

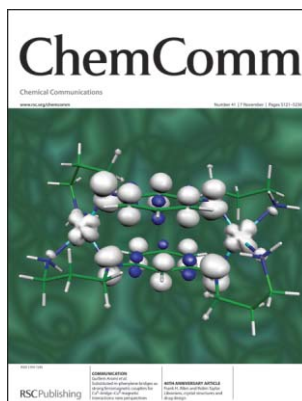
IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (41) 5121-5236 (2005)



Cover

See Takanori Suzuki *et al.*, page 5154. The macrocyclic hosts twist upon complexation only with a guest of the "right" handedness. Image reproduced by permission of Ryo Katoono, Hidetoshi Kawai, Kenshu Fujiwara and Takanori Suzuki from *Chem. Commun.*, 2005, 5154.



Inside cover

See Guillem Aromí *et al.*, page 5172. Spin density map of a model dinuclear Cu(II) complex predicted from DFT calculations to display very strong ferromagnetic coupling. Image reproduced by permission of Alok Ranjan Paital, Tamoghna Mitra, Debashis Ray, Wing Tak Wong, Jordi Ribas-Ariño, Juan J. Novoa, Joan Ribas and Guillem Aromí from *Chem. Commun.*, 2005, 5172.

CHEMICAL SCIENCE

C81

In this issue...

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

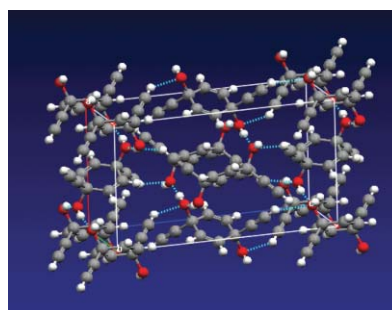
40TH ANNIVERSARY ARTICLE

5135

Librarians, crystal structures and drug design

Frank H. Allen and Robin Taylor

Crystal structure data are fundamental to our understanding of chemical structure, and make important contributions to rational drug design. However, high-quality scientific research based on these data requires high-quality crystal-structure databases, and these cannot be assembled without the expenditure of time, effort and money.



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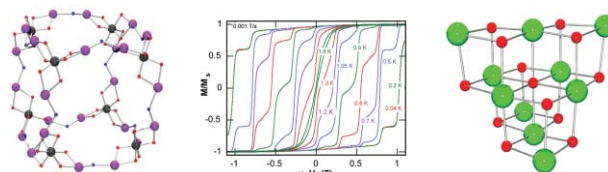
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Using tripodal alcohols to build high-spin molecules and single-molecule magnets

Euan K. Brechin*

The combination of tripodal alcohols with paramagnetic 3d transition metal ions leads to the isolation of a host of new clusters, high spin molecules and single-molecule magnets ranging in nuclearity from two to thirty-two.



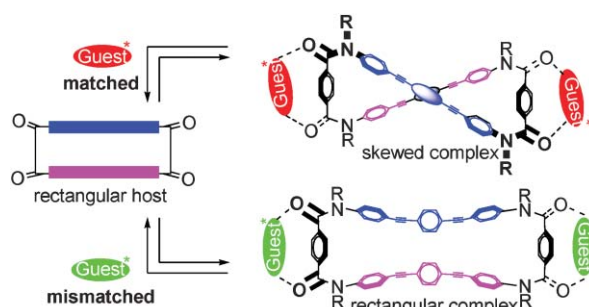
COMMUNICATIONS

5154

Stereospecific change in conformation upon complexation of an exoditopic tetraamide host with a bis(ammonium) guest: chiral recognition and strong CD signaling

Ryo Katoono, Hidetoshi Kawai, Kenshu Fujiwara and Takanori Suzuki*

The chiral macrocyclic host undergoes “stereospecific chiroptical modulation”, and the diastereomeric complexes exhibit quite different CD spectra since only the matched enantiomer of the guest induces the geometrical change of the host.

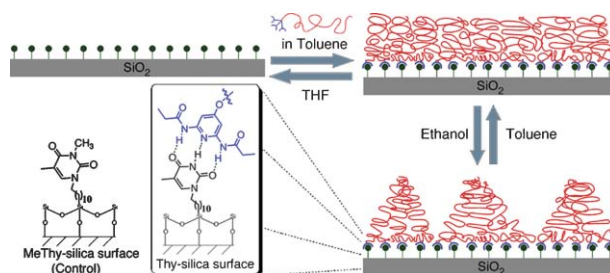


5157

Stimuli responsive surfaces through recognition-mediated polymer modification

Hao Xu, Tyler B. Norsten, Oktay Uzun, Eunhee Jeoung and Vincent M. Rotello*

Readily renewable stimuli-responsive surfaces were fabricated *via* recognition-mediated polymer modification using “brush-like” multi-recognition-unit terminated polystyrene.

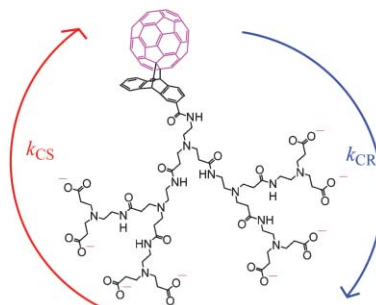


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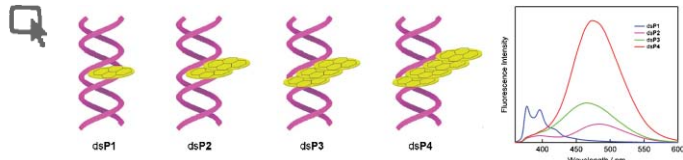
Photoinduced charge separation and charge recombination of fullerene bearing dendritic poly(amidoamine) with carboxylates at the terminal in aqueous media

Atula S. D. Sandanayaka, Huimin Zhang, Yutaka Takaguchi, Yuuki Sako, Mitsuhiro Tamura, Yasuyuki Araki and Osamu Ito

Photoinduced charge separation and charge recombination of fullerenes bearing dendritic poly(amidoamine)s with carboxylates at the terminal site in aqueous media.



5163

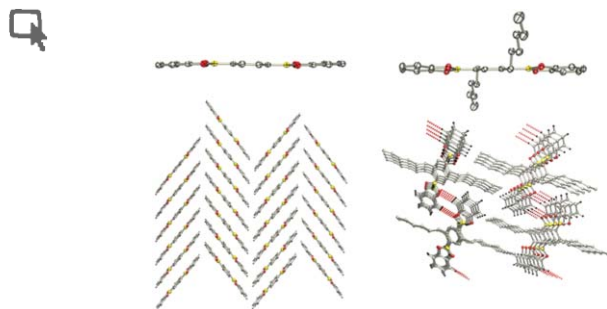


Helical pyrene-array along the outside of duplex RNA

Mitsunobu Nakamura,* Yukinori Ohtoshi and Kazushige Yamana*

A helical pyrene-array was formed by incorporation of multiple pyrenes into the sugar residues of duplex RNA leading to strong excimer fluorescence.

5166

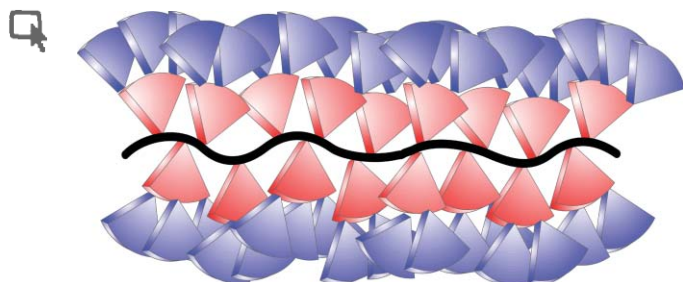


Substituent effects on the structure and supramolecular assembly of bis(dioxaborole)s

Weijun Niu, Brett Rambo, Mark D. Smith and John J. Lavigne*

Substitution on the central phenyl ring of bis(dioxaborole)s does not alter the conjugation through the borole but does significantly alter the supramolecular assembly of these materials.

5169

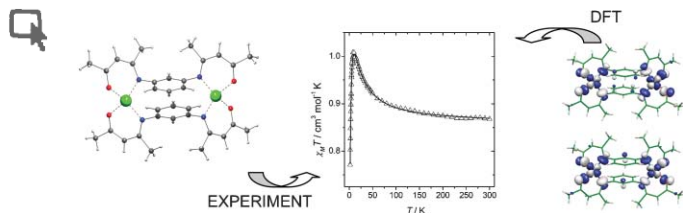


Doubly-dendronized linear polymers

Justin L. Mynar, Tae-Lim Choi, Masaru Yoshida, Victor Kim, Craig J. Hawker and Jean M. J. Fréchet*

Doubly-dendronized polymers were synthesized by grafting polybenzyl ether dendrons onto a poly(hydroxy) styrene polymer with polyaliphatic esters.

5172



Substituted *m*-phenylene bridges as strong ferromagnetic couplers for Cu^{II}-bridge-Cu^{II} magnetic interactions: new perspectives

Alok Ranjan Paital, Tamoghna Mitra, Debashis Ray,* Wing Tak Wong, Jordi Ribas-Ariño, Juan J. Novoa, Joan Ribas and Guillem Aromí*

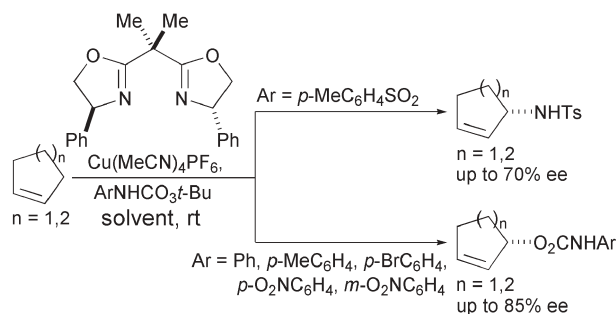
The nature of the *m*-phenylene bridge as a tuneable ferromagnetic coupler between Cu^{II} centers is established through DFT calculations and this is supported experimentally in the form of the new complex [Cu₂(L3)] (3).

5175

Tuneable asymmetric copper-catalysed allylic amination and oxidation reactions

J. Stephen Clark* and Caroline Roche

Asymmetric allylic amination or oxidation of simple alkenes can be achieved by reaction with a peroxycarbamate in the presence of chiral copper *bis*-oxazoline complex. The reaction can be tuned to give either the amination or oxidation product by choice of peroxycarbamate. Amination can be performed to give allylic amines with ee levels of up to 70% and oxidation can be accomplished to deliver allylic carbamates with ee levels of up to 85%.

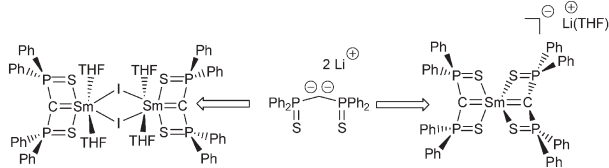


5178

New mono- and bis-carbene samarium complexes: synthesis, X-ray crystal structures and reactivity

Thibault Cantat, Florian Jaroschik, François Nief, Louis Ricard, Nicolas Mézailles and Pascal Le Floch*

Synthesis of new samarium complexes featuring a carbenic SCS-based pincer ligand is reported and the first homoleptic bis-carbene samarium complex is described. The electronic nature of the carbene-samarium bond was established by both X-ray analyses and reactivity towards benzophenone. Interestingly, these new complexes exhibit Schrock-like character.

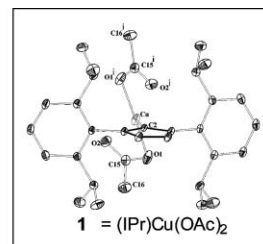
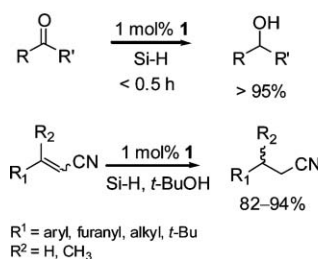


5181

A new alternative to Stryker's reagent in hydrosilylation: synthesis, structure, and reactivity of a well-defined carbene-copper(II) acetate complex

Jaesook Yun,* Daesung Kim and Hoseop Yun

A new, air stable and well-defined carbene-copper(II) complex has been prepared, which is an efficient precatalyst for the 1,2- and 1,4-reduction of carbonyl compounds under hydrosilylation conditions.

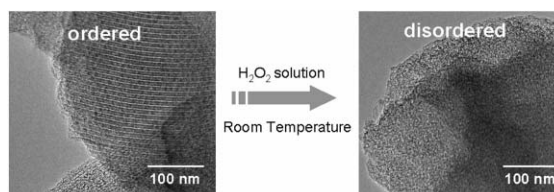


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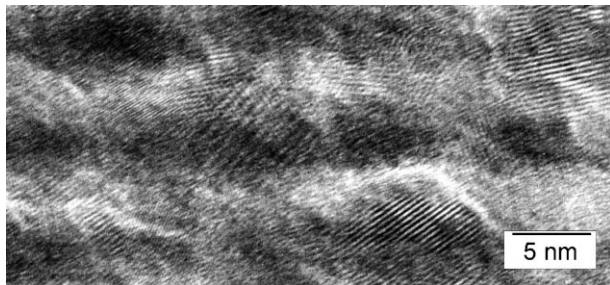
Evidence for C–C bond cleavage by H₂O₂ in a mesoporous CMK-5 type carbon at room temperature

An-Hui Lu, Wen-Cui Li, Nelli Muratova, Bernd Spliethoff and Ferdi Schüth*

The structure of ordered tubular carbon of the CMK-5 type is destroyed by the mild oxidizing agent H₂O₂, as evidenced by X-ray diffraction and TEM analysis. As a product of the reaction, small hydrocarbon species form at room temperature which shows that C–C-bond cleavage occurs.



5187

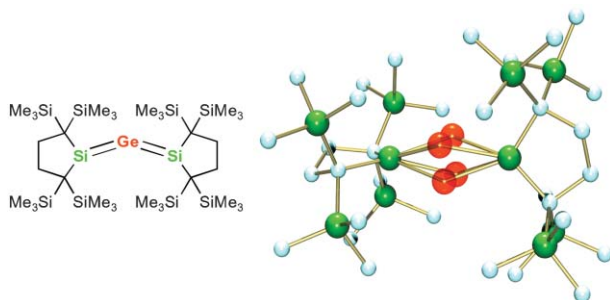


Hexagonally ordered mesoporous ternary $\text{Li}_2\text{O-TiO}_2\text{-P}_2\text{O}_5$ oxides with high lithium content

Donglin Li, Haoshen Zhou,* Itaru Honma and Masaki Ichihara

High lithium content mesoporous ternary $\text{Li}_2\text{O-TiO}_2\text{-P}_2\text{O}_5$ oxides have been synthesized, with a variety of microstructures including a nanocomposite, amorphous multicomponent oxide, and almost fully nanocrystalline anatase.

5190

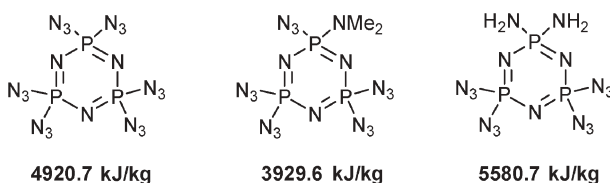


A missing allene of heavy Group 14 elements: 2-germadisilaallene

Takeaki Iwamoto, Takashi Abe, Chizuko Kabuto and Mitsuo Kira*

The first stable 2-germadisilaallene was synthesized by the reduction of a 2 : 1 mixture of a stable dialkylsilylene and dichlorogermylene-dioxane complex with KC_8 . The 2-germadisilaallene showed dynamic disorder similar to the corresponding trisilaallene in the solid state.

5193

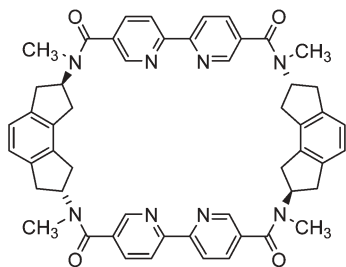


High energy density materials from azido cyclophosphazenes

K. Muralidharan, Bamidele A. Omotowa, Brendan Twamley, Crystal Piekarski and Jean'ne M. Shreeve*

Azido substituted cyclophosphazenes were prepared and their standard heats of formation were calculated based on experimentally determined heats of combustion.

5196



A computer-designed macrocyclic zinc receptor

Haidong Huang and Dale G. Drueckhammer*

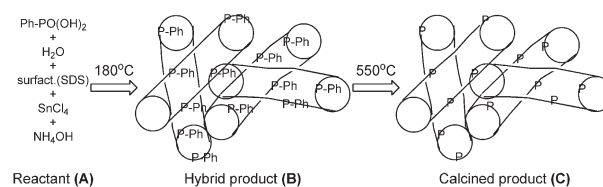
A novel computer-based strategy was used for the design of a receptor exhibiting unique selectivity for zinc ion.

5199

Synthesis of organic–inorganic hybrid mesoporous tin oxophosphate in the presence of anionic surfactant

Nawal Kishor Mal, Masahiro Fujiwara* and Masahiko Matsukata

A wormhole mesoporous hybrid tin oxophenylphosphate (B) was prepared using phenylphosphonic acid as a single source of phosphorus with anionic surfactant, which gave a stable mesoporous tin oxophosphate (C) after calcination.

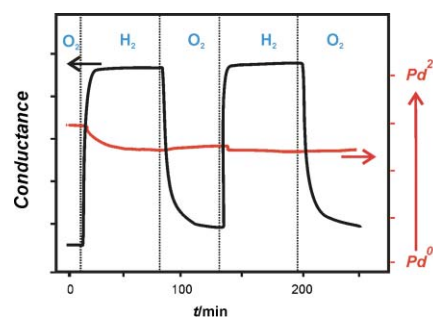


5202

Characterization of the H₂ sensing mechanism of Pd-promoted SnO₂ by XAS *in operando* conditions

Olga V. Safonova,* Thomas Neisius, Andrey Ryzhikov, Bernard Chenevier, Aleksandre M. Gaskov and Michel Labeau

The effect of Pd nanoparticles on the H₂ sensitivity of SnO₂ thin films was studied in real working conditions using X-ray Absorption Spectroscopy (XAS), electrical conductivity measurements and mass-spectrometry.

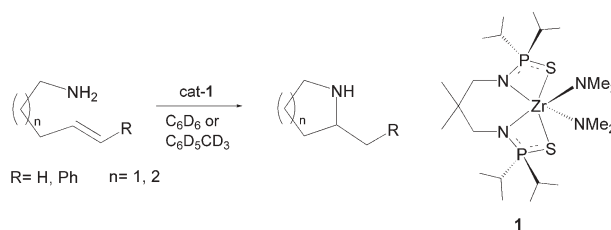


5205

Intramolecular alkene hydroaminations catalyzed by a bis(thiophosphinic amidate) Zr(IV) complex

Hyunseok Kim, Phil Ho Lee* and Tom Livinghouse*

A neutral Zr(IV) complex has been shown to be an effective precatalyst for intramolecular alkene hydroaminations that provide cyclic amines in good to excellent yields.

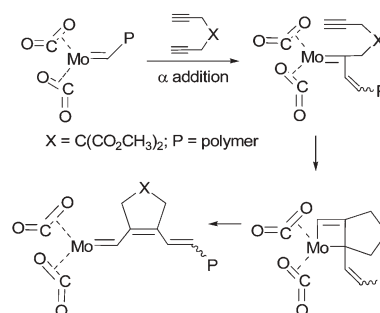


5208

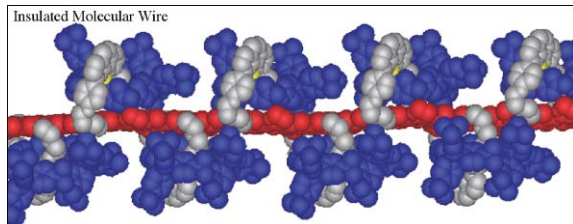
Cyclopolymerization of dimethyl dipropargylmalonate in supercritical carbon dioxide to give a highly regular polyene containing predominantly five-membered rings

Ji Won Park, Young-Jae Hur, Hwayong Kim and Youn-Woo Lee*

Poly(dimethyl dipropargylmalonate) synthesized in scCO₂ contained more than 95% five-membered rings, *i.e.*, highly regular polyene was produced, which shows carbon dioxide as a reaction medium plays a significant role in determining a highly selective polymer structure.



5211

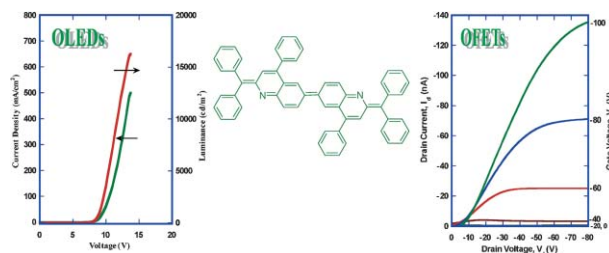


Insulated conducting polymers: manipulating charge transport using supramolecular complexes

Phoebe H. Kwan and Timothy M. Swager*

Conducting polymers that are enshrouded with rotaxanes are shown to behave as insulated molecular wires. Copper ions placed in the rotaxane structures can mediate conduction between polymer chains.

5214

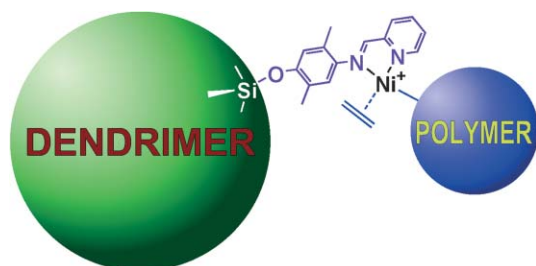


Quinoidal oligoquinoline: a novel quinodimethane exhibiting high electroluminescence efficiency and p-channel field effect charge transport

Christopher J. Tonzola, Jessica M. Hancock, Amit Babel and Samson A. Jenekhe*

A novel tetraphenylquinodimethane based on electron-deficient 4-phenylquinoline oligomer was used as a p-channel semiconductor in thin-film transistors and as an emitter to achieve very bright and high efficiency green light-emitting diodes.

5217

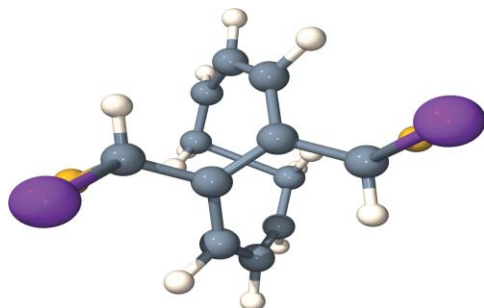


Generation effects on the microstructure and product distribution in ethylene polymerization promoted by dendritic nickel catalysts

José M. Benito, Ernesto de Jesús,* F. Javier de la Mata, Juan C. Flores* and Rafael Gómez

Nickel catalysts supported on carbosilane dendrimers polymerize ethylene generating a mixture of oligomers and polymers, the microstructure and distribution of which are significantly affected by the generation of the dendritic precursor.

5220



Double-twist Möbius aromaticity in a $4n + 2$ electron electrocyclic reaction

Henry S. Rzepa

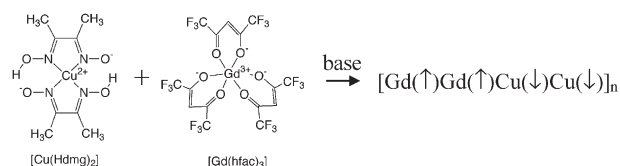
A 5,6-di-*t*-Bu substituted decapentaene is predicted to react *via* a transition state in the form of a double-twist Möbius strip in preference to the competitive six-electron electrocycloislation.

5223

The first A_2B_2 -heterometal ferrimagnetic chain. Structures and magnetic properties of polymeric $[Gd_2Cu_2]_n$ and the corresponding monomer

Sohei Ueki, Yasuko Kobayashi, Takayuki Ishida* and Takashi Nogami

We utilized oxime derivatives to explore adjustable and short bridging ligands for 3d/4f heterometallic magnetic materials, and actually prepared and characterized glyoximate-bridged polymeric $[Gd_2Cu_2]_n$ and tetranucleating $[CuGd_2Cu]$, both showing ground ferrimagnetic states.

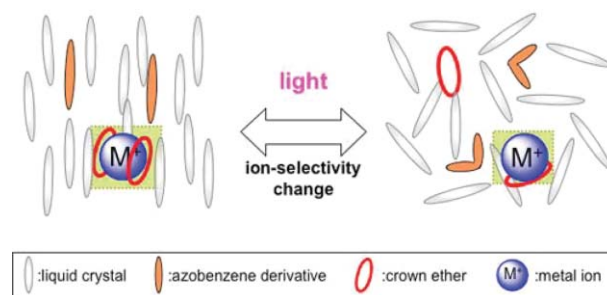


5226

Photocontrol of ion-sensor performances in neutral-carrier-type ion sensors based on liquid-crystalline membranes

Syusuke Oosaki, Hisanobu Hayasaki, Yoshiaki Sakurai, Setsuko Yajima and Keiichi Kimura*

Neutral-carrier-type ion sensors based on liquid-crystalline membranes containing an azobenzene derivative showed photo-tunable ion selectivities, which were synchronized by the photoinduced phase transition of the ion-sensing membranes.

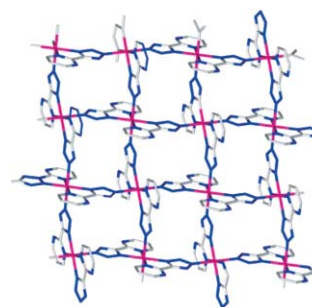


5228

Unique self-assembled 2D metal-tetrazolate networks: crystal structure and magnetic properties of $[M(\text{pmtz})_2]$ ($M = \text{Co(II)}$ and Fe(II)); Hpmtz = 5-(pyrimidyl)tetrazole

Antonio Rodríguez, Raikko Kivekäs and Enrique Colacio*

Reaction of M^{II} salts ($M^{II} = \text{Co}^{II}$ and Fe^{II}) with 5-(pyrimidyl)tetrazole under hydrothermal conditions yields the title compounds which have a square-grid-like 2D structure; the cobalt complex is a spin-canted antiferromagnet with $T_c = 15$ K.

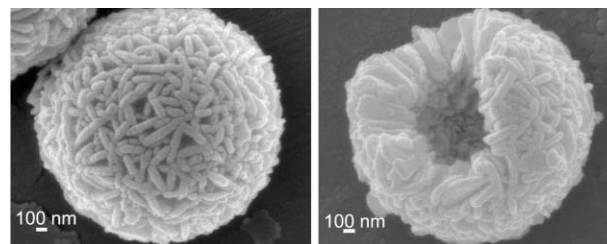


5231

Fabrication of β -Ni(OH)₂ and NiO hollow spheres by a facile template-free process

Yong Wang, Qingshan Zhu* and Huigang Zhang

Ni(OH)_2 hollow microspheres with β -Ni(OH)₂ nanosheets as the *in situ* formed building units were fabricated *via* a novel template-free approach in a strong alkaline solution of glycine, and can be converted into NiO hollow microspheres by a thermal decomposition process.



Transition-metal-catalyzed rearrangement of 5-alkynals to γ -alkynylketones and 1-cyclopentenylketones

Ken Tanaka, Kaori Sasaki, Kenzo Takeishi and Koudai Sugishima


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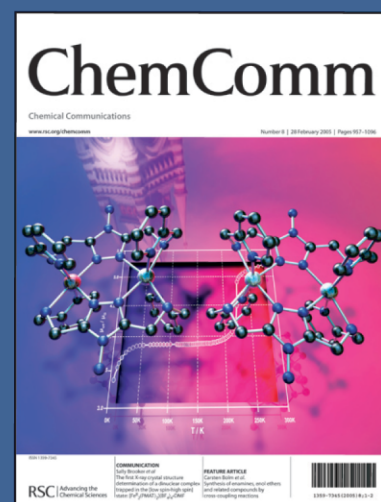
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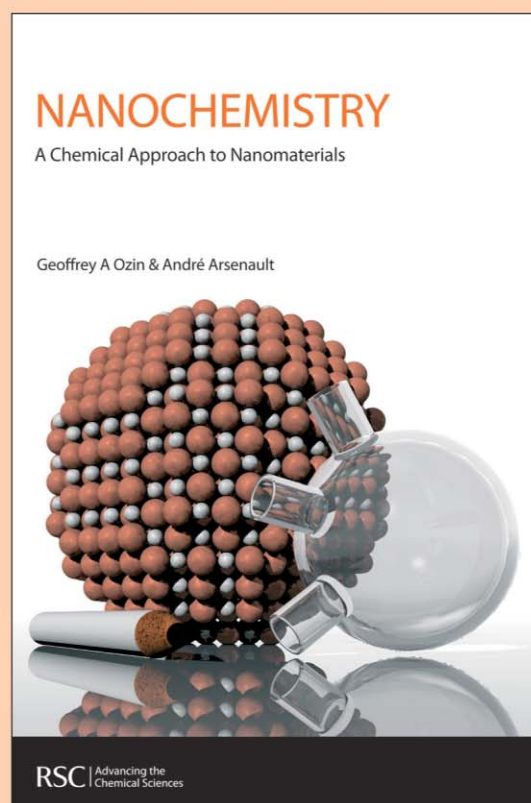
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