

# ChemComm

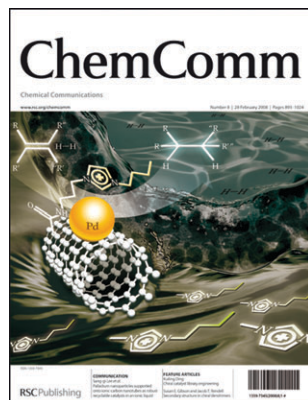
Chemical Communications

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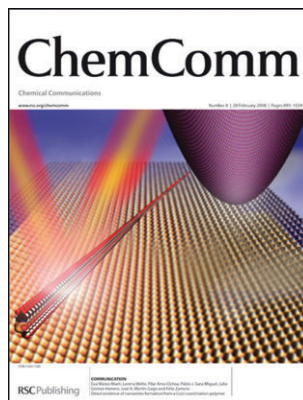
## IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (8) 893-1024 (2008)



### Cover

See Sang-gi Lee *et al.*, pp. 942–944. Palladium nanoparticles supported on imidazolium-functionalized ionic CNTs showed extraordinary stability in an ionic liquid, providing a robust recyclable ionic liquid-based catalytic system. Image reproduced by permission of Yu Sung Chun, Ju Yeon Shin, Choong Eui Song and Sang-gi Lee from *Chem. Commun.*, 2008, 942.



### Inside cover

See Félix Zamora *et al.*, pp. 945–947. Spectroscopic and morphological evidence of nanowires formation from a Cu(I) coordination polymer on surfaces. Image reproduced by permission of Eva Mateo-Martí, Lorena Welte, Pilar Amo-Ochoa, Pablo J. Sanz Miguel, Julio Gómez-Herrero, José A. Martín-Gago and Félix Zamora from *Chem. Commun.*, 2008, 945.

## FEATURE ARTICLES

909

### Synergistic effect of binary component ligands in chiral catalyst library engineering for enantioselective reactions

Kuiling Ding

The synergistic effect of binary ligands was taken as the basis for chiral catalyst library design by assembling the component ligands with metal ions. This article highlights the most relevant examples for development of highly efficient and cost-effective chiral catalysts in asymmetric hetero-Diels–Alder, carbonyl–ene, alkylation, and hydrogenation reactions, respectively.

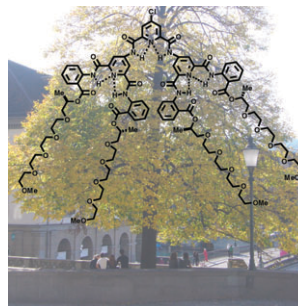


922

### The quest for secondary structure in chiral dendrimers

Susan E. Gibson\* and Jacob T. Rendell

This review highlights important developments in the pursuit of chiral conformational order in dendritic structures. To be able to create and control chiral secondary structure necessitates a thorough understanding of how chiral subunits influence the macroscopic structure.



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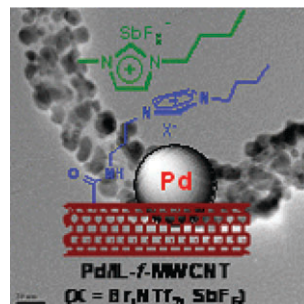
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942

### Palladium nanoparticles supported onto ionic carbon nanotubes as robust recyclable catalysts in an ionic liquid

Yu Sung Chun, Ju Yeon Shin, Choong Eui Song and Sang-gi Lee\*

Combination of palladium nanoparticles deposited onto imidazolium-functionalized ionic MWCNTs with an ionic liquid created a new recyclable ionic liquid-based catalytic system allowing up to 50 times recycling.

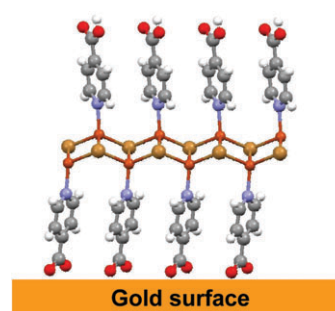


945

### Direct evidence of nanowires formation from a Cu(I) coordination polymer

Eva Mateo-Martí, Lorena Welte, Pilar Amo-Ochoa, Pablo J. Sanz Miguel, Julio Gómez-Herrero, José A. Martín-Gago and Félix Zamora\*

Spectroscopic and morphological evidences showing the one-dimensional organization of [CuBr(HIN)]<sub>n</sub> (HIN = isonicotinic acid) on selected surfaces are reported.

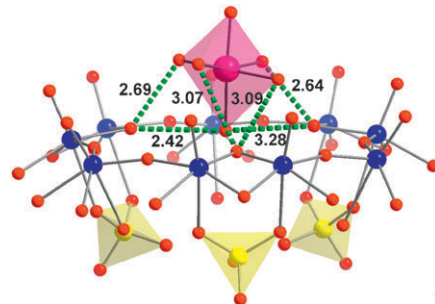


948

### Cation behavior at an artificial cell interface: binding distinguished by ion hydration energetics and size

Alice Merca, Hartmut Bögge, Marc Schmidtman, Yunshan Zhou, Erhard T. K. Haupt, M. Khaled Sarker, Craig L. Hill\* and Achim Müller\*

Whereas alkali cations forming less stable aqua complexes can cross the channels of molybdenum oxide-based nanoporous capsules, the stable [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> get trapped above the pores interacting with the latter *via* hydrogen bonds.

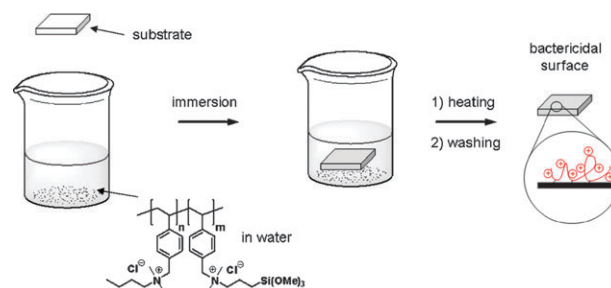


951

### A new, simple approach to confer permanent antimicrobial properties to hydroxylated surfaces by surface functionalization

Othman Bouloussa, Francis Rondelez and Vincent Semetey\*

A new, simple method to obtain ultrathin polycationic monolayers on hydroxylated surfaces is described which uses a bifunctional copolymer comprising a reactive part (trimethoxysilane) and positive charges (quaternary ammonium salts) to confer antimicrobial properties.



# A decade shedding light on crystal engineering



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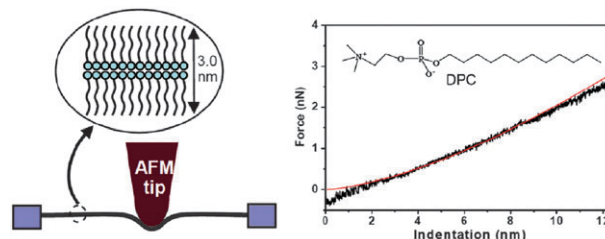
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954

### Nanomechanical properties of reversed surfactant bilayers formed in micrometre-sized holes

Jian Jin, Yukihiko Sugiyama, Keita Mitsui, Hideo Arakawa and Izumi Ichinose\*

Nanomechanical properties of free-standing reversed surfactant bilayers, dried foam films, were examined *via* AFM by fitting local force-indentation curves with a Hertzian model. The Young's moduli of four kinds of bilayers were in the range 10–30 MPa.

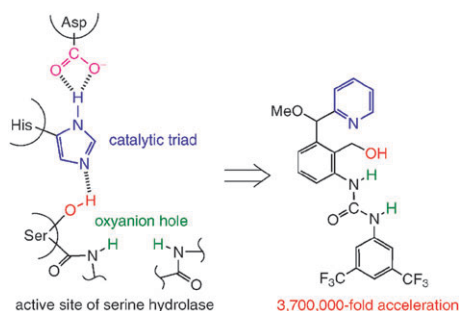


957

### Biomimetic trifunctional organocatalyst showing a great acceleration for the transesterification between vinyl ester and alcohol

Tadashi Ema,\* Daisuke Tanida, Tatsuya Matsukawa and Takashi Sakai\*

Trifunctional organocatalysts mimicking the active site of serine hydrolases showed high catalytic activity with up to a 3 700 000-fold acceleration for the acyl-transfer reactions from vinyl trifluoroacetate to alcohol.

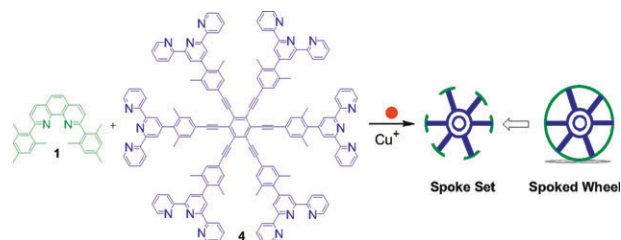


960

### Towards technomimetic spoked wheels: dynamic hexakis-heteroleptic coordination at a hexakis-terpyridine scaffold

Michael Schmittl\* and Prasenjit Mal

The synthesis of hexakis-terpyridine **4** and an expedient approach to a dynamic hexakis-heteroleptic spoke set are elaborated, the latter being readily accessible precursors for the construction of technomimetic molecular spoked wheels.

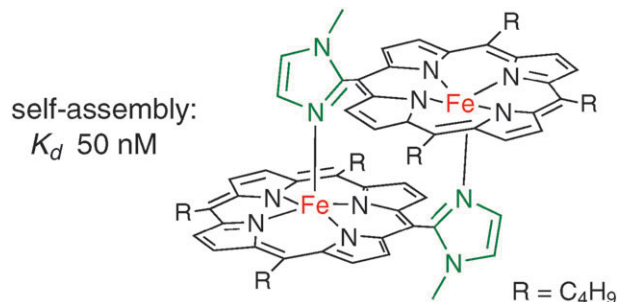


963

### Simple dimer containing dissociatively stable mono-imidazole ligated ferrohemes

Qing-Zheng Yang, Daria Khvostichenko, John D. Atkinson and Roman Boulatov\*

Easily accessible Fe<sup>II</sup> meso-(*N*-methylimidazol-2-yl)porphine exists as a stable dimer that binds ligands without breaking apart and is presently the simplest complex in which the mono-imidazole ligation of a ferroheme is enforced without excess imidazole in solution.





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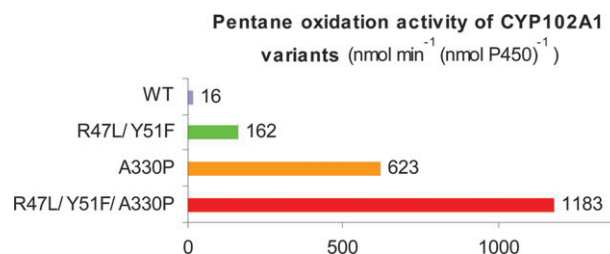
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966

### Evolved CYP102A1 (P450<sub>BM3</sub>) variants oxidise a range of non-natural substrates and offer new selectivity options

Christopher J. C. Whitehouse, Stephen G. Bell, Henry G. Tufton, Richard J. P. Kenny, Lydia C. I. Ogilvie and Luet-Lok Wong\*

A simple screening procedure identified new CYP102A1 (P450<sub>BM3</sub>) variants that significantly enhanced the oxidation rates of a range of non-natural substrates and gave unusual product distributions.

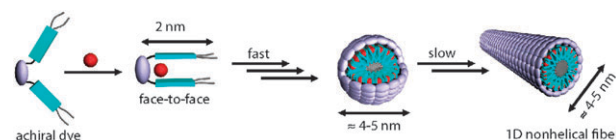


969

### Controlled self-assembly of squaraines to 1D supramolecular architectures with high molar absorptivity

Ayyappanpillai Ajayaghosh,\* Parayalil Chithra, Reji Varghese and Kizhumuri P. Divya

A tailor made squaraine dye in the presence of Ca<sup>2+</sup> self-assembles to form spherical micelles that reorganise to cylindrical rods with high molar absorptivity.

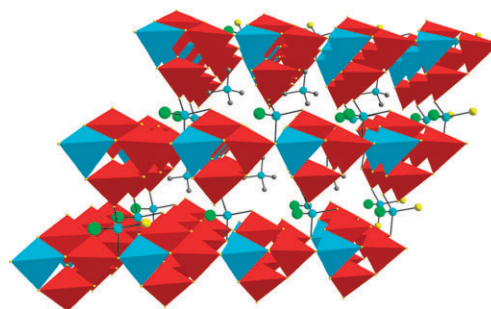


972

### [Zn(H<sub>2</sub>O)<sub>4</sub>][Zn<sub>2</sub>Sn<sub>3</sub>Se<sub>9</sub>(MeNH<sub>2</sub>)]: a robust open framework chalcogenide with a large nonlinear optical response

Manolis J. Manos, Joon I. Jang, John B. Ketterson and Mercuri G. Kanatzidis\*

[Zn(H<sub>2</sub>O)<sub>4</sub>][Zn<sub>2</sub>Sn<sub>3</sub>Se<sub>9</sub>(MeNH<sub>2</sub>)] has a structure based on supertetrahedra with double connectivity and exhibits a large second harmonic generation response, excellent acid stability and proton exchange capacity.

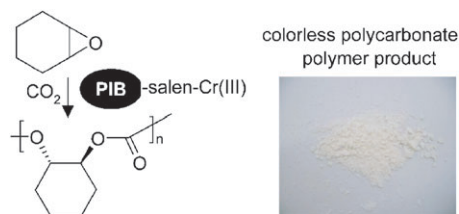


975

### A phase separable polycarbonate polymerization catalyst

Chayanant Hongfa, Jianhua Tian, Jeremy Andreatta, Donald J. Darensbourg\* and David E. Bergbreiter\*

Salen ligands containing a polyisobutyl group facilitate separation of the colored Cr(III) catalyst from a polycarbonate product in a polymerization of CO<sub>2</sub> and cyclohexene oxide.



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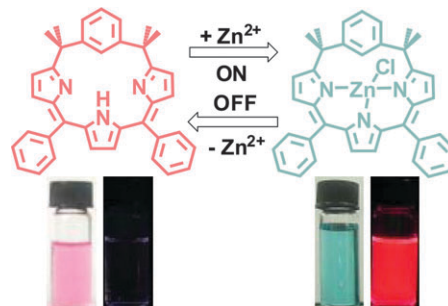


978

***m*-Benziporphodimethene: a new porphyrin analogue fluorescence zinc(II) sensor**

Chen-Hsiung Hung,\* Gao-Fong Chang, Anil Kumar, Geng-Fong Lin, Li-Yang Luo, Wei-Min Ching and Eric Wei-Guang Diao

*m*-Benziporphodimethene, a long-wavelength Zn<sup>2+</sup> specific chemosensor, shows fluorescence switch-on upon Zn<sup>2+</sup> binding with no apparent background fluorescence. The fluorescence quantum yield ( $\Phi_F$ ) of 0.34 for the zinc complex is higher than that of the zinc complex of tetraphenylporphyrin.

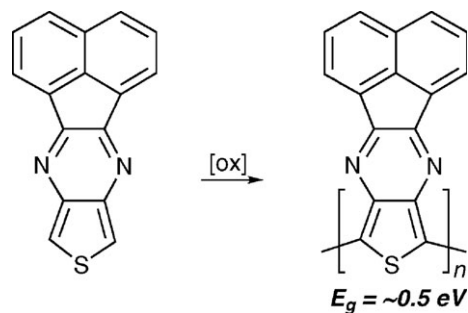


981

**Poly(acenaphtho[1,2-*b*]thieno[3,4-*e*]pyrazine): a new low band gap conjugated polymer**

Jon P. Nietfeld, Christopher L. Heth and Seth C. Rasmussen\*

Electropolymerization of acenaphtho[1,2-*b*]thieno[3,4-*e*]pyrazine results in the production of a new conjugated polymer exhibiting a low band gap of  $\sim 0.5$  eV and increased stability.

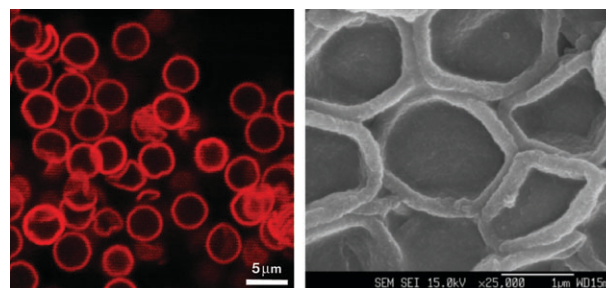


984

**A facile approach to synthesize uniform hydrogel shells with controllable loading and releasing properties**

Joo-Hyun Han, Bo-Mi Koo, Jin-Woong Kim\* and Kyung-Do Suh\*

We introduce a facile method to synthesize uniform hydrogel shells by using *in situ* hydrolysis and subsequent creation of covalent bonds. These hydrogel shells can load active ingredients and release them through pH changes.

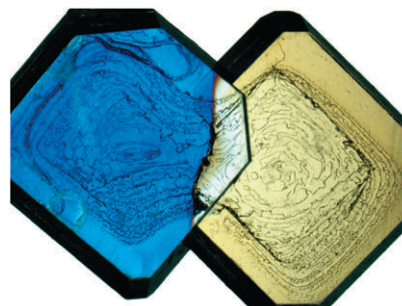


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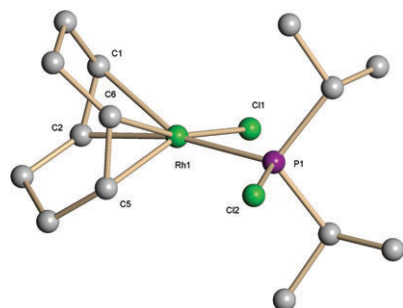
**Complete asymmetric amplification of ethylenediammonium sulfate using an abrasion/grinding technique**

Pui Shan Monica Cheung, Jacinthe Gagnon, Jamie Surprenant, Ye Tao, Huiwen Xu and Louis A. Cuccia\*

Complete asymmetric amplification of ethylenediammonium sulfate was achieved under continuous dissolution/crystallization conditions using an abrasion/grinding technique. *Levorotatory* (left) and *dextrorotatory* (right) ethylenediammonium sulfate crystals are shown as viewed between polarizing filters at 30°.



990

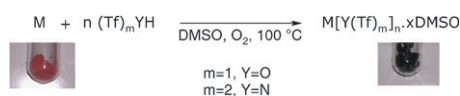


### Simple rhodium–chlorophosphine pre-catalysts for the ortho-arylation of phenols

Robin B. Bedford,\* Michael Betham,  
Andrew J. M. Caffyn,\* Jonathan P. H. Charmant,  
Lesley C. Lewis-Alleyne, Philip D. Long,  
Dorian Polo-Cerón and Sanjiv Prashar\*

Simple chlorodiisopropylphosphine adducts of rhodium, either pre-formed or formed *in situ*, prove to be highly effective catalysts for the ortho-arylation of phenols.

993

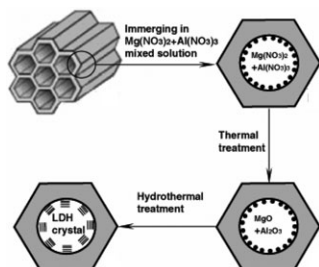


### Facile preparation of metallic triflates and triflimidates by oxidative dissolution of metal powders

Sylvain Antoniotti and Elisabet Duñach\*

Various metallic triflates and triflimidates were prepared by the oxidative dissolution of the corresponding metal powder in DMSO under O<sub>2</sub> in the presence of stoichiometric amounts of triflic or triflimidic acid.

996

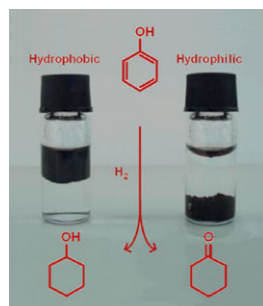


### *In situ* assembly of layered double hydroxide nano-crystallites within silica mesopores and its high solid base catalytic activity

Liang Li and Jianlin Shi\*

Mg–Al layered double hydroxide (LDH) nanocrystallites with a lateral size less than 9 nm were *in situ* synthesized within the pore channels of mesoporous silica materials, creating one of the most active heterogeneous base catalysts owing to the high number of active edge sites.

999



### Selective partial hydrogenation of hydroxy aromatic derivatives with palladium nanoparticles supported on hydrophilic carbon

Philippe Makowski, Rezan Demir Cakan,  
Markus Antoniotti, Frédéric Goettmann\* and  
Maria-Magdalena Titirici\*

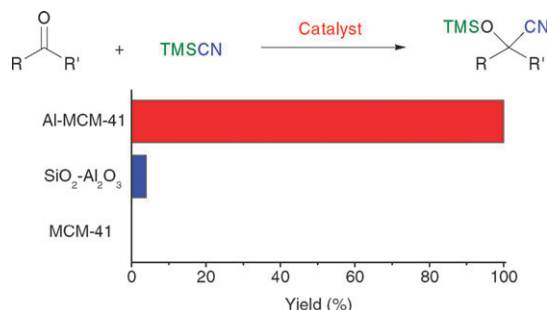
The palladium catalyst was obtained in one step, by hydrothermal carbonisation of an aqueous solution of furfural and palladium acetate.

1002

**Remarkable acceleration of cyanosilylation by the mesoporous Al-MCM-41 catalyst**

Katsuyuki Iwanami, Jun-Chul Choi, Baowang Lu, Toshiyasu Sakakura and Hiroyuki Yasuda\*

The very significant catalytic effect of mesoporous aluminosilicate Al-MCM-41 in the cyanosilylation of carbonyl compounds is described. The Al-MCM-41 catalyst shows overwhelming superiority in this reaction over amorphous aluminosilicates.

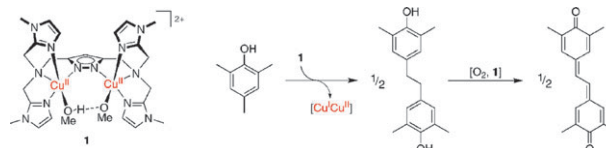


1005

**Selective benzylic C–C coupling catalyzed by a bioinspired dicopper complex**

Angelina Prokofieva, Alexander I. Prikhod'ko, Sebastian Dechert and Franc Meyer\*

A highly preorganized bioinspired dicopper complex with imidazole ligation catalyzes the selective benzylic *para*-C–H activation of 2,4,6-trimethylphenol under aerobic conditions, yielding either the stilbenequinone or 4-methoxymethyl-2,6-dimethylphenol depending on the solvent used.

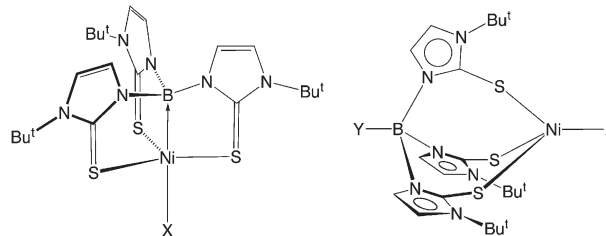


1008

**Reactivity of the Ni→B dative σ-bond in the nickel boratrane compounds [κ<sup>4</sup>-B(mim<sup>Bu<sup>t</sup>)</sup>]<sub>3</sub>NiX (X = Cl, OAc, NCS, N<sub>3</sub>): synthesis of a series of B-functionalized tris(2-mercapto-1-*tert*-butylimidazolyl)borato complexes, [YTm<sup>Bu<sup>t</sup></sup>]NiZ**

Keliang Pang, Joseph M. Tanski and Gerard Parkin\*

The reactivity of nickel boratrane complexes [κ<sup>4</sup>-B(mim<sup>Bu<sup>t</sup>)</sup>]<sub>3</sub>NiX provides a means of synthesizing nickel complexes that feature B-functionalized tris(mercaptoimidazolyl)borate derivatives, [YTm<sup>Bu<sup>t</sup></sup>]NiZ.

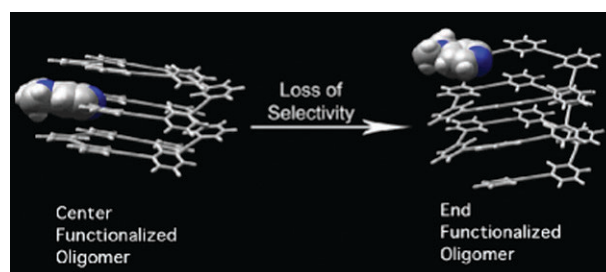


1011

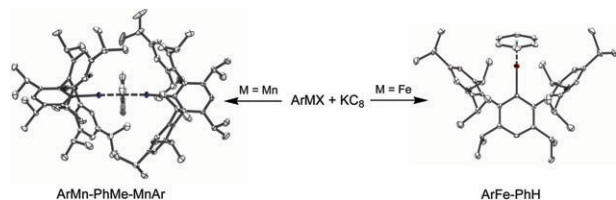
**Sequence dependence of methylation rate enhancement in *meta*-phenyleneethynylene foldamers**

Ronald A. Smaldone and Jeffrey S. Moore\*

The methylation rates of a *meta*-phenyleneethynylene (*m*PE) oligomer with a terminally-attached 4-dimethylaminopyridine (DMAP) residue are reported for a series of linear and branched methyl sulfonates.



1014

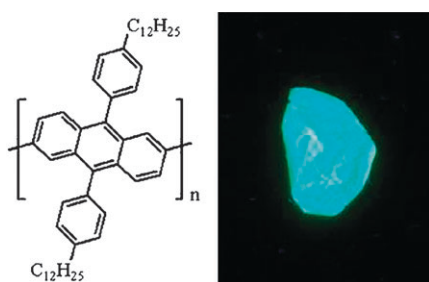


### Univalent transition metal complexes of arenes stabilized by a bulky terphenyl ligand: differences in the stability of Cr(i), Mn(i) or Fe(i) complexes

Chengbao Ni, Bobby D. Ellis, James C. Fettinger, Gary J. Long and Philip P. Power\*

Unlike their Cr(i) counterpart, the arene complexes of the univalent MAr moieties (M = Mn or Fe, Ar = terphenyl) are stable under ambient conditions.

1017

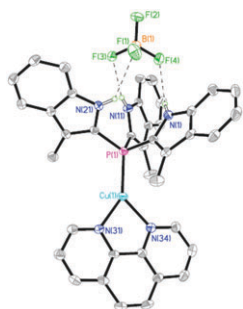


### The first soluble conjugated poly(2,6-anthrylene): synthesis and properties

Weibin Cui, Yubo Wu, Hongkun Tian, Yanhou Geng\* and Fosong Wang

The first soluble conjugated poly(2,6-anthrylene) with 9,10-diphenyl-anthracene as the repeating unit is reported, which represents a novel well-conjugated system.

1020



### Tris-2-(3-methylindolyl)phosphine as an anion receptor

Joanne O. Yu, C. Scott Browning\* and David H. Farrar


The  $C_3$ -symmetric ligand tris-2-(3-methylindolyl)phosphine (**1**) demonstrates the ability to hydrogen bond anions through the NH sites of its indolyl substituents. The ligand binds  $\text{BF}_4^-$  while P-bonded to the metal centre in its  $[\text{Cu}(\text{1})(\text{phen})]\text{BF}_4$  complex.

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