# IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (6) 681-812 (2005)

# In this issue.

More efficient solar cells can be made using a new ionic liquid and iodine in place of the usual organic solvent-based dyes. See Yuji Wada et al., pp. 740-742





#### Cover

Ultimate miniaturization in electronics: A nanowire of gold clusters. See p. 697.

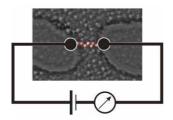
### **FEATURE ARTICLE**

697

#### Gold nanoparticles: assembly and electrical properties in 1–3 dimensions

G. Schmid\* and U. Simon

The defined assembly of gold nanoparticles in different dimensions leads to size-specific electrical properties governed by Coulomb charging effects which may be utilized in nanoelectronic applications.



# **COMMUNICATIONS**

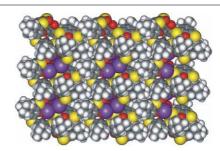
711



# Potassium-thiacalix[8]arene assembly: structure and guest sorption profiles

Yoshihiko Kondo, Ken Endo and Fumio Hamada\*

The thiacalix[8]arene-K complex shows highly-extensive coordination that gives rise to a zeolitic structure, which can adsorb such gaseous organic guests as methanol and benzene.



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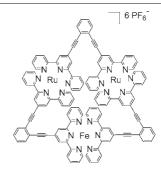
#### COMMUNICATIONS

713

Construction of triangular metallomacrocycles:  $[M_3(1,2-bis(2,2':6',2''-terpyridin-4-yl-ethynyl)benzene)_3]$ [M = Ru(II), Fe(II), 2Ru(II)Fe(II)]

Seok-Ho Hwang, Charles N. Moorefield, Frank R. Fronczek, Olena Lukoyanova, Luis Echegoyen and George R. Newkome\*

Novel bis(terpyridine) building blocks lead to the creation of triangular metallocycles with differing metal centers and unique properties.



716

A porphyrin nanochannel: formation of cationic channels by a protonated saddle-distorted porphyrin and its inclusion behavior

Ryosuke Harada and Takahiko Kojima\*

A highly saddle-distorted dodecaphenylporphyrin dication  $(H_4DPP^{2+})$  was revealed by X-ray crystallography to form positively charged porphyrin nanochannels which were 1 nm in diameter; chloride anion and redox-active hydroquinone could be incorporated in the channels.

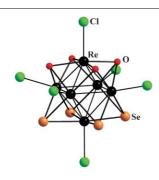


719

Unexpected ligand substitutions in the cluster core {Re<sub>6</sub>Se<sub>8</sub>}: synthesis and structure of the novel cluster compound  $Cs_{11}(H_3O)[Re_6Se_4O_4Cl_6]_3 \cdot 4H_2O$ 

S. S. Yarovoi, Y. V. Mironov, S. F. Solodovnikov, D. Y. Naumov, N. K. Moroz, S. G. Kozlova, A. Simon and V. E. Fedorov\*

The compound Cs<sub>11</sub>(H<sub>3</sub>O)[Re<sub>6</sub>Se<sub>4</sub>O<sub>4</sub>Cl<sub>6</sub>]<sub>3</sub>·4H<sub>2</sub>O containing a novel cluster core  $\{Re_6Se_4O_4\}$  with ordered ligands, where the 4 positions of one face of a Se<sub>4</sub>O<sub>4</sub> cube are occupied exclusively by Se atoms and 4 O atoms lie in the opposite face was synthesized via the interaction of solid Re<sub>6</sub>Se<sub>8</sub>Br<sub>2</sub> with molten KOH.

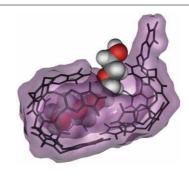


722

Encapsulation of oligoethylene glycols and perfluoro-n-alkanes in a cylindrical host molecule

Byron W. Purse and Julius Rebek, Jr.\*

Oligoethylene glycols and perfluoro-n-alkanes are suitable guests for a cylindrical dimeric molecular capsule. The former must coil to fill the cavity, the latter are bound in their native conformation.



#### **COMMUNICATIONS**

725

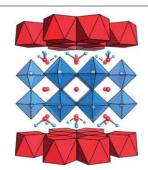


Phosphate anion-selective recognition by boron complex having plural hydrogen bonding sites

Naohiro Kameta and Kazuhisa Hiratani\*

A boron complex having plural proton donors (OH, amide NH) and proton acceptors (quinoline) can act as a selective chromo-ionophore toward phosphate anions among halogen, acetate, hydrogensulfate, and phosphate anions in CH<sub>3</sub>CN.

728

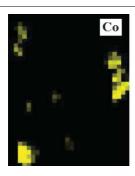


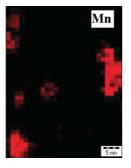
Sr<sub>11</sub>Ge<sub>4</sub>N<sub>6</sub>: a new nitride composed of [GeN<sub>2</sub>Sr<sub>7</sub>]<sup>4+</sup> antiperovskite-type slabs and  $[Sr_4Ge]^{4+}$  layers, separated by sheets of bent  $[Ge^{II}N_2]^{4-}$  ions

Zoltán A. Gál and Simon J. Clarke\*

The layered nitride  $Sr_{11}Ge_4N_6$  contains  $Ge^{4-}$  Zintl anions in both  $[Sr_4Ge]^{4+}$  layers and  $[GeN_2Sr_7]^{4+}$  antiperovskite-type slabs which are separated by sheets of bent  $[Ge^{II}N_2]^{4-}$  ions; the observed range of formal germanium oxidation states in nitrides thus extends between +4 and -4.

731

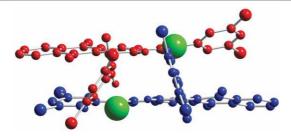




Cobalt on carbon nanofiber catalysts: auspicious system for study of manganese promotion in Fischer–Tropsch

G. Leendert Bezemer, Uwe Falke, A. Jos van Dillen and Krijn P. de Jong\*

STEM-EELS and XPS investigation shows manganese oxide to be closely associated with cobalt nanoparticles supported on carbon nanofibers thereby improving selectivity in Fischer-Tropsch catalysis.



'Twisted' isophthalamide analogues

Simon J. Brooks, Louise S. Evans, Philip A. Gale,\* Michael B. Hursthouse and Mark E. Light

1,3-Dicarboxamidoanthraquinones provide a 'twisted' isophthalamide-like hydrogen-bonding array allowing the formation of a '2 + 2' fluoride containing molecular box.



### A new class of organic donor-acceptor molecules with large third-order optical nonlinearities

Tsuyoshi Michinobu, Joshua C. May, Jin H. Lim, Corinne Boudon, Jean-Paul Gisselbrecht, Paul Seiler, Maurice Gross, Ivan Biaggio\* and François Diederich\*

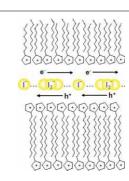
New donor-acceptor molecules with 4-(dimethylamino)phenyl donor and 1,1,4,4-tetracyanobuta-1,3-diene acceptor groups were prepared and their efficient intramolecular chargetransfer interactions and potent third-order nonlinear optical properties investigated.

#### 740

## Ionic liquid crystal as a hole transport layer of dye-sensitized solar cells

Noriyo Yamanaka, Ryuji Kawano, Wataru Kubo, Takayuki Kitamura, Yuji Wada, Masayoshi Watanabe and Shozo Yanagida\*

Use of a new ionic liquid crystal as a hole transport layer of dye-sensitized solar cells leads to a high short circuit photocurrent density, due to a self-assembled structure of the imidazolium cations.

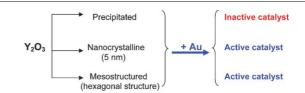


#### 743

# Nanocrystalline and mesostructured Y<sub>2</sub>O<sub>3</sub> as supports for gold catalysts

Javier Guzman and Avelino Corma\*

The structure of yttrium oxide influences the CO oxidation activity of  $Au/Y_2O_3$  catalysts; nanocrystalline  $Y_2O_3$  stabilizes more active species of gold and increases the activity of the gold catalyst in comparison with mesostructured and precipitated  $Y_2O_3$ .



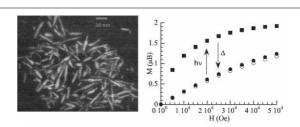
#### 746



#### Photomagnetic nanorods of the Mo(CN)<sub>8</sub>Cu<sub>2</sub> coordination network

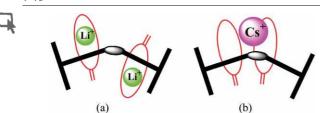
Laure Catala,\* Corine Mathonière, Alexandre Gloter, Odile Stephan, Thierry Gacoin, Jean-Pierre Boilot and Talal Mallah\*

Nanorods of the photomagnetic coordination network Mo(CN)<sub>8</sub>Cu<sub>2</sub> coated with polyvinylpyrrolidone were prepared and exhibit an enhanced effect upon irradiation when compared to the bulk.



#### **COMMUNICATIONS**

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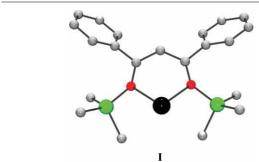


# [3]Rotaxane synthesized via covalent bond formation can recognize cations forming a sandwich structure

Yoshinobu Nagawa,\* Jun-ichi Suga, Kazuhisa Hiratani,\* Emiko Koyama and Masatoshi Kanesato

A [3]rotaxane which was successfully synthesized via covalent bond formation makes a 1:1 complex with caesium ion, forming a sandwich-type structure.

752

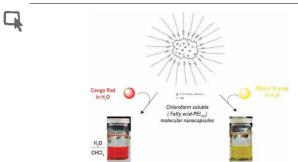


# Synthesis and characterisation of two monomeric crystalline thallium(I) β-diketiminates

Yanxiang Cheng, Peter B. Hitchcock, Michael F. Lappert\* and Meisu Zhou

The first structurally characterised thallium(I) β-diketiminates are the monomeric crystalline complexes TlL (1) and TlL' (2) [L = {N(SiMe<sub>3</sub>)C(Ph)}<sub>2</sub>CH, L' =  $\{N(C_6H_3Pr^i_2-2,6)C(H)\}_2CPh\}$ .

755

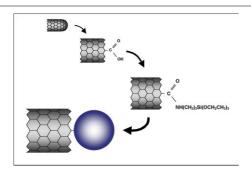


# Synergistic assembly of hyperbranched polyethylenimine and fatty acids leading to unusual supramolecular nanocapsules

Yu Chen, Zhong Shen, Holger Frey, Julia Pérez-Prieto and Salah-Eddine Stiriba\*

The self-assembly of hyperbranched polyethylenimine (PEI) and fatty acids leads to unusual supramolecular inverted micellar structures that are able to irreversibly transfer watersoluble guest molecules into organic solvents on a large scale.

758



# Covalent decoration of multi-walled carbon nanotubes with silica nanoparticles

Massimo Bottini, Lutz Tautz, Huong Huynh, Edvard Monosov, Nunzio Bottini, Marcia I. Dawson, Stefano Bellucci and Tomas Mustelin\*

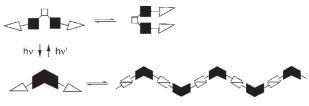
A novel tunable approach for the synthesis of carbon nanotube-silica nanobead composites is described. Silica nanobeads were synthesized directly onto carbon nanotubes to form a novel and useful material.

#### ¬ DI

## Photoreversible supramolecular polymer formation

Michinori Takeshita,\* Miyuki Hayashi, Souichi Kadota, Kamrul Hossain Mohammed and Takehiko Yamato

Particle sizes of a supramolecular polymer composed of a diarylethene having two quadruple hydrogen bonding moieties were changed photoreversibly.



supramolecular polymer

delocalised N<sup>1/2+</sup>••N<sup>1/2+</sup>

localised

N+••N

50

#### 764

## A mixed-valence bis(diarylamino)stilbene: crystal structure and comparison of electronic coupling with biphenyl and tolane analogues

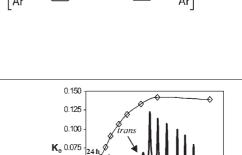
Stephen Barlow,\* Chad Risko, Veaceslav Coropceanu, Neil M. Tucker, Simon C. Jones, Zerubba Levi, Viktor N. Khrustalev, Mikhail Yu. Antipin, Tiffany L. Kinnibrugh, Tatiana Timofeeva, Seth R. Marder and Jean-Luc Brédas

The first vinylene-bridged bis(triarylamine) mixed-valence species has been characterised by crystallography and spectroscopy (EPR, vibrational and electronic); it is a class-III symmetric species, in contrast to its class-II ethynylene-bridged analogue.

# Photoinduced isomerisation of *cis*-[M(L-S,O)<sub>2</sub>] (M = Pt<sup>II</sup> and Pd<sup>II</sup>) complexes of N,N-diethyl-N'-3,4,5-trimethoxybenzoyl-thiourea: key to preparation of the *trans* isomer

Dirk Hanekom, Jean M. McKenzie, Nocky M. Derix and Klaus R. Koch\*

In CH<sub>3</sub>CN solutions at room temperature, cis-[M(L-S,O)<sub>2</sub>] (M = Pt<sup>II</sup> and Pd<sup>II</sup>) complexes of N,N-diethyl-N'-3,4,5-trimethoxybenzoylthiourea undergo reversible photoinduced isomerisation to the trans isomer upon irradiation with visible light. In the dark trans-[M(L-S,O)<sub>2</sub>] cleanly reverts back to the cis complex at a rate dependent on the solution temperature, indicating a thermally controlled reverse process.



10 20

0.050

0.025

0.000

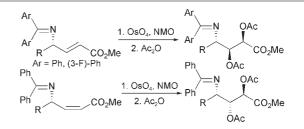
0

 $Ar = p-MeOC_6H_4$ 

# Stereoselective dihydroxylation reactions of $\gamma$ -amino- $\alpha,\beta$ -unsaturated esters via their aryl ketimine derivatives

Joon Seok Oh, Jongho Jeon, Do Yeon Park and Young Gyu Kim\*

Dihydroxylation reactions of the ketimine derivatives of (*E*)- $\gamma$ -amino- $\alpha$ , $\beta$ -unsaturated esters gave *anti* selectivity from 6.7:1 to 19:1. Opposite *syn* selectivity was observed with the (*Z*)-esters (5.4:1 to >100:1).



30 40

exposure time/h

4

Design and synthesis of a new class of arginine analogues with an improved anion binding site in the side chain

Carsten Schmuck\* and Lars Geiger

Four new arginine analogues 2a–d with an improved anion binding site in the side chain are synthesized. Their Fmoc derivatives can be applied in standard solid phase peptide synthesis (SPPS) to probe the role of arginine in biologically active peptides.

775

First catalytic allyltitanation reactions

Laurianne Bareille, Pierre Le Gendre\* and Claude Moïse\*

Catalytic allyltitanation reactions were accomplished from dienes and aldehydes with only 5% of titanocene complexes at the expense of employing stoichiometric amounts of PMHS.

//8



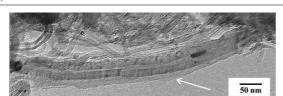
Generation and aromaticity of 2-silaimidazolium ion, a new  $\pi$ -conjugated silylium ion

Shintaro Ishida, Tohru Nishinaga, Robert West and Koichi Komatsu\*

The first 2-silaimidazolium ion having a planar five-membered ring was generated in solution and was shown to possess the  $6\pi$ -electron Hückel aromaticity.

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Supported coordination polymerization: a unique way to potent polyolefin carbon nanotube nanocomposites

Daniel Bonduel, Michaël Mainil, Michaël Alexandre, Fabien Monteverde and Philippe Dubois\*

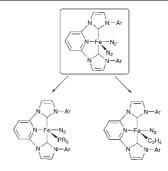
Homogeneous surface coating of long carbon nanotubes is achieved by *in situ* polymerization of ethylene as catalyzed directly from the nanotube surface-treated by a metallocene-based complex. The *in situ* grown polyolefinic chains embedding the carbon nanotubes allow for the break-up of the native nanotube bundles. TEM displays a typical multi-walled carbon nanotube surface-coated by *ca.* 70 wt% polyethylene (see white arrow).



## Molecular N<sub>2</sub> complexes of iron stabilised by N-heterocyclic 'pincer' dicarbene ligands

Andreas A. Danopoulos,\* Joseph A. Wright and William B. Motherwell

The first dinitrogen complexes stabilised by N-heterocyclic carbenes are reported. They show unusual structures and undergo interesting substitution reactions.

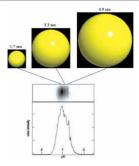


787

# Size-selective separation of gold nanoparticles using isoelectric focusing electrophoresis (IEF)

Isabelle Arnaud, Jean-Pierre Abid, Christophe Roussel and Hubert H. Girault\*

A size-selective separation of gold nanoparticles derivatised with mercaptosuccinic acid using an isoelectric focusing electrophoresis technique is used for improving the monodispersity of colloidal samples.



789

# The facile and efficient Michael addition of indoles and pyrrole to α,β-unsaturated electron-deficient compounds catalyzed by aluminium dodecyl sulfate trihydrate [Al(DS)<sub>3</sub>]·3H<sub>2</sub>O in water

Habib Firouzabadi,\* Nasser Iranpoor\* and Farhad Nowrouzi

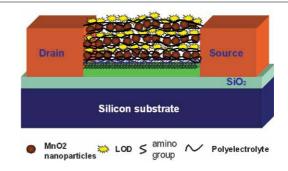
Aluminium dodecyl sulfate trihydrate [Al(DS)<sub>3</sub>]·3H<sub>2</sub>O is a new effective non-corrosive Lewis acid surfactant combined catalyst for the efficient Michael addition of indoles and pyrrole to structurally diverse electron-deficient olefins at room temperature in aqueous media. Pyrrole as an acid sensitive compound undergoes Michael addition in high yields without any polymerization reactions occurring.

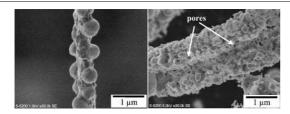


# A sensitive biosensor for lactate based on layer-by-layer assembling MnO<sub>2</sub> nanoparticles and lactate oxidase on ion-sensitive field-effect transistors

Jing-Juan Xu,\* Wei Zhao, Xi-Liang Luo and Hong-Yuan Chen

A sensitive enzyme-based FET biosensor for lactate has been obtained by introducing MnO<sub>2</sub> nanoparticles at the gate surface with a layer-by-layer assembling method. The sensitivity of the ENFET with MnO<sub>2</sub> nanoparticles is 50 times higher than that without MnO<sub>2</sub> nanoparticles.



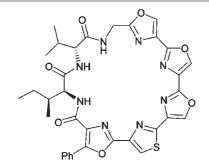


# Porous and nonporous Ag nanostructures fabricated using cellulose fiber as a template

Junhui He, Toyoki Kunitake\* and Takeshi Watanabe

Porous and nonporous Ag nanostructures were fabricated with ease by using cellulose fiber as a template.

797

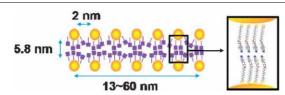


# Synthesis and establishment of stereochemistry of the unusual polyoxazole-thiazole based cyclopeptide YM-216391 isolated from *Streptomyces nobilis*

Jon Deeley and Gerald Pattenden\*

A concise total synthesis of the unusual oxazole-based cyclopeptide structure YM-216391, which also establishes the stereochemistry of the natural product, is described.

800

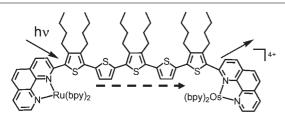


# Spontaneous one dimensional arrangement of spherical Au nanoparticles with liquid crystal ligands

Insik In, Young-Wook Jun, Yun Jun Kim and Sang Youl Kim\*

Spontaneous 1D arrangements of spherical Au nanoparticles were accomplished by using a liquid crystalline thiol ligand, 4'-(12-mercaptododecyloxy)biphenyl-4-carbonitrile. Simple thermal treatment of Au nanoparticles with the ligands showed 1D ordering of the Au nanoparticles.

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# Exciton-like energy collection in an oligothiophene wire end-capped by Ru- and Os-polypyridine chromophores

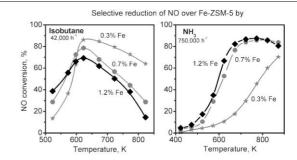
Raymond Ziessel,\* Peter Bäuerle, Martin Ammann, Andrea Barbieri and Francesco Barigelletti\*

Ru(II)- and Os(II)-polypyridine *termini* are linked by a quinquethiophene bridge wherein a conductive level conveys excitation energy into the luminescent Os-based unit.

# Active sites for NO reduction over Fe-ZSM-5 catalysts

M. Schwidder, M. Santhosh Kumar, A. Brückner and W. Grünert\*

A series of Fe-ZSM-5 catalysts with varying distribution of mononuclear, oligomeric and particulate Fe oxide species has been prepared and characterised, which allows derivation of definite conclusions on the role of these sites in the selective catalytic reduction of NO.



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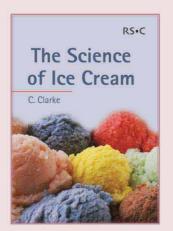


Chemiluminescence in molecular recognition: base-induced decomposition of optically active dioxetanes bearing a bisnaphthol moiety with a complex of optically active crown ether—potassium *tert*-butoxide

Masakatsu Matsumoto,\* Koji Hamaoka, Yuji Takashima, Mizuki Yokokawa, Kazutaka Yamada, Nobuko Watanabe and Hisako K. Ijuin

Optically active dioxetane-based chemiluminescent substrates were triggered in an optically anisotropic microenvironment to give light, the color of which was varied with the configuration of the substrates.

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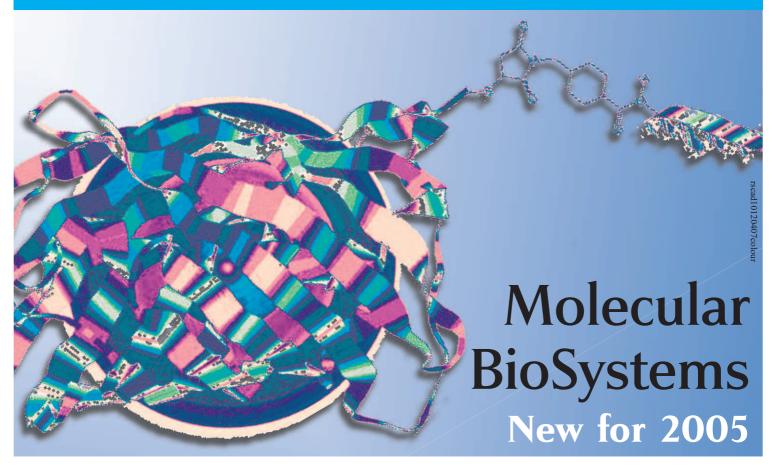
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