#### IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (30) 3745-3876 (2005)



#### Cover

See Philip A. Gale, Mark E. Light, Beth McNally, Korakot Navakhun, Kate E. Sliwinski and Bradley D. Smith, page 3773. The cover image depicts a lipid bilayer rendered permeable to chloride by a synthetic prodigiosin mimic. The authors would like to thank Christopher J. Woods for this excellent cover illustration. Image reproduced by permission of Philip A. Gale et al., from Chem. Commun., 2005, 3773.



# Inside cover

See Radiy R. Islangulov, Denis V. Kozlov and Felix N. Castellano, page 3776. Efficient green-to-blue photon upconversion is realized from selective excitation of a Ru(II) chromophore in the presence of anthracene or diphenylanthracene. Image reproduced by permission of Felix N. Castellano et al., from Chem. Commun., 2005, 3776.

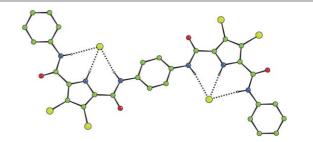
#### FEATURE ARTICLE

#### 3761

#### Amidopyrroles: from anion receptors to membrane transport agents

Philip A. Gale\*

Amidopyrroles have been employed in a variety of anion receptors and sensors and in membrane transport agents for HCl.



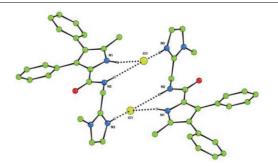
#### COMMUNICATIONS

#### 3773

#### Co-transport of $H^+/Cl^-$ by a synthetic prodigiosin mimic

Philip A. Gale,\* Mark E. Light, Beth McNally, Korakot Navakhun, Kate E. Sliwinski and Bradley D. Smith\*

An amidopyrrole with appended imidazole group can bind and co-transport H<sup>+</sup>/Cl<sup>-</sup> across vesicle membranes much more effectively than an analogue with an appended pyridyl group.



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#### 3776

#### Low power upconversion using MLCT sensitizers

Radiy R. Islangulov, Denis V. Kozlov and Felix N. Castellano\*

Selective low energy excitation of the metal-to-ligand charge transfer (MLCT) transition in  $[Ru(dmb)_3]^{2+}$  (dmb = 4,4'-dimethyl-2,2'-bipyridine) in the presence of anthracene or 9,10-diphenylanthracene yields easily visualized green-to-blue upconverted singlet fluorescence resulting from triplet-triplet annihilation at low excitation power.

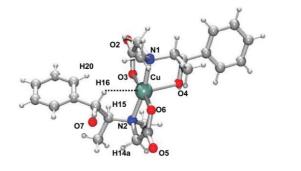
#### 3779

# On the CH…Cu agostic interaction: chiral copper(II) compounds with ephedrine and pseudoephedrine derivatives

Miguel Castro,\* Julián Cruz, Horacio López-Sandoval and Norah Barba-Behrens\*

The structure of  $[Cu(Hceph)_2]$  has a  $Cu(II) \cdots H$  agostic bond. This bond was characterized by the atoms in molecules formalism.





N N

Zr

σ= 15400

A

Zn

Zn

 $\sigma = 10600$ 

N N

N N

#### 3782

# Enlarged $\pi$ -electronic network of a *meso-meso*, $\beta$ - $\beta$ , $\beta$ - $\beta$ triply linked dibenzoporphyrin dimer that exhibits a large two-photon absorption cross section

Yasuhide Inokuma, Noboru Ono, Hidemitsu Uno, Deok Yun Kim, Soo Bum Noh, Dongho Kim\* and Atsuhiro Osuka\*

A *meso-meso*,  $\beta$ - $\beta$ ,  $\beta$ - $\beta$  triply linked dibenzoporphyrin dimer that exhibits a large two-photon absorption (TPA) cross section was prepared in two different ways.

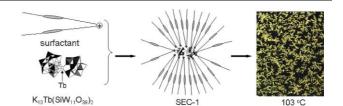
#### 3785

#### A surfactant-encapsulated polyoxometalate complex towards a thermotropic liquid crystal

Wen Li, Weifeng Bu, Haolong Li, Lixin Wu\* and Min Li

A novel surfactant-encapsulated terbium-substituted heteropolyoxotungstate complex

 $[L1]_{13}[Tb(SiW_{11}O_{39})_2] \cdot 30H_2O$  (SEC-1) bearing mesomorphous groups was successfully prepared by the ionic self-assembling route, exhibiting characteristic thermotropic liquid-crystalline behavior.

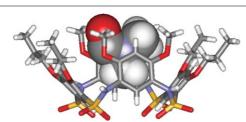


TPA σ-value increase

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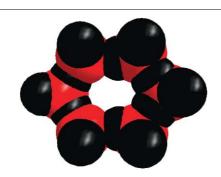


## Macrocyclic aromatic tetrasulfonamides with a stable cone conformation

Lan He,\* Yu An, Lihua Yuan, Kazuhiro Yamato, Wen Feng, Oksana Gerlitz, Chong Zheng and Bing Gong\*

Aromatic tetrasulfonamide macrocycles carrying alkoxy side chains adopt a stable cone conformation in both the solid state and solution.

3793



Drug

230 nm

# A previously unrecognised hydronium di-cation in the crystal structure of a cucurbituril derivative

Ivan Bernal,\* Uday Mukhopadhyay, Alexander V. Virovets, Vladimir P. Fedin and William Clegg

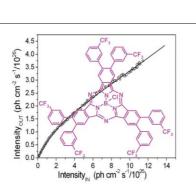
The novel di-hydronium di-cation  $(H_{14}O_6)^{2+}$ , or  $[(H_3O)_2(H_2O)_4]^{2+}$ , is found in the crystal structure of a complex containing the cavitand cucurbit[6]uril; the formation of the cation cluster, with its almost planar  $O_6H_6$  ring, is templated by hydrogen bonding to the  $O_6$  portal of the cavitand.

# High-density doxorubicin-conjugated polymeric nanoparticles *via* ring-opening metathesis polymerization

Paul A. Bertin, DeeDee Smith and SonBinh T. Nguyen\*

High-density doxorubicin-conjugated polymeric nanoparticles are prepared *via* ring-opening metathesis polymerization and sustained release of nearly 50% of the anticancer agent is observed after 24 h in mildly acidic aqueous solution.





### Nonlinear optical effects related to saturable and reverse saturable absorption by subphthalocyanines at 532 nm

Danilo Dini,\* Sergej Vagin, Michael Hanack, Vincenzo Amendola and Moreno Meneghetti

It is found that both effects of saturable absorption and reverse saturable absorption are obtained with a solution of subphthalocyanine 2 at 532 nm depending on the intensity of 9 ns laser pulses.

#### 3799

# Synthetic gecko foot-hairs from multiwalled carbon nanotubes

Betul Yurdumakan, Nachiket R. Raravikar, Pulickel M. Ajayan and Ali Dhinojwala\*

We report a fabrication process for constructing polymer surfaces with multiwalled carbon nanotube hairs, with strong nanometer-level adhesion forces that are 200 times higher than those observed for gecko foot-hairs. This process can be adapted to create structures that are found in nature on the gecko's foot and offer excellent potential for applications as dry adhesives for space, microelectronics and MEMS devices.

#### 3802

3805

#### Highly enantioselective organocatalysis of the Hajos–Parrish–Eder–Sauer–Wiechert reaction by the β-amino acid cispentacin

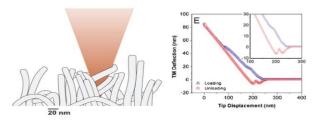
Stephen G. Davies,\* Ruth L. Sheppard, Andrew D. Smith\* and James E. Thomson

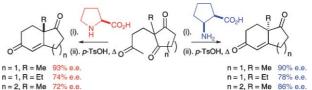
The  $\beta$ -amino acid cispentacin promotes the Hajos–Parrish– Eder–Sauer–Wiechert reaction with levels of enantioselectivity comparable to or higher than proline.

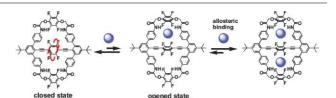
Allosteric binding of anionic guests to a bicyclic host

Osamu Hirata, Masayuki Takeuchi\* and Seiji Shinkai\* A bicyclic host which has a diethynyl tetrafluorophenyl axis and is expected to behave as an anion-binding 'turnstile' has

which imitates the action of a 'turnstile'







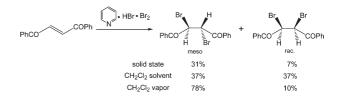
#### 3808

been designed.

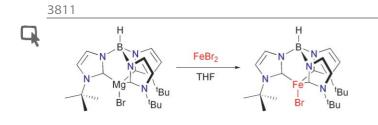
The important role of solvent vapor in an organic solid state reaction

Seiken Nakamatsu, Shinji Toyota, William Jones and Fumio Toda\*

Some organic reactions in the solid state proceeded very efficiently and selectively in the presence of a small amount of solvent vapor.





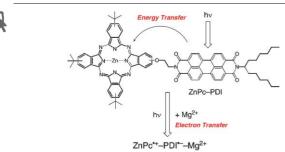


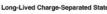
# A new synthetic route to bulky "second generation" tris(imidazol-2-ylidene)borate ligands: synthesis of a four coordinate iron(II) complex

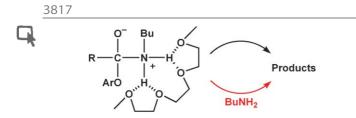
Ismael Nieto, Francisco Cervantes-Lee and Jeremy M. Smith\*

A new synthetic route provides access to coordinatively unsaturated metal complexes of bulky tris(carbene)borate ligands.

#### 3814







#### Formation of a long-lived charge-separated state of a zinc phthalocyanine-perylenediimide dyad by complexation with magnesium ion

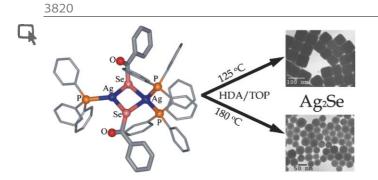
Shunichi Fukuzumi,\* Kei Ohkubo, Javier Ortiz, Ana M. Gutiérrez, Fernando Fernández-Lázaro\* and Ángela Sastre-Santos\*

Photoexcitation of a zinc phthalocyanine–perylenediimide (ZnPc–PDI) dyad affords the triplet excited state, whereas addition of  $Mg^{2+}$  to the photoexcited ZnPc–PDI results in formation of a long-lived charge-separated state.

## Novel catalytic effects in ester aminolysis in chlorobenzene

Nuno Basilio, Luís García-Río,\* J. Ramón Leis, Juan C. Mejuto and Moisés Pérez-Lorenzo

A new pathway should be included in the reaction scheme for ester aminolysis catalyzed by glymes.



# Shape and size control of Ag<sub>2</sub>Se nanocrystals from a single precursor [(Ph<sub>3</sub>P)<sub>3</sub>Ag<sub>2</sub>(SeC{O}Ph)<sub>2</sub>]

Meng Tack Ng, Chris Boothroyd and Jagadese J. Vittal\*

Monodispersed Ag<sub>2</sub>Se nanocubes and faceted crystals have been synthesized by using one-pot hexadecylamine (HDA)-controlled decomposition of [(PPh<sub>3</sub>)<sub>3</sub>Ag<sub>2</sub>(SeC{O}Ph)<sub>2</sub>]. The morphology of the nanocrystals induces self-assembly of these nanoparticles, which is a property required for photonic studies.

#### 3823

#### Axial bis(terpyridoxy)phosphorus(V) porphyrin: Modulation of PET and EET by $Zn^{2+}$ or $Cd^{2+}$ ions

P. Prashanth Kumar,\* G. Premaladha and Bhaskar G. Maiya

Axial bis(terpyridoxy)phosphorus(V) porphyrin was prepared and its photophysical properties were investigated. Excitation at 566 nm, with addition of  $Zn^{2+}/Cd^{2+}$ , inhibited PET from terpyridine to excited porphyrin, whereas at 300 nm EET dominated over PET from excited terpyridine to the porphyrin.

#### 3826

# Structure and reactivity of a new anionic *N*-heterocyclic carbene silver(I) complex

Claude Y. Legault, Christopher Kendall and André B. Charette\*

The efficient synthesis of a *N*-benzoyliminoimidazolium ylide provides access to a new type of *N*-heterocyclic anionic carbene, from which air stable Ag(I) and Cu(II) complexes and a catalytically active Rh(I) complex were formed.



# Photocatalytic overall water splitting under visible light by TaON and WO<sub>3</sub> with an $IO_3^-/I^-$ shuttle redox mediator

Ryu Abe,\* Tsuyoshi Takata, Hideki Sugihara and Kazunari Domen

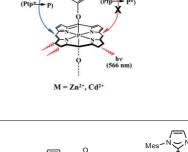
The oxynitride TaON was applied for the first time to the two-step overall splitting of water under visible light through combination with WO<sub>3</sub> using an  $IO_3^-/I^-$  shuttle redox mediator.

#### 3832

# Catalytic phosphorylation using a bifunctional imidazole derived nucleophilic catalyst

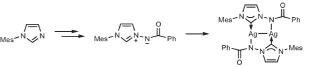
#### Simon Jones,\* Julian Northen and Alan Rolfe

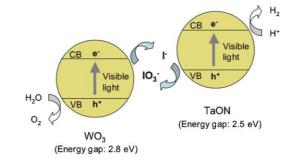
Polyether/imidazole hybrid catalysts have been prepared and shown to function as bifunctional catalysts in the presence of group 1 and 2 cations for the phosphorylation of alcohols using phosphoryl chlorides.

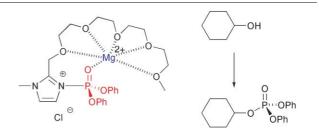


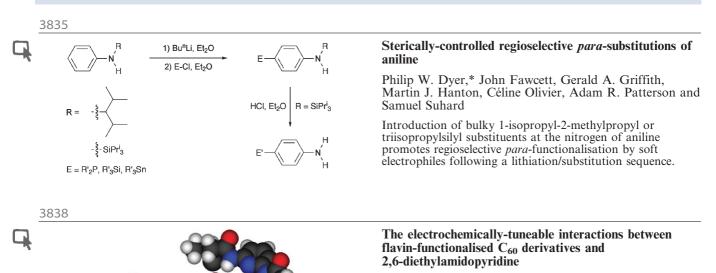
hv(300

EET









Joseph B. Carroll, Graeme Cooke,\* James F. Garety, Brian J. Jordan, Suhil Mabruk and Vincent M. Rotello

We report the electrochemically-tuneable interactions between flavin-functionalised  $C_{60}$  derivatives and a diamidopyridine derivative.

## Single-crystalline Sb-doped $SnO_2$ nanowires: synthesis and gas sensor application

Q. Wan\* and T. H. Wang

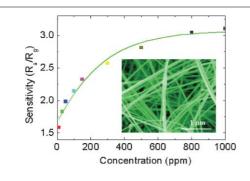
The synthesis of semiconducting transparent Sb-doped  $\text{SnO}_2$ nanowires in mass production by an *in situ* doping approach is reported, and the ethanol sensing results demonstrated that Sb-doped  $\text{SnO}_2$  nanowires have a promising application for the fabrication of gas sensors with low resistance, and quick response and recovery times.

#### A preliminary observation of additive thermodynamic contribution of pendant arms to the complexation of calixarene derivatives with mercury(II)

Angela F. Danil de Namor,\* Samir Chahine, Eduardo E. Castellano, Oscar E. Piro and H. Donald Brooke Jenkins

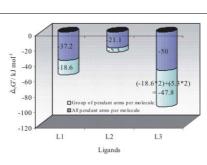
The first demonstration of an additive thermodynamic contribution of pendant arms in calixarene–mercury(II) complexation.





3844

Ч



#### 3847

#### Fabrication of polyimide nanotubes and carbon nanotubes containing magnetic iron oxide in confinement

#### Jyongsik Jang,\* Kyung Jin Lee and Younggeun Kim

Polyimide nanotubes and their carbonized product with tunable wall thickness were fabricated by a precursor impregnation method and subsequent carbonization process using an AAO template. Magnetic properties could also be introduced into carbon nanotubes by carbonizing the Fe-embedded polyimide nanotube precursor.

#### 3850

#### A microporous scandium terephthalate, $Sc_2(O_2CC_6H_4CO_2)_3$ , with high thermal stability

S. R. Miller, P. A. Wright,\* C. Serre, T. Loiseau, J. Marrot and G. Férey

The first porous scandium carboxylate,  $Sc_2(O_2CC_6H_4CO_2)_3$ , has a framework of isolated ScO<sub>6</sub> octahedra and fully connected terephthalate ligands that has high thermal stability and a pore volume of  $0.26 \text{ cm}^3 \text{ g}^-$ 

#### 3853

2,2-Dimethyl cyclopentanones by acid catalyzed ring expansion of isopropenylcyclobutanols. A short synthesis of  $(\pm)$ - $\alpha$ -cuparenone and  $(\pm)$ -herbertene

Angela M. Bernard, Angelo Frongia, Francesco Secci and Pier P. Piras\*

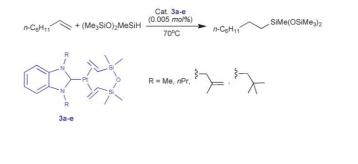
New access to 2,2-dimethyl cyclopentanones by acid catalyzed ring expansion of isopropenylcyclobutanols. The method allows a straightforward synthesis of  $(\pm)$ - $\alpha$ -cuparenone and  $(\pm)$ -herbertene.

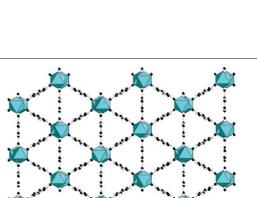
#### 3856

#### Second generation N-heterocyclic carbene–Pt(0) complexes as efficient catalysts for the hydrosilylation of alkenes

Olivier Buisine, Guillaume Berthon-Gelloz, Jean-François Brière, Sébastien Stérin, Gérard Mignani, Paul Branlard, Bernard Tinant, Jean-Paul Declercq and István E. Markó\*

A new class of benzimidazolylidene carbene-Pt(0) complexes was developed and used to efficiently catalyse the hydrosilylation of alkenes.



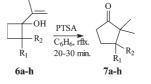


Carbonization

50 nm

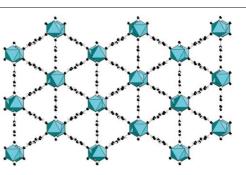
(b)

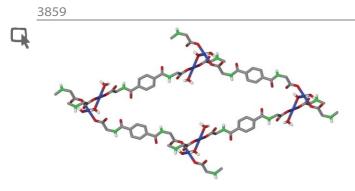
50 nm



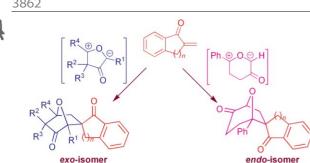
(a)

 $\mathbf{R}_1 = Me, H$  $\mathbf{R}_2 = -(CH_2)_2C_6H_5$ ,  $-CH(CH_3)CH_2SC_6H_5$ , -C<sub>6</sub>H<sub>4</sub>-*p*-Me,-C<sub>6</sub>H<sub>4</sub>-*m*-Me, -CH<sub>2</sub>O-C<sub>6</sub>H<sub>4</sub>-p-OMe, -CH2O-C6H4-m-OMe

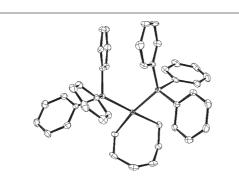




3862



3865



Interpenetrated networks from a novel nanometer-sized pseudopeptidic ligand, bridging water, and transition metal ions with cds topology

George E. Kostakis, Luigi Casella, Nick Hadjiliadis,\* Enrico Monzani, Nikolaos Kourkoumelis and John C. Plakatouras\*

A new approach has been initiated combining coordination chemistry and biomimetic ligands to synthesize metal organic polymers.  $TBG^{2-}$  coordinates to metal ions to form 3D polymers with cds structures and reversible loss of water molecules.

#### Highly regio-, chemo- and diastereoselective synthesis of oxa-bridged spirocycles: A novel observation of reverse selectivity

Sengodagounder Muthusamy,\* Janagiraman Krishnamurthi and Munirathnam Nethaji

The reverse regio- and diastereoselectivities are observed between the reactions involving 5- and 6-membered-ring cyclic carbonyl ylide dipoles with  $\alpha$ -methylene ketones. A mild catalytic route to synthesize spirocyclic systems with high regio-, chemo- and diastereoselectivities is described.

#### A new route to metallacycloalkanes

Katja Dralle, Nastassia L. Jaffa, Tanya le Roex, John R. Moss,\* Susan Travis, Nicholas D. Watermeyer and Akella Sivaramakrishna

The platinacycloheptane  $Pt(PPh_3)_2(CH_2)_6$  has been obtained in high yield from the hydrogenation of the platinacycloheptene  $Pt(PPh_3)_2(CH_2CH_2CH=CHCH_2CH_2).$ 

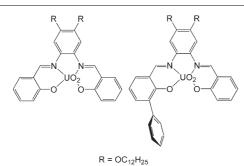
#### Exclusive transition state stabilization in the supramolecular catalysis of Diels-Alder reaction by a uranyl salophen complex

Antonella Dalla Cort, Luigi Mandolini\* and Luca Schiaffino

Whereas the parent uranyl salophen is catalytically inactive, its phenyl derivative effectively catalyses with turnover the reaction of benzoquinone with 1,3-cyclohexadiene, while showing no appreciable affinity toward reactants and product.



G



3870

Non-steady-state living polymerization: a new route to control cationic ring-opening polymerization (CROP) of oxetane *via* an activation chain end (ACE) mechanism at ambient temperature

Hassen Bouchékif,\* Marcia I. Philbin, Eamon Colclough and Allan J. Amass\*

Well-defined polyoxetane with low polydispersivity has been synthesized *via* a novel living polymerisation process using 3-phenoxypropyl 1,4-dioxanium hexafluoroantimonate (3-PPD) as a model of a living "monomeric polyoxetane" initiator, in 1,4-dioxane at 35 °C.

#### ADDITION AND CORRECTION

#### 3873

Non-steady-state living polymerization: a new route to control cationic ring-opening polymerization (CROP) of oxetane *via* an activation chain end (ACE) mechanism at ambient temperature

Hassen Bouchékif, Marcia I. Philbin, Eamon Colclough and Allan J. Amass

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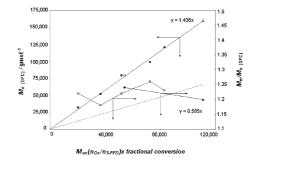
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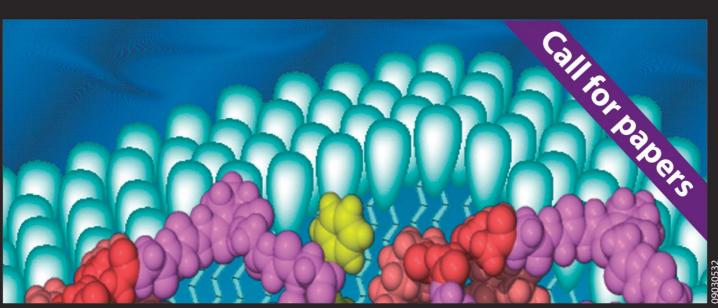
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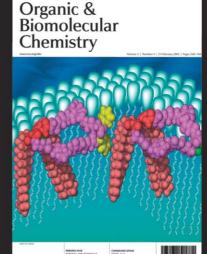


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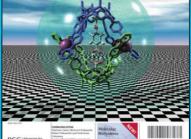
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