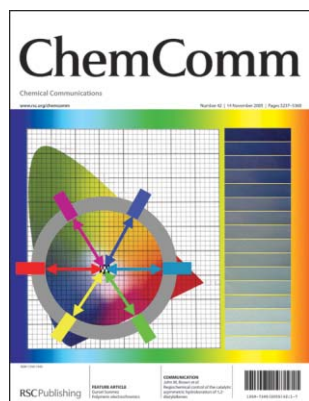


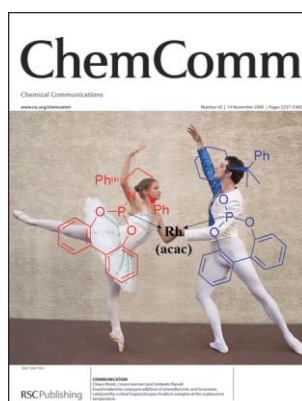
## IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (42) 5237-5360 (2005)



### Cover

See Gursel Sonmez, page 5251. Realization of additive and subtractive colours in polymeric electrochromics is one of the most important steps for the materialization of these substances. Image reproduced by permission of Gursel Sonmez from *Chem. Commun.*, 2005, 5251.



### Inside cover

See Cesare Gennari *et al.*, *Chem. Commun.*, 2005, 5281. A rhodium pre-catalyst is constituted of a free-to-rotate biphenol-derived phosphite and two coalescing biphenol-derived phosphoramidites, like in a ballet. The photograph of the two dancers is reproduced by permission of Bob Shomler.

## CHEMICAL SCIENCE

C81

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

November 2005/Volume 2/Issue 11

[www.rsc.org/chemicalscience](http://www.rsc.org/chemicalscience)

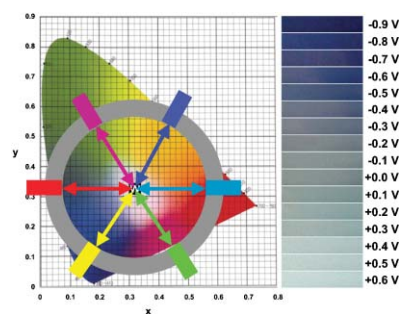
## FEATURE ARTICLE

5251

### Polymeric electrochromics

Gursel Sonmez

The properties of electrochromic polymers are easily modified through changes in the polymeric backbone, which has resulted in their completion of the additive primary colour space, red, green and blue (RGB).



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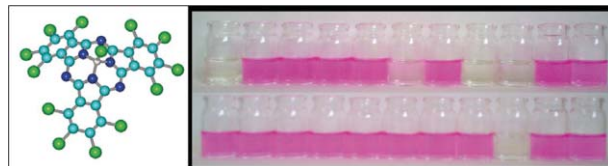
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### Subphthalocyanines as fluoro-chromogenic probes for anions and their application to the highly selective and sensitive cyanide detection

Jose V. Ros-Lis, Ramón Martínez-Máñez\* and Juan Soto

The use of a subphthalocyanine derivative as a selective and sensitive chromo-fluorogenic reporter for the anion cyanide in mixed aqueous solution is reported.

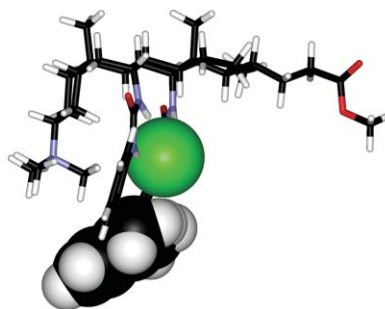


5263

### Contra-Hofmeister anion extraction by cyclosteroidal receptors

Adam L. Sisson, John P. Clare and Anthony P. Davis\*

Steroid-based receptors with enclosed binding sites, formed from quaternary ammonium and macrocyclic bis-urea units, can substantially override the Hofmeister series in anion phase transfer experiments.

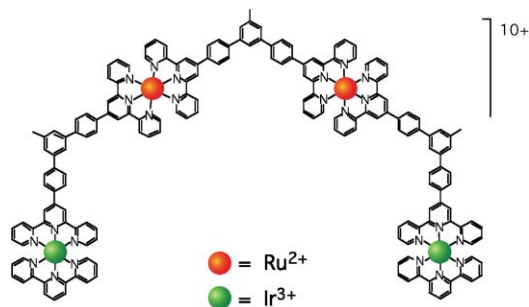


5266

### Two-color luminescence from a tetranuclear Ir(III)/Ru(II) complex

Marco Cavazzini, Paola Pastorelli, Silvio Quici,\*  
Frédérique Loiseau\* and Sebastiano Campagna

Independent excited-state decays of the Ir-based and Ru-based subunits lead to two-color luminescence in the title species at room temperature. At 77 K, efficient energy transfer from the Ir(III) chromophores to the Ru(II) ones occurs.

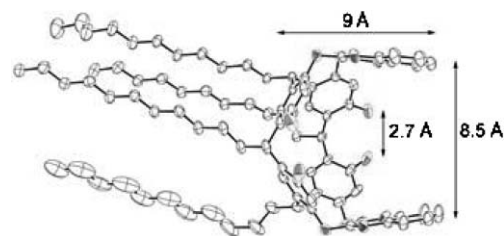


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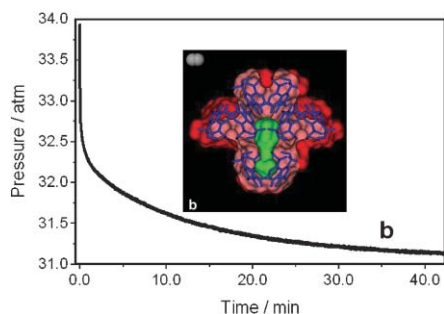
### Selective steroid recognition by a partially bridged resorcin[4]arene cavitand

Martina Cacciarini, Vladimir A. Azov, Paul Seiler,  
Hermann Künzer and François Diederich\*

A partially bridged resorcin[4]arene cavitand featuring a cleft-shaped recognition site formed by two *anti*-quinoxaline bridges and four convergent phenolic HO-groups was found to be an efficient, selective receptor for steroidal substrates.



5272

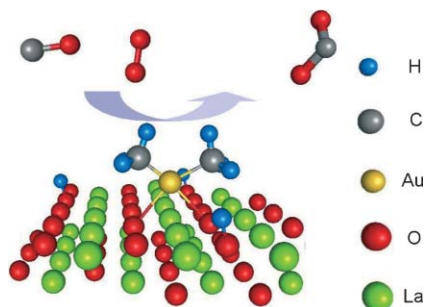


### Organic crystals absorb hydrogen gas under mild conditions

Praveen K. Thallapally, Gareth O. Lloyd, Trevor B. Wirsig, Martin W. Breidenkamp, Jerry L. Atwood\* and Leonard J. Barbour\*

We have studied the hydrogen sorption on three well-known organic hosts that possess vacant lattice voids large enough to accommodate  $H_2$  molecules.

5275

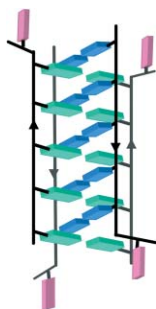


### A highly active catalyst for CO oxidation at 298 K: mononuclear $Au^{III}$ complexes anchored to $La_2O_3$ nanoparticles

Juan C. Fierro-Gonzalez, Vinesh A. Bhirud and Bruce C. Gates\*

$La_2O_3$ -supported  $Au^{III}$  complexes synthesised from  $Au^{III}(CH_3)_2(C_5H_7O_2)$  are active, stable CO oxidation catalysts at room temperature, demonstrating that zerovalent gold is not needed for these properties.

5278

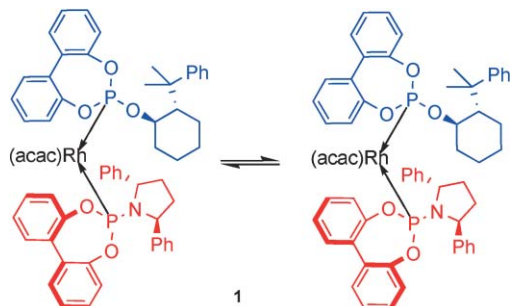


### PNA forms an i-motif

Yamuna Krishnan-Ghosh, Elaine Stephens and Shankar Balasubramanian\*

A C-rich PNA hexanucleotide, p(C<sub>5</sub>T), has been shown to form an i-motif by nanoelectrospray ionization mass spectrometry coupled with H/D exchange.

5281



### Enantioselective conjugate addition of phenylboronic acid to enones catalysed by a chiral tropos/atropos rhodium complex at the coalescence temperature

Chiara Monti, Cesare Gennari\* and Umberto Piarulli\*

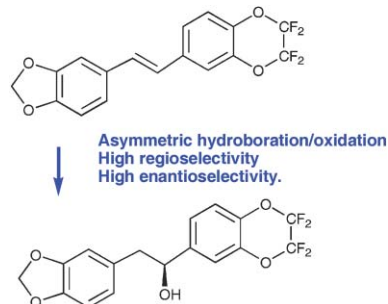
Mixed pre-catalyst **1** is constituted of a free-to-rotate (tropos) biphenol-derived phosphite and a tropos/atropos biphenol-derived phosphoramidite (coalescence temperature = 310 K) and provides excellent results in the Rh-catalysed asymmetric conjugate addition of phenylboronic acid to cyclic enones.

5284

**Regiochemical control of the catalytic asymmetric hydroboration of 1,2-diarylethenes**

Antonia Black, John M. Brown\* and Christophe Pichon

The hydroboration of stilbenes and related disubstituted alkenes catalysed by QUINAP complexes may proceed with high enantio- and regioselectivity; rhodium and iridium catalysts give the same product regioisomer but opposite enantiomers.

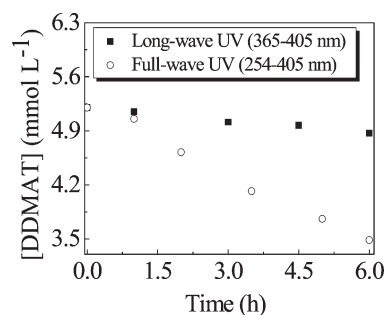


5287

**Well-controlled reversible addition–fragmentation chain transfer radical polymerisation under ultraviolet radiation at ambient temperature**

Lican Lu, Nianfa Yang\* and Yuanli Cai\*

Controlled/“living” reversible addition–fragmentation chain transfer radical polymerisation of methyl acrylate was carried out under long-wave ( $\lambda \geq 365$  nm) ultraviolet radiation using an acylphosphine oxide as a photoinitiator at ambient temperature.

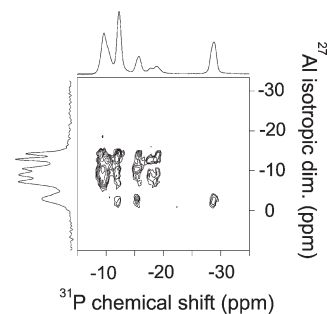


5289

**Phase identification and quantification in a devitrified glass using homo- and heteronuclear solid-state NMR**

Grégory Tricot, Laurent Delevoye,\* Gérard Palavit and Lionel Montagne

A complex mixture resulting from the devitrification of an aluminophosphate glass has been studied for the first time using a combination of homo- and heteronuclear solid-state NMR sequences that offers the advantage of subsequent quantification.

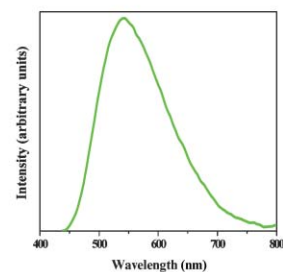
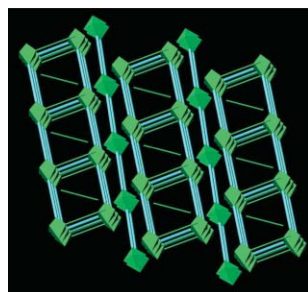


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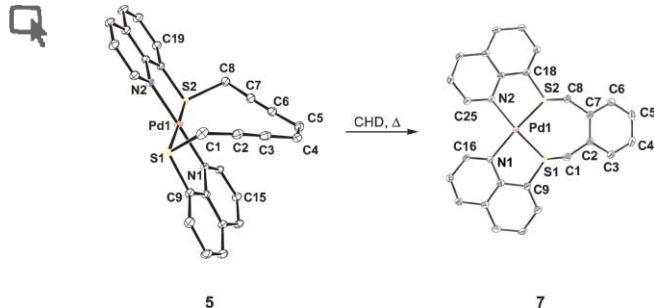
**Assembled bright green fluorescent zinc coordination polymer**

Ruibiao Fu, Shengchang Xiang, Shengmin Hu, Longsheng Wang, Yaming Li, Xihe Huang and Xintao Wu\*

A fluorescent brightener (disodium 4,4'-bis(2-sulfonatostyryl)biphenyl) was assembled with a zinc/4,4'-bipyridine framework to form a coordination polymer, possessing strong green fluorescence at 542 nm.



5295

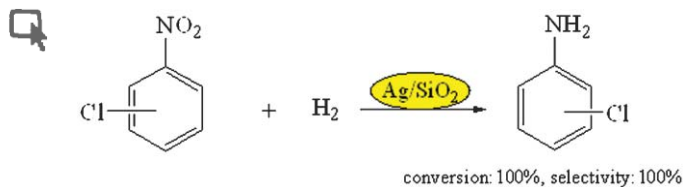


### A geometric switching approach toward thermal activation of metalloenediynes

Sibaprasad Bhattacharyya, David F. Dye, Maren Pink and Jeffrey M. Zaleski\*

Non-rigid geometric coordination of an enediyne about a metal within a given oxidation state, can be used as a switch to drive Bergman cyclization by converting stable enediyne conformations to their reactive counterparts.

5298

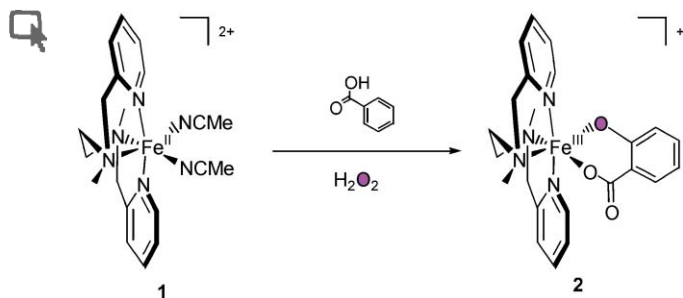


### Ag/SiO<sub>2</sub>: a novel catalyst with high activity and selectivity for hydrogenation of chloronitrobenzenes

Yangying Chen, Chuang Wang, Hongyang Liu, Jieshan Qiu\* and Xinhe Bao

Ag/SiO<sub>2</sub> catalysts prepared by an *in situ* reduction method are found, for the first time, to be highly effective and recyclable for the selective hydrogenation of a range of chloronitrobenzenes to their corresponding chloroanilines, which are of great potential as industrially viable and cheap novel catalysts for the production of chloroanilines.

5301

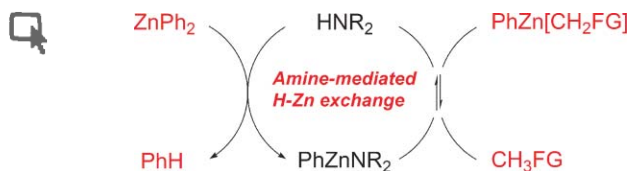


### *ortho*-Hydroxylation of benzoic acids with hydrogen peroxide at a non-heme iron center

Sonia Taktak, Margaret Flook, Bruce M. Foxman, Lawrence Que, Jr. and Elena V. Rybak-Akimova\*

Aromatic hydroxylation is yet another transformation catalyzed by the versatile Fe(bpmen)/H<sub>2</sub>O<sub>2</sub> combination. Hydroxylation of benzoates occurs within seconds at room temperature regiospecifically at the position *ortho* to the carboxylate function affording salicylates in high stoichiometric yield. Potent and selective metal-based oxidants can thus be obtained in simple non-heme iron systems.

5304



### The direct $\alpha$ -zincation of amides, phosphonates and phosphine oxides by H-Zn exchange

Mark L. Hlavinka, Jeffrey F. Greco and John R. Hagadorn\*

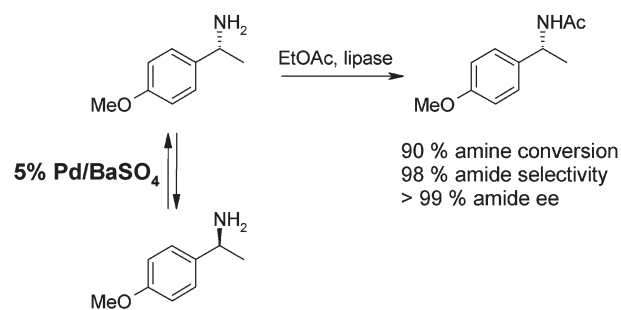
Stoichiometric or catalytic quantities of simple 2° amines greatly increase the rate of H-Zn exchange between ZnPh<sub>2</sub> and a range of relatively non-acidic substrates, allowing for the convenient and direct preparation of  $\alpha$ -functionalized organozincs.

5307

**Efficient dynamic kinetic resolution of secondary amines with Pd on alkaline earth salts and a lipase**

Andrei Parvulescu, Dirk De Vos and Pierre Jacobs\*

Combination of Pd, supported on alkaline earth type supports with a lipase results in a selective catalytic system for dynamic kinetic resolution of benzylic amines.

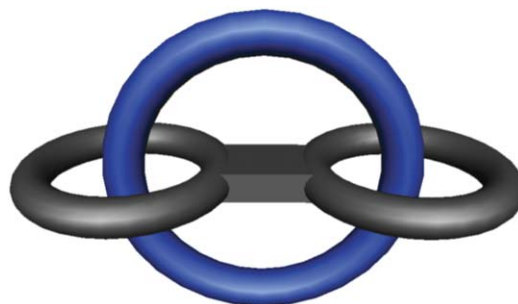


5310

**A catenane consisting of a large ring threaded through both cyclic units of a handcuff-like compound**

Julien Frey, Tomáš Kraus, Valérie Heitz and Jean-Pierre Sauvage\*

A new catenane has been prepared in good yield which consists of a bis-macrocycle and a large central ring.

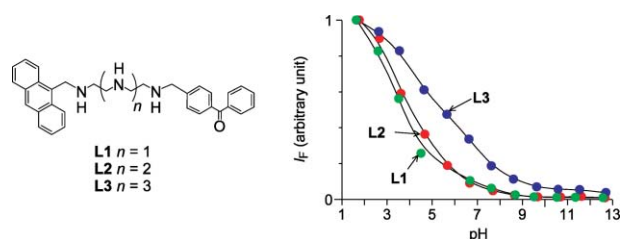


5313

**A fluorescent chemosensor for wide-range pH detection**

Go Nishimura, Yasuhiro Shiraishi\* and Takayuki Hirai

Simple-structured polyamines, **L1–L3**, bearing anthracene and benzophenone units at respective ends, behave as a fluorescent pH sensor applicable to wide-range pH detection: the pH–fluorescence intensity profile of the molecules demonstrate a “gentle slope” over pH 2–10 range.

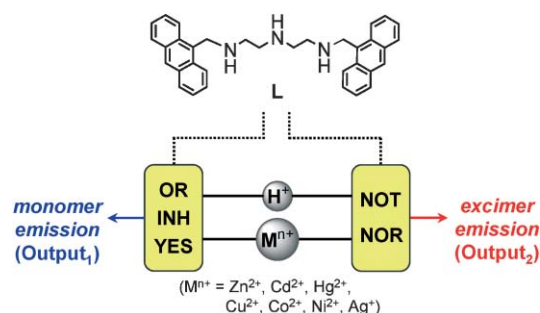


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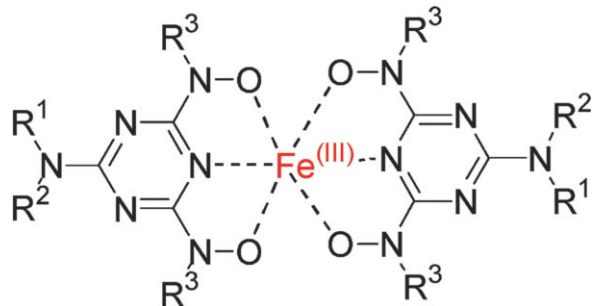
**A fluorescent molecular logic gate with multiply-configurable dual outputs**

Yasuhiro Shiraishi,\* Yasufumi Tokitoh and Takayuki Hirai

A simple molecule, **L**, diethylenetriamine bearing anthracene fragments at both ends, behaves as a fluorescent molecular logic gate with “multiply-configurable dual outputs”, capable of demonstrating five different logic functions operated by proton ( $H^+$ ) and transition metal cations ( $M^{n+}$ ) as inputs.



5319

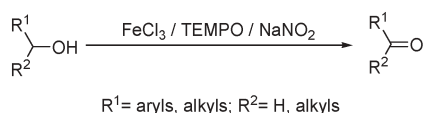


### Bis-(hydroxyamino)triazines: highly stable hydroxylamine-based ligands for iron(III) cations

Jenny Gun, Irina Ekeltchik, Ovadia Lev, Rimma Shelkov and Artem Melman\*

Bis-(hydroxyamino)triazines (BHT) constitute a new, general and versatile group of tridentate iron(III) chelating agents exhibiting high affinity to iron(III) and iron(III) over iron(II) selectivity.

5322

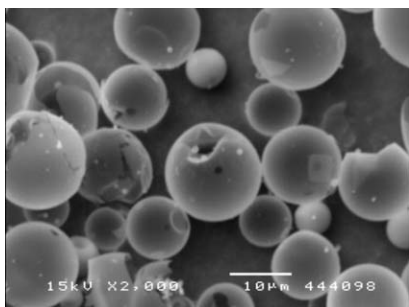


### NaNO<sub>2</sub>-activated, iron-TEMPO catalyst system for aerobic alcohol oxidation under mild conditions

Naiwei Wang, Renhua Liu,\* Jiping Chen and Xinmiao Liang\*

FeCl<sub>3</sub>-TEMPO-NaNO<sub>2</sub> catalyses the selective and mild aerobic oxidation of a broad range of alcohols, which may bear N and S heteroatoms or carbon-carbon double bond, to the corresponding aldehydes and ketones.

5325

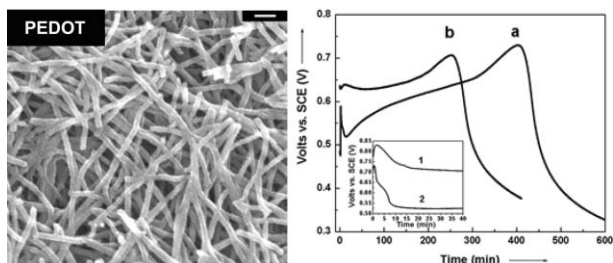


### Synthesis of protein-silica hybrid hollow particles through the combination of protein catalysts and sonochemical treatment

Toru Shiomi, Tatsuo Tsunoda, Akiko Kawai, Hiroyuki Chiku, Fujio Mizukami and Kengo Sakaguchi\*

Hollow spherical particles with protein-silica hybrid shell structures have been synthesized through the combination of the catalytic activity of the protein and sonochemical treatment. The morphologies of the particles were controlled by varying the protein concentration.

5328



### Chemical synthesis of PEDOT nanofibers

Xinyu Zhang, Alan G. MacDiarmid and Sanjeev K. Manohar\*

Nanofibers of PEDOT can be synthesized in bulk quantities, in one step, by chemical oxidative polymerization of EDOT using V<sub>2</sub>O<sub>5</sub> nanofibers as sacrificial seed templates.

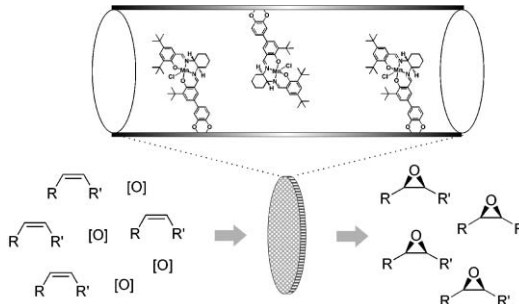


5331

### Anodic aluminium oxide catalytic membranes for asymmetric epoxidation

So-Hye Cho, Nolan D. Walther, SonBinh T. Nguyen\* and Joseph T. Hupp\*

Catechol-functionalized (salen)Mn complexes can be supported on mesoporous anodized aluminium oxide disks to yield catalytic membranes that are highly active in the enantioselective epoxidation of olefins when being deployed in a forced-through-flow reactor.

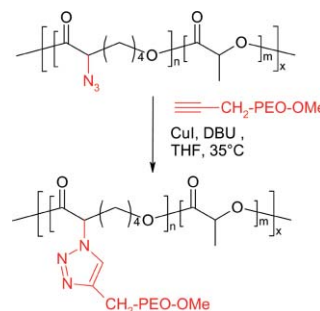


5334

### Combination of ring-opening polymerization and “click” chemistry towards functionalization of aliphatic polyesters

Raphaël Riva, Stéphanie Schmeits, François Stoffelbach, Christine Jérôme, Robert Jérôme\* and Philippe Lecomte

Azide-containing aliphatic polyesters have been reacted with various alkynes by “click” reaction. The experimental conditions have been optimized, such that the aliphatic polyesters are not degraded, including even poly(lactide) which is very sensitive to nucleophilic attack.

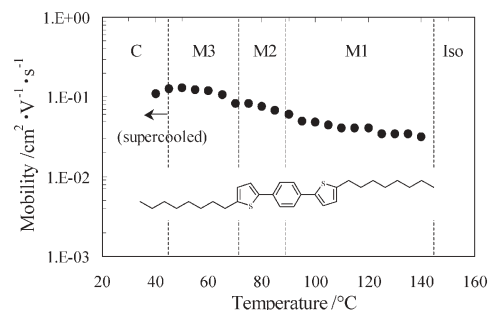


5337

### A novel calamitic mesophase semiconductor with the fastest mobility of charged carriers: 1,4-di(5'-octyl-2'-thienyl)benzene

Kazuma Oikawa,\* Hirosato Monobe, Junpei Takahashi, Kazuhiko Tsuchiya, Benoît Heinrich, Daniel Guillon and Yo Shimizu\*

The carrier mobility of highly ordered lamellar mesophases was evaluated by a Time-of-Flight (TOF) method for 1,4-di(5'-octyl-2'-thienyl)benzene (8-TPT-8) to show the fastest mobility ever reported for calamitic systems.

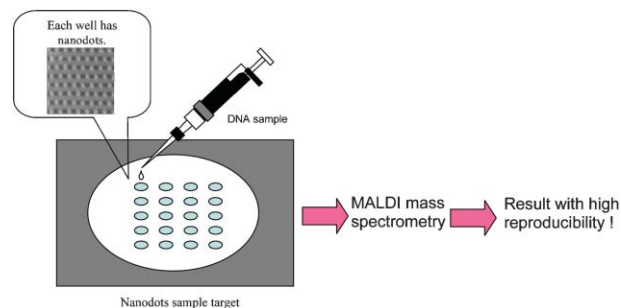


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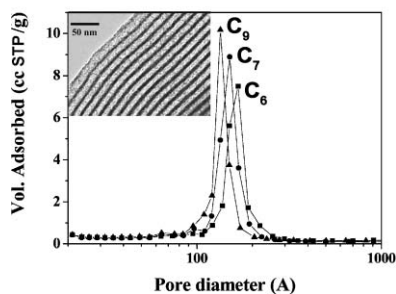
### Improved method of the MALDI-TOF analysis of DNA with nanodot sample target plate

Aki Honda, Hideki Sonobe, Akiko Ogata and Koji Suzuki

A newly developed sample target plate for MALDI-TOF mass spectrometry made of SiO<sub>2</sub> with 30 nm Pt dots provided highly reproducible DNA analysis without any modification of sample preparation.



5343

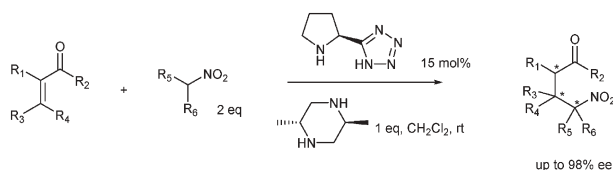


### Alkanes-assisted low temperature formation of highly ordered SBA-15 with large cylindrical mesopores

Junming Sun, He Zhang, Ding Ma, Yangying Chen, Xinhe Bao,\* Achim Klein-Hoffmann, Norbert Pfänder and Dang Sheng Su

Highly ordered SBA-15 silicas with large cylindrical mesopores (~15 nm) are successfully obtained with the help of  $\text{NH}_4\text{F}$  by controlling the initial reaction temperatures in the presence of excess amounts of alkanes.

5346

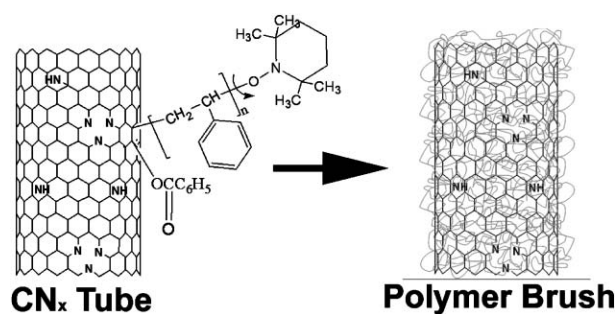


### A versatile organocatalyst for the asymmetric conjugate addition of nitroalkanes to enones

Claire E. T. Mitchell, Stacey E. Brenner and Steven V. Ley\*

5-Pyrrolidin-2-yltetrazole performs as an improved catalyst for the asymmetric addition of a range of nitroalkanes to cyclic and acyclic enones, with good to excellent enantioselectivity.

5349

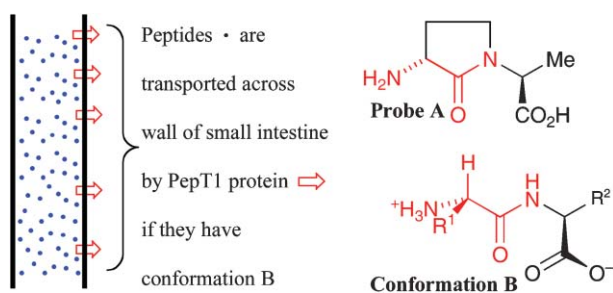


### Nanotube brushes: polystyrene grafted covalently on $\text{CN}_x$ nanotubes by nitroxide-mediated radical polymerization

M. Dehonor,\* K. Masenelli-Varlot, A. González-Montiel, C. Gauthier, J. Y. Cavallé, H. Terrones and M. Terrones\*

Polymer brushes consisting of polystyrene (PS) chains bonded covalently to N-doped multiwalled carbon nanotubes ( $\text{CN}_x$ ) were synthesized by a “grafting from” route using nitroxide mediated radical polymerization (NMRP). The materials were compared with composites fabricated by blending PS and  $\text{CN}_x$  nanotubes.

5352



### Conformational and spacial preferences for substrates of PepT1

Patrick D. Bailey,\* C. A. Richard Boyd, Ian D. Collier, John. G. George, George L. Kellett, David Meredith, Keith M. Morgan, Rachel Pettecrew, Richard A. Price and Robin G. Pritchard

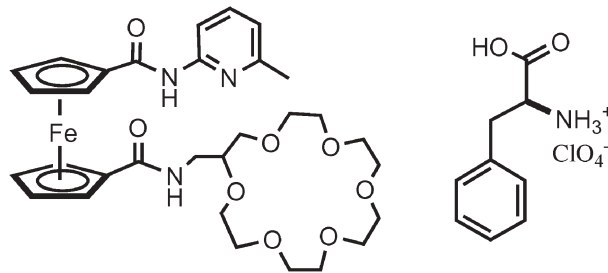
By using constrained peptide analogues (*e.g.* probe A), the active conformation of the N-terminal region of di- and tri-peptides (*e.g.* red region of conformation B) for transport by PepT1 has been determined.

5355

**Selective electrochemical sensing of acidic organic molecules *via* a novel guest-to-host proton transfer reaction**

Hidekazu Miyaji, Gilles Gasser, Stephen J. Green,\*  
Yann Molard, Sharon M. Strawbridge and  
James H. R. Tucker\*

Mono- and heteroditopic ferrocene receptors selectively bind and sense carboxylic acid derivatives such as the amino acid phenylalanine *via* a novel guest-to-host proton transfer reaction in acetonitrile solution.



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