**Synthesis and structures of a 3-sila-β-diketiminatomagnesium bromide, ketenimide and triflate**

James D. Farwell, Peter B. Hitchcock, Michael F. Lappert\* and Andrey V. Protchenko

Four crystalline 3-sila-β-diketiminatomagnesium compounds  $\text{Mg}(\text{L})\text{X}$  have been obtained:  $[\text{Mg}(\text{Br})(\text{L})(\text{thf})] \cdot 0.5\text{Et}_2\text{O}$  **1** from the bis(imido)silane  $\text{L}-\text{Br}$  and Mg,  $[\text{Mg}(\text{L})(\text{A})(\text{D})_2]$  **2** (D = NCAr) and **3** (D = thf) from  $[\text{Mg}(\text{SiR}_3)_2(\text{thf})_2]$  and ArCN, and  $[\{\text{Mg}(\text{L})\}_2\{\mu\text{-OSO}(\text{CF}_3)\text{O}-\mu\}_2]$  **4** from **2** and ROTf with R-A (**5**) as coproduct; **2**, **3** and **5** contain the ketenimido ligand A.

2274

**Silicon-based nanowires from silicon wafers catalyzed by cobalt nanoparticles in a hydrogen environment**

Joshua D. Carter, Yongquan Qu, Rhiannon Porter, Luke Hoang, Daniel J. Masiel and Ting Guo\*

Bulk quantities of Si-based nanowires are produced from reactions between Co or Co silicide nanoparticle catalysts, Si wafers and hydrogen gas.

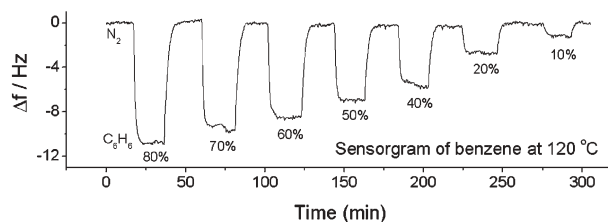


2277

**Ionic liquid high temperature gas sensors**

Lei Yu, Diego Garcia, Rex Ren and Xiangqun Zeng\*

An ionic liquid piezoelectric gas sensor was demonstrated for detection of polar and nonpolar organic vapors at high temperature with fast, linear and reversible response.

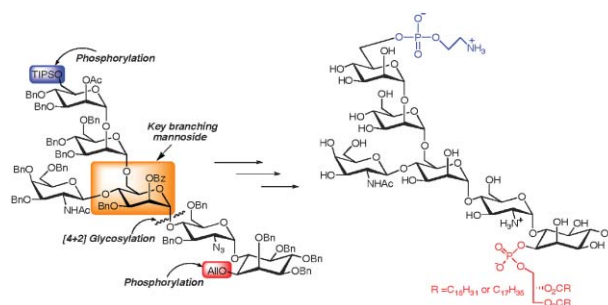


2280

 **Total syntheses of fully lipidated glycosylphosphatidylinositol anchors of *Toxoplasma gondii***

Yong-Uk Kwon, Xinyu Liu and Peter H. Seeberger\*

Convergent syntheses of the glycosylphosphatidylinositol anchors of *T. gondii* were achieved. Such a modular approach can be also applied to the synthesis of various GPIs with branching carbohydrate moieties along the oligomannose chain.

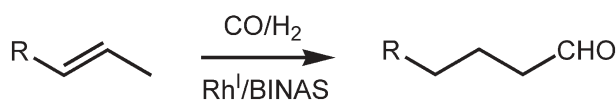


2283

**Synthesis of linear aldehydes from internal olefins in water**

Holger Klein, Ralf Jackstell and Matthias Beller\*

The carbonylation of internal olefins to linear aldehydes in a biphasic water system is possible with unprecedented regioselectivity.

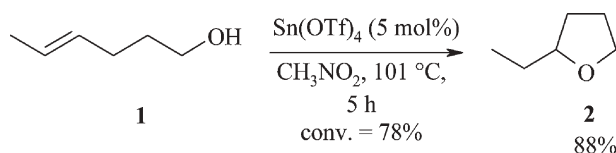


2286

**Catalytic formation of C–O bonds by alkene activation: Lewis acid-cycloisomerisation of olefinic alcohols**

Lydie Coulombel, Isabelle Favier and Elisabet Duñach\*

Tin(IV) trifluoromethanesulfonate has been found to be an excellent catalyst for the cycloisomerisation of non-activated and differently substituted olefinic alcohols to cyclic ethers.




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