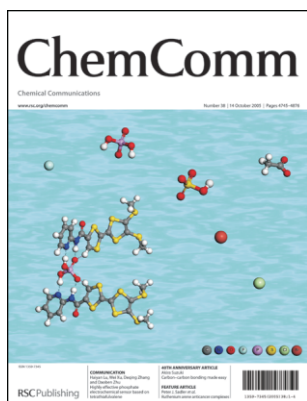


## IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (38) 4745–4876 (2005)



### Cover

See Haiyan Lu, Wei Xu, Deqing Zhang and Daoben Zhu, page 4777. A neutral electrochemical chemosensor based on tetrathiafulvalene exhibited high selectivity for  $\text{H}_2\text{PO}_4^-$  over a wide range of anions. Image reproduced by permission of Wei Xu *et al.*, from *Chem. Commun.*, 2005, 4777.



### Inside cover

See Kazuhisa Fujimoto, Yu Muto and Masahiko Inouye, page 4780. A water-soluble potassium sensor was developed based on the structural motif of antibodies, which consists of benzo-15-crown-5 ether, DNA and pyrene. Image reproduced by permission of Kazuhisa Fujimoto *et al.*, from *Chem. Commun.*, 2005, 4780.

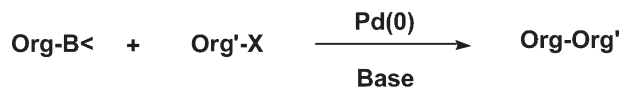
## 40TH ANNIVERSARY ARTICLE

4759

### Carbon–carbon bonding made easy

Akira Suzuki

C–C bond formation, Pd catalysts, ligands, bases.



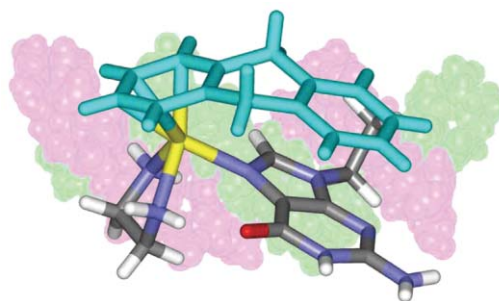
## FEATURE ARTICLE

4764

### Organometallic chemistry, biology and medicine: ruthenium arene anticancer complexes

Yaw Kai Yan, Michael Melchart, Abraha Habtemariam and Peter J. Sadler

Certain ruthenium(II) arene complexes exhibit promising anticancer activity, and illustrate rapidly evolving research into bioorganometallic chemistry.



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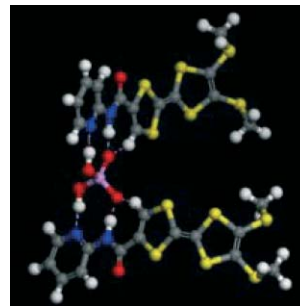
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4777

### Highly effective phosphate electrochemical sensor based on tetrathiafulvalene

Haiyan Lu, Wei Xu,\* Deqing Zhang and Daoben Zhu\*

A neutral electrochemical chemosensor **1** based on TTF exhibited high selectivity for  $\text{H}_2\text{PO}_4^-$  over a wide range of anions and the significant  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonding between  $\text{C}=\text{C}-\text{H}$  of the TTF unit and  $\text{H}_2\text{PO}_4^-$  played an important role in regulating the selectivity.

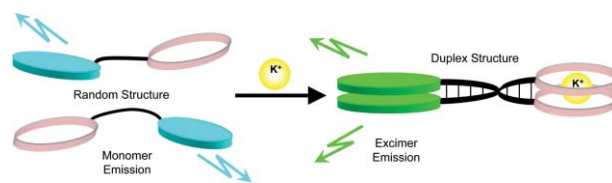


4780

### A general and versatile molecular design for host molecules working in water: a duplex-based potassium sensor consisting of three functional regions

Kazuhisa Fujimoto,\* Yu Muto and Masahiko Inouye\*

A general and versatile molecular design for host molecules was proposed based on the structural motif of antibodies. A water-soluble potassium sensor was developed by this molecular design.

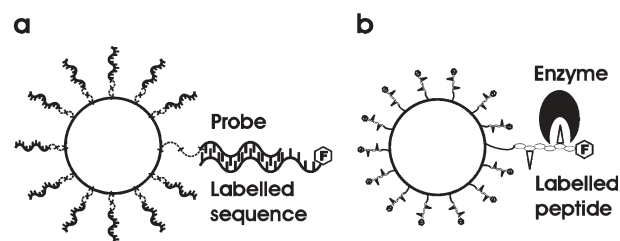


4783

### Biomolecular screening with novel organosilica microspheres

Chris R. Miller, Robert Vogel, Peter P. T. Surawski, Simon R. Corrie, Andreas Rühmann and Matt Trau\*

Organosilica microspheres synthesised *via* a novel surfactant-free emulsion-based method show applicability towards optical encoding, solid-phase synthesis and high-throughput screening of bound oligonucleotide and peptide sequences.

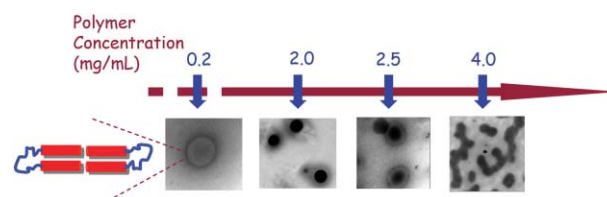


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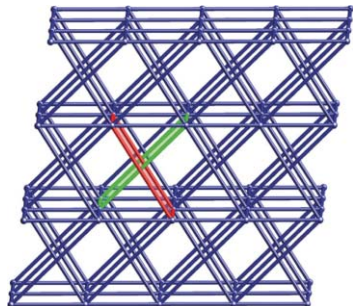
### Multiple self-assembled nanostructures from an oligo(*p*-phenyleneethynylene) containing rod-coil-rod triblock copolymer

Kun Li and Qing Wang\*

A well-defined rod-coil-rod triblock copolymer consisting of polystyrene as the coil-like segment and conjugated oligo(*p*-phenyleneethynylene) as the rod-like segment has been synthesized. Systematic variation of polymer concentration in toluene gives diverse morphologies of aggregates including vesicles, spheres, onion-like structures, worm-like fibers, and interconnected rod-like fibers.



4789

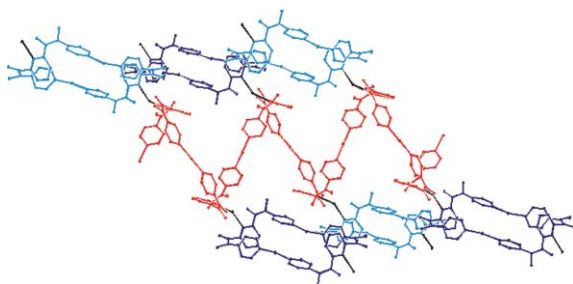


### An unprecedented eight-connected self-penetrating network based on pentanuclear zinc cluster building blocks

Xin-Long Wang, Chao Qin, En-Bo Wang,\*  
Zhong-Min Su,\* Lin Xu and Stuart R. Batten\*

An unprecedented eight-connected self-penetrating network is constructed based on pentanuclear zinc cluster building blocks and linear dicarboxylate linkers. This 3D network defines a new self-penetrating topology for eight-connected networks and represents the highest connected topology presently known for self-penetrating systems.

4792

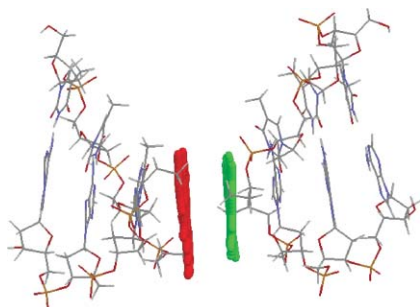


### Ring-opening polymerisation of coordination compounds: a silver(I) network with both ring and polymer components

Nancy L. S. Yue, Michael C. Jennings and  
Richard J. Puddephatt\*

Supramolecular isomers related by ring-opening polymerisation are present in the complex  $[\{Ag_3(\mathbf{1})_2\}_n][CF_3SO_3]_{3n}$ ,  $\mathbf{1} = 2,6-C_5H_3N\{C(=O)N(Me)-4-C_5H_4N\}_2$ , whose structure contains polymer chains  $[\{Ag(\mu-\mathbf{1})\}_n]^{n+}$  sandwiched between sheets of macrocycles  $[Ag_2(\mu-\mathbf{1})_2]^{2+}$ .

4795

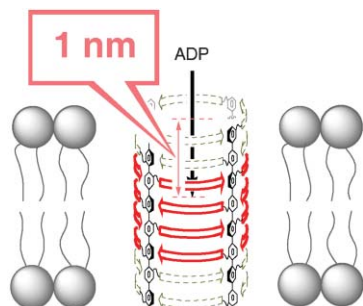


### Duplex and hairpin dimer structures for perylene diimide–oligonucleotide conjugates

Yan Zheng, Hai Long, George C. Schatz and  
Frederick D. Lewis\*

Perylene diimide–oligonucleotide conjugates can form either duplex or hairpin dimer structures; a combination of optical spectroscopy and molecular modeling was used to investigate the structures of the duplex and hairpin dimer.

4798



### The depth of molecular recognition: voltage-sensitive blockage of synthetic multifunctional pores with refined architecture

Yoann Baudry, Dario Pasini, Masamichi Nishihara,  
Naomi Sakai and Stefan Matile\*

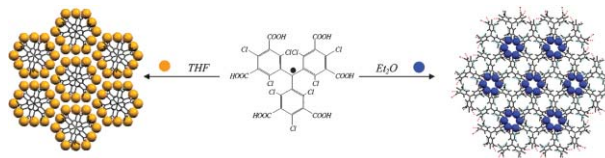
Neither size nor charge nor number of active sites: it is the depth of guest inclusion that accounts for magnitude and voltage sensitivity of molecular recognition by synthetic multifunctional pores.

4801

### Hydrogen-bonded self-assemblies in a polychlorotriphenylmethyl radical derivative substituted with six *meta*-carboxylic acid groups

Nans Roques, Daniel MasPOCH, Neus Domingo, Daniel Ruiz-Molina, Klaus Wurst, Javier Tejada, Concepció Rovira and Jaume Veciana\*

The synthesis, self assembly and magnetic properties of a polychlorotriphenylmethyl radical, substituted with six *meta*-carboxylic groups, are reported showing that radical-radical hydrogen bonds in the solid state yield to very weak intermolecular ferromagnetic interactions.

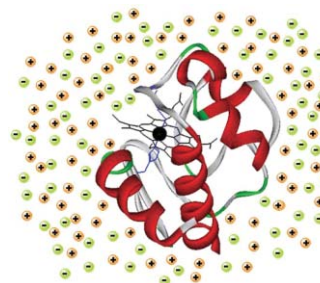


4804

### Protein solubilising and stabilising ionic liquids

Kyoko Fujita, Douglas R. MacFarlane\* and Maria Forsyth

We report a family of biocompatible ionic liquids (ILs) which are able to dissolve significant amounts of proteins such as cytochrome c and in which ATR-FTIR spectroscopy results show retention of secondary structure to extreme temperatures.

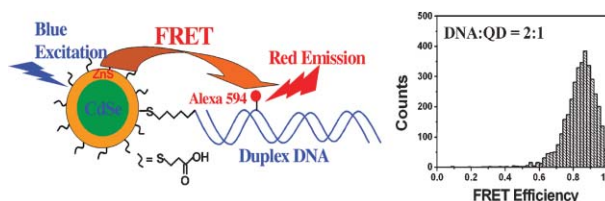


4807

### Fluorescence resonance energy transfer between a quantum dot donor and a dye acceptor attached to DNA

Dejian Zhou,\* Joe D. Piper, Chris Abell, David Klenerman, Dae-Joon Kang\* and Liming Ying\*

Direct coupling of a dye-labelled DNA (acceptor) to a quantum dot (QD) donor significantly reduces the donor-acceptor distance and improves the FRET efficiency in quantum dot bioconjugates.

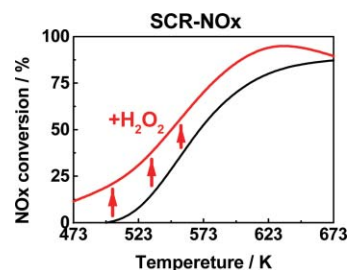


4810

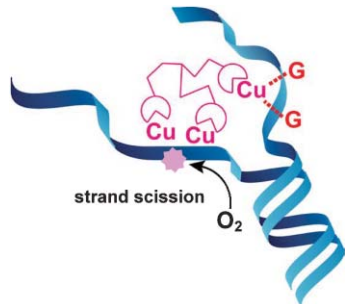
### Selective catalytic reduction of NO<sub>x</sub> by hydrocarbons enhanced by hydrogen peroxide over silver/alumina catalysts

Petr Sazama and Blanka Wichterlová\*

It is shown that hydrogen peroxide enhances substantially selective reduction of NO<sub>x</sub> to nitrogen with hydrocarbons over Ag/alumina catalysts.



4812

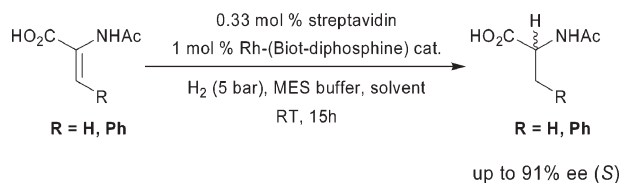


### Recognition of guanines at a double helix–coil junction in DNA by a trinuclear copper complex

Takeo Ito, Sunita Thyagarajan, Kenneth D. Karlin and Steven E. Rokita\*

Selective oxidation and cleavage of DNA promoted by a trinuclear copper complex is guided by recognition of the N7 position of guanines that are extended in a 5'-direction from a helix–coil junction. Related bulge- and loop-containing structures of DNA are not targets of reaction.

4815

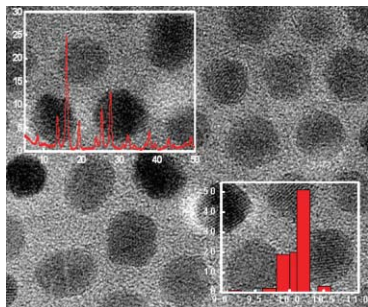


### Chemical optimization of artificial metalloenzymes based on the biotin-avidin technology: (*S*)-selective and solvent-tolerant hydrogenation catalysts *via* the introduction of chiral amino acid spacers

Myriem Skander, Christophe Malan, Anita Ivanova and Thomas R. Ward\*

Incorporation of biotinylated-[rhodium(diphosphine)]<sup>+</sup> complexes, with enantiopure amino acid spacers, in streptavidin affords solvent-tolerant and selective artificial metalloenzymes.

4818

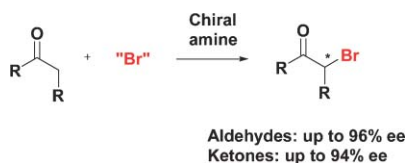


### One step synthesis of highly crystalline and high coercive cobalt-ferrite nanocrystals

Sanjib Bhattacharyya,\* Jean-Paul Salvétat, Romain Fleurier, Anke Husmann, Thomas Cacciaguerra and Marie-Louise Saboungi

Highly crystalline and almost monodisperse spinel cobalt-ferrite nanocrystals are synthesized in a one step process, which has very high coercivity at 10 K and exhibits superparamagnetic behaviour at 300 K.

4821



### Organocatalytic asymmetric $\alpha$ -bromination of aldehydes and ketones

Søren Bertelsen, Nis Halland, Stephan Bachmann, Mauro Marigo, Alan Braunton and Karl Anker Jørgensen\*

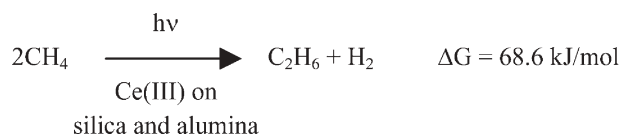
A  $C_2$ -symmetric diphenylpyrrolidine catalyst afforded the  $\alpha$ -brominated aldehydes in good yields and up to 96% ee, while ketones were  $\alpha$ -brominated by a  $C_2$ -symmetric imidazolidine in up to 94% ee; furthermore, the organocatalytic enantioselective  $\alpha$ -iodination of aldehydes is also demonstrated to proceed with up to 89% ee.

4824

### Highly dispersed Ce(III) species on silica and alumina as new photocatalysts for non-oxidative direct methane coupling

Leny Yuliati, Tomoyo Hamajima, Tadashi Hattori and Hisao Yoshida\*

Highly dispersed cerium oxide species on silica and alumina, which mainly exist as Ce(III) species, promote non-oxidative direct methane coupling photocatalytically around room temperature, while Ce(IV) species as CeO<sub>2</sub> particles do not behave as a catalyst for this reaction.

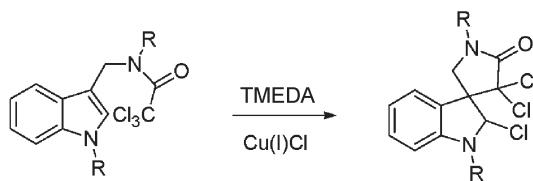


4827

### Synthesis of highly functionalised spiro-indoles by a halogen atom transfer radical cyclization

Christian V. Stevens,\* Ellen Van Meenen, Yves Eeckhout, Bart Vanderhoydonck and Wim Hooghe

Halogenated 3,3-spiro-3H-indoles were formed by halogen atom transfer radical cyclization by a 5-*exo*-trig ring closure in moderate to good yields.

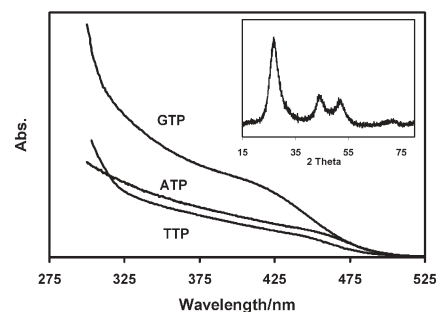


4830

### Nucleotide passivated cadmium sulfide quantum dots

Mark Green,\* David Smyth-Boyle, Joanna Harries and Robin Taylor

The preparation of nucleotide passivated nanoparticles is described. The orientation of the nucleotides on the particle surface is examined and the effects on the optical properties and stability reported.

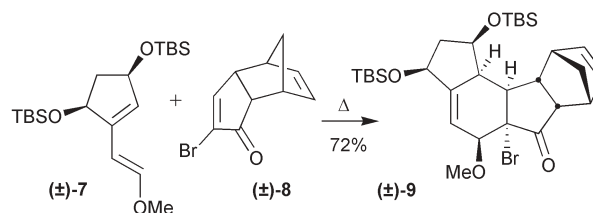


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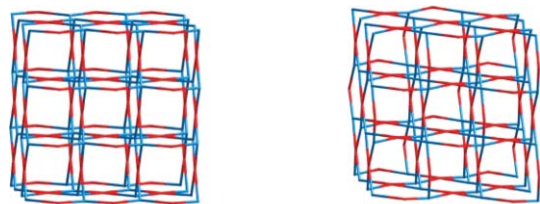
### Reversal of facial selectivity in complex Diels–Alder reactions

Jacques-Alexis Funel, Louis Ricard and Joëlle Prunet\*

A complex Diels–Alder reaction between a semi-cyclic diene with allylic silyloxy substituents and a bromo enone presented an unusual *syn* diastereoselectivity.



4836



pts net

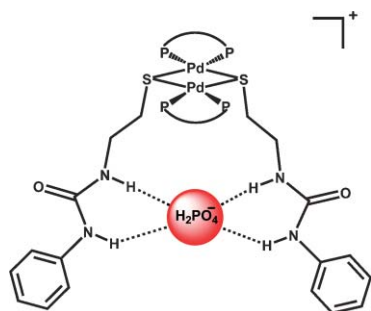
lvt net

### Direction of topological isomers of silver(I) coordination polymers induced by solvent, and selective anion-exchange of a class of PtS-type host frameworks

Miao Du,\* Xiao-Jun Zhao, Jian-Hua Guo and Stuart R. Batten\*

Coordination polymers with closely related 4-connected nets (pts and lvt) were constructed, and the topological differences only result from the stereochemistry of silver(I) coordination. Selective anion-exchange of the PtS-type frameworks with different anions was identified.

4839

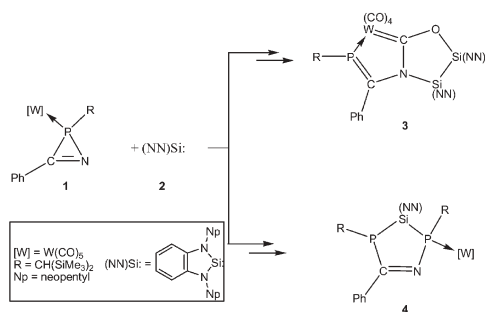


### A di-palladium urea complex as a molecular receptor for anions

Jorge A. Tovilla, Ramón Vilar\* and Andrew J. P. White

A new di-nuclear palladium complex containing urea-substituted thiolate bridging ligands has been prepared and structurally characterized. Its interaction with anionic species has been studied in solution demonstrating that this complex acts as a good metalla-host for anionic guests.

4842

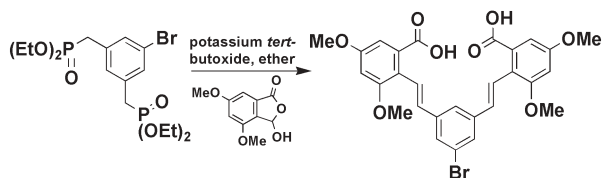


### Surprising reactions of a 2H-azaphosphirene complex with a silylene

Emanuel Ionescu, Barbara Gehrus, Peter B. Hitchcock, Martin Nieger and Rainer Streubel\*

Bicyclic carbene complex **3** and 1,2,4,3-azadiphosphasilol-5-ene complex **4** were obtained using 2H-azaphosphirene complex **1** and kinetically stable silylene **2** as starting materials.

4845



### Synthesis of stilbene carboxylic acids as scaffolds for calcium sensors

Heather A. Behanna and Samuel I. Stupp\*

The synthesis and characterization of calcium binding stilbene carboxylic acids for use as sensors are described.

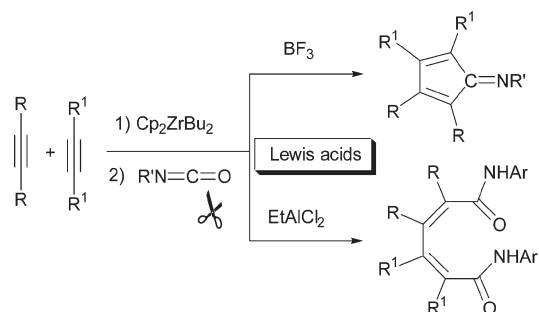


4848

**Lewis acid-promoted reactions of zirconacyclopentadienes with isocyanates. A one-pot three-component synthesis of multiply-substituted iminocyclopentadienes from one isocyanate and two alkynes**

Jiang Lu, Guoliang Mao, Wenxiong Zhang and Zhenfeng Xi\*

A three-component one-pot procedure leading to cyclopentadienylimines was developed *via* intermolecular coupling of two alkynes and one isocyanate. Site selective cleavage of the C=O double bond in the isocyanate and Lewis acid-dependent formation of products were observed.

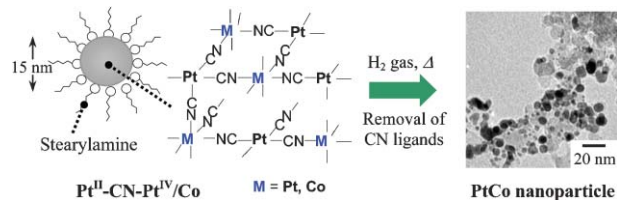


4851

**Novel synthetic approach to creating PtCo alloy nanoparticles by reduction of metal coordination nano-polymers**

Mami Yamada,\* Masayuki Maesaka, Masato Kurihara, Masatomi Sakamoto and Mikio Miyake\*

PtCo alloy nanoparticles with different metal elemental ratios were prepared by a novel synthetic approach using the transformation reaction of nanometer-sized platinum<sup>II</sup>/cobalt tetracyanoplatinate metal coordination polymers (Pt<sup>II</sup>-CN-Pt<sup>IV</sup>/Co) through a H<sub>2</sub> gas-phase reduction.

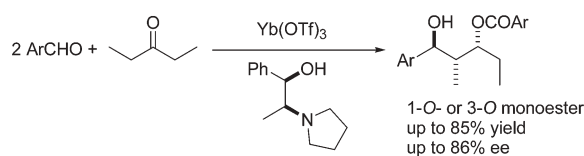


4854

**Direct asymmetric aldol-Tishchenko reaction of aliphatic ketones catalyzed by *syn*-aminoalcohol-Yb(III) complexes**

Jacek Mlynarski,\* Joanna Jankowska and Bartosz Rakiel

The asymmetric direct aldol condensation of aldehydes with ethyl- and propylketones is catalyzed by *syn*- $\alpha$ -aminoalcohol-Yb(OTf)<sub>3</sub> complexes, yielding the *anti*-1,3-diol monoesters with high diastereocontrol and good enantioselectivity. Three adjacent stereogenic centers are created in a simultaneous aldol condensation and Evans-Tishchenko reduction in an acyclic system.

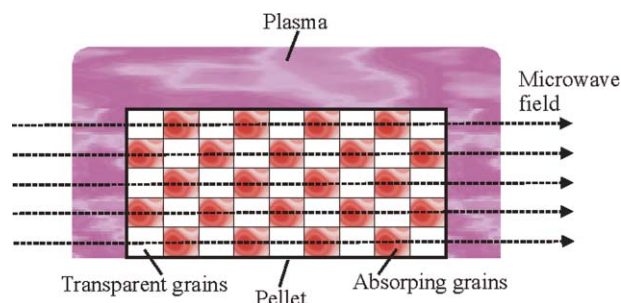


4857

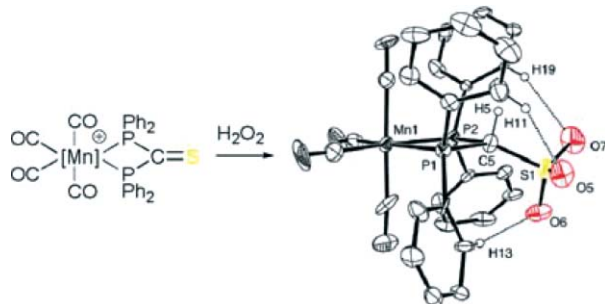
**Plasma-promoted dielectric heating in the microwave synthesis of spinels**

David J. Brooks, Richard E. Douthwaite\* and Lisa J. Gillie

A microwave-induced plasma has been used to drive reactions between oxide precursors that do not exhibit microwave dielectric heating at room temperature. Comparison between reaction rates using conventional and plasma methods indicates that the plasma promotes dielectric heating of the reaction mixture at elevated temperatures.



4860

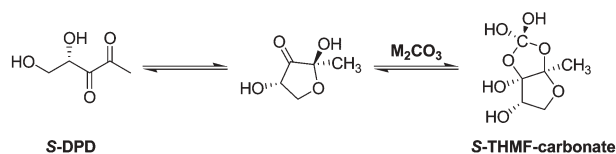


### New approach to sulfonated diphosphine complexes: synthesis and amphoteric behaviour of zwitterionic $[\text{Mn}^+(\text{CO})_4\{(\text{PPh}_2)_2\text{C}(\text{H})\text{SO}_3^-\}]$

Javier Ruiz,\* Mario Ceroni, Marilín Vivanco, Marta P. Gonzalo, Santiago García-Granda and Francisco van der Maelen

Oxidation of the thioether residue in the complex  $[\text{Mn}(\text{CO})_4\{(\text{PPh}_2)_2\text{C}=\text{S}\}]^+$  with  $\text{H}_2\text{O}_2$  affords the sulfonate derivative  $[\text{Mn}(\text{CO})_4\{(\text{PPh}_2)_2\text{C}(\text{H})\text{SO}_3^-\}]$ , providing access to new sulfonated diphosphines under very mild conditions.

4863

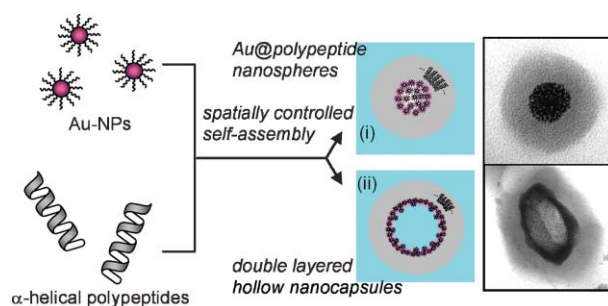


### A furanosyl-carbonate autoinducer in cell-to-cell communication of *V. harveyi*

Kathleen M. McKenzie, Michael M. Meijler, Colin A. Lowery, Grant E. Boldt and Kim D. Janda\*

A previously unidentified autoinducer S-THMF-carbonate, arising from reaction of cyclized S-DPD and carbonate, is found to induce light in *V. harveyi*, thus adding to the ever expanding AI-2 family of autoinducers.

4866

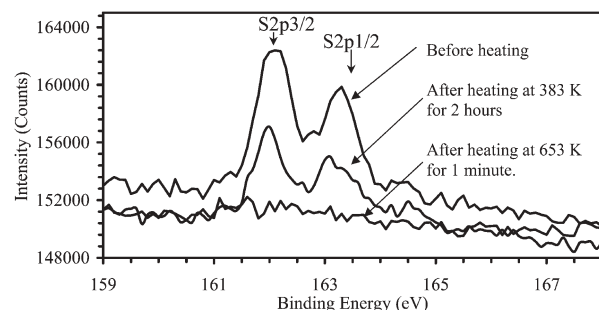


### Spatially controlled self-assembly of gold nanoparticles encased in $\alpha$ -helical polypeptide nanospheres

Masa-aki Morikawa and Nobuo Kimizuka\*

Gold nanoparticles (Au-NPs) are encased in aqueous nanospheres of  $\alpha$ -helical poly( $\gamma$ -benzyl L-glutamate)s, with spatially controlled self-assembly structures of (i) solid core-shell nanospheres or (ii) double-layered hollow nanocapsules.

4869



### Kinetics of alkanethiol monolayer desorption from gold in air

Mohammad Reza Shadnam and A. Amirfazli\*

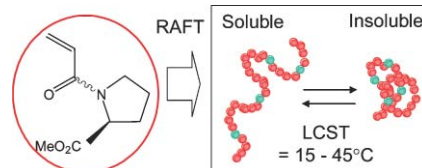
Desorption of an alkanethiol monolayer in gas is investigated using XPS and it is shown that the rate of desorption strongly increases with temperature. A quantitative analysis shows that there exist 2 consecutive 1st order kinetics regimes for desorption.

4872

### Controlled synthesis of thermoresponsive polymers derived from L-proline *via* RAFT polymerization

Hideharu Mori,\* Hideyuki Iwaya, Atsushi Nagai and Takeshi Endo\*

Well-defined polymers derived from L-proline are synthesized using reversible addition–fragmentation chain transfer (RAFT) polymerization and the amino acid-based polymers exhibit thermosensitive phase separation at lower critical solution temperatures (LCST = 15–45 °C) in aqueous medium.



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