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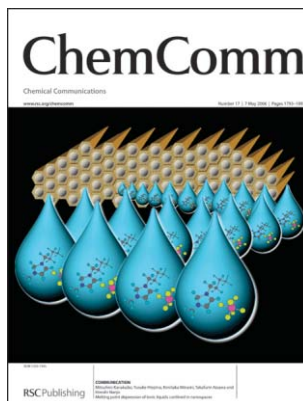
IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (17) 1793–1892 (2006)



Cover

See Pierangelo Metrangolo, Giuseppe Resnati *et al.*, page 1819. Supramolecular *n*-Borromean rings of different dimensions can be engineered through a modular approach based on the self assembly of fluorinated tectons *via* halogen bonding. Image reproduced by permission of Rosalba Liantonio, Pierangelo Metrangolo, Franck Meyer, Tullio Pilati, Walter Navarrini and Giuseppe Resnati from *Chem. Commun.*, 2006, 1819.



Inside cover

See Mitsuhiro Kanakubo *et al.*, page 1828. Controllable nano-ionic liquids; confinement is a unique physical approach. Image reproduced by permission of Mitsuhiro Kanakubo, Yusuke Hiejima, Kimitaka Minami, Takafumi Aizawa and Hiroshi Nanjo from *Chem. Commun.*, 2006, 1828.

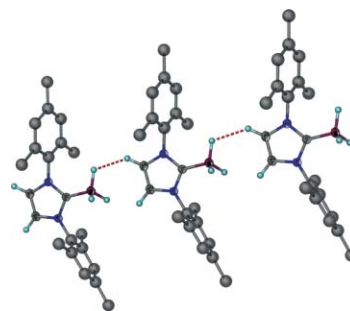
FEATURE ARTICLE

1809

From the reactivity of *N*-heterocyclic carbenes to new chemistry in ionic liquids

John P. Canal, Taramatee Ramnial, Diane A. Dickie and Jason A. C. Clyburne*

The reactivity and chemistry of *N*-heterocyclic carbenes, including investigations into their reactions with small reagents, and of related imidazolium salts are discussed.



COMMUNICATIONS

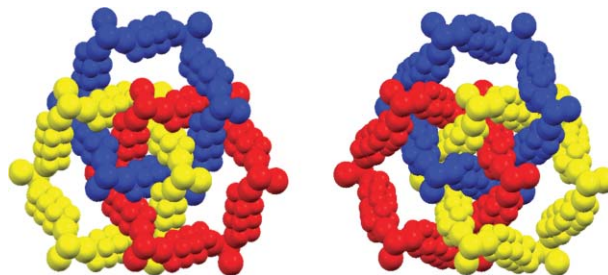
1819



Metric engineering of supramolecular Borromean rings

Rosalba Liantonio, Pierangelo Metrangolo,* Franck Meyer, Tullio Pilati, Walter Navarrini and Giuseppe Resnati*

The first case of homology in the topology of Borromean rings is found in supramolecular networks based on halogen bonding.



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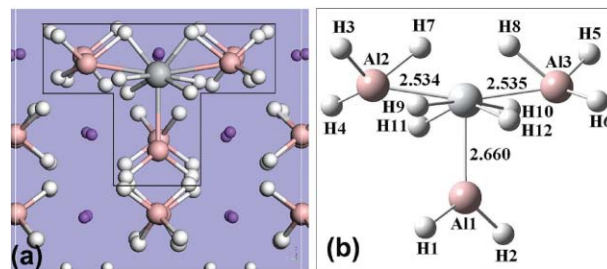
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1822

A precursor state for formation of TiAl_3 complex in reversible hydrogen desorption/adsorption from Ti-doped NaAlH_4

Jianjun Liu and Qingfeng Ge*

A complex structure, TiAl_3H_x , with Ti occupying an interstitial site and interacting directly with three neighboring $(\text{AlH}_4)^-$ groups in a slab simulating $\text{NaAlH}_4(001)$, is believed to be a precursor state for the formation of a TiAl_3 binary phase observed experimentally and plays an important role in hydrogen release/uptake in Ti-doped NaAlH_4 .

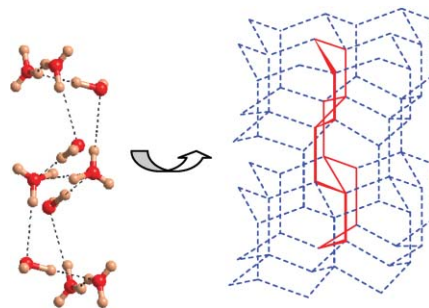


1825

First example of an ice-like water hexamer boat tape structure in a supramolecular organic host

Binoy K. Saha and Ashwini Nangia*

A T6(2) tape of water molecules in the boat cyclohexane conformation, a 1D structural motif in natural ice I_h , is characterized by X-ray diffraction in the channel framework of dibromophloroglucinol tetrahydrate.

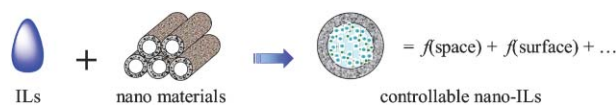


1828

Melting point depression of ionic liquids confined in nanospaces

Mitsuhiro Kanakubo,* Yusuke Hiejima, Kimitaka Minami, Takafumi Aizawa and Hiroshi Nanjo

A new physical method was proposed to control the liquid properties of room temperature ionic liquids (RT-ILs) in combination with nanoporous materials; the melting point of ILs confined in nanopores remarkably decreases in proportion to the inverse of the pore size.

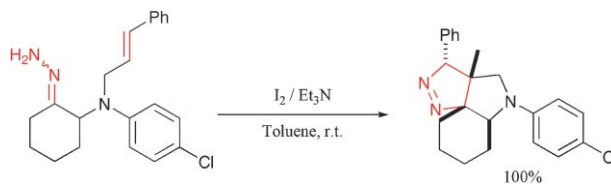


1831

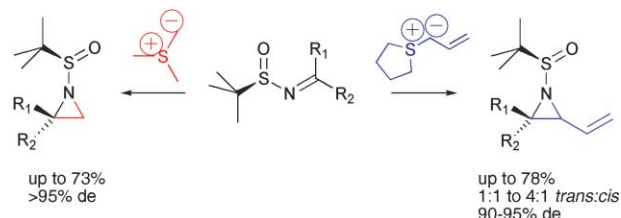
Observations on the reaction of hydrazones with iodine: interception of the diazo intermediates

Béatrice Quiclet-Sire* and Samir Z. Zard*

The reaction of hydrazones with iodine/base leads to diazo intermediates which are readily trapped by an internal alkene or alkyne.



1833

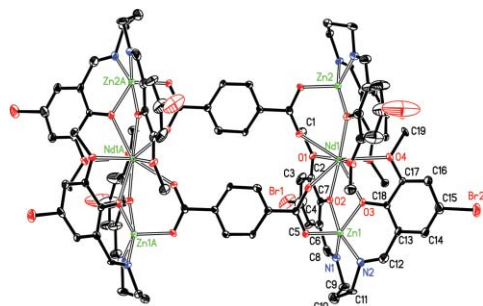


Direct synthesis of chiral aziridines from *N*-*tert*-butyl-sulfinylketimines

Daniel Morton, David Pearson, Robert A. Field and Robert A. Stockman*

Reaction of *tert*-butyl-sulfinylketimines with sulfur ylides yields highly substituted chiral aziridines in up to 78% yield and > 90% d.e.

1836

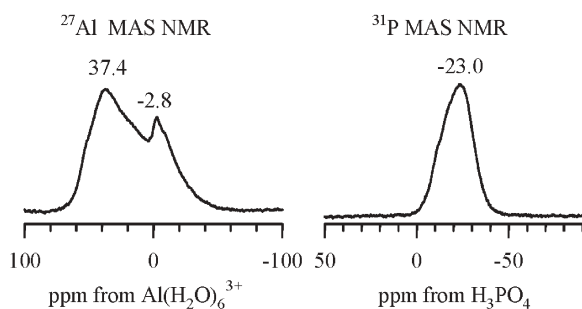


Design and synthesis of a near infra-red luminescent hexanuclear Zn–Nd prism

Xiao-Ping Yang, Richard A. Jones,* Wai-Kwok Wong,* Vince Lynch, Michael M. Oye and Archie L. Holmes

The use of the Schiff-base ligand *N,N'*-bis(5-bromo-3-methoxysalicylidene)propylene-1,3-diamine (H_2L) and 1,4-benzenedicarboxylate (BDC) enables the construction of the hexanuclear luminescent Zn–Nd complex $[Zn_4Nd_2L_4(1,4-BDC)_2] \cdot [Nd(NO_3)_5(H_2O)] \cdot Et_2O \cdot 2EtOH \cdot 3H_2O$.

1839

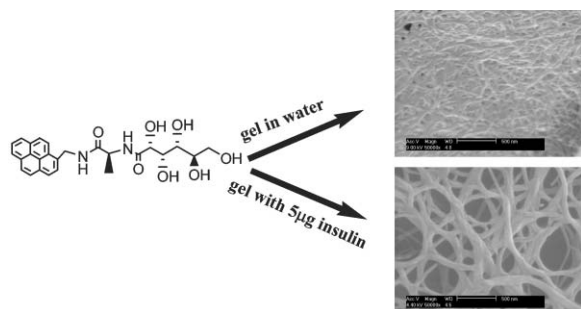


Synthesis and characterization of novel mesoporous aluminosilicate MCM-41 containing aluminophosphate building units

Tomás D. Conesa, Robert Mokaya, Juan M. Campelo and Antonio A. Romero*

A new approach for the synthesis of mesoporous SAPO materials with high Si loading *via* the addition of aluminophosphate precursor to preformed mesoporous Al-MCM-41 phases is reported.

1842



An insulin-sensing sugar-based fluorescent hydrogel

Sankarprasad Bhuniya and Byeang Hyeon Kim*

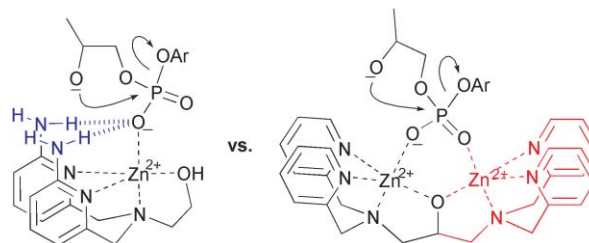
A small library of amphiphiles consisting of a polar carbohydrate “headgroup” attached to the N-termini of amino acids, which is linked with a nonpolar pyrene tail group have been prepared and it is found that one of them has insulin sensitivity in aqueous media.

1845

Comparing a mononuclear Zn(II) complex with hydrogen bond donors with a dinuclear Zn(II) complex for catalysing phosphate ester cleavage

Guoqiang Feng, Juan C. Mareque-Rivas* and Nicholas H. Williams*

A comparison between making a Zn(II) complex dinuclear or introducing H-bond donors to improve its efficiency for phosphate diester cleavage shows that both lead to similar observed rates of cleavage; however, using H-bond donors can lead to higher turnover numbers.



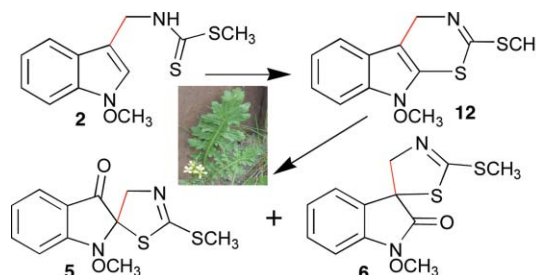
How do H-bond donors compare to making a Zn(II) complex **dinuclear** in improving its efficiency for catalysing phosphate diester cleavage?

1848

En route to erucalexin: a unique rearrangement in the crucifer phytoalexin biosynthetic pathway

M. Soledade C. Pedras* and Denis P. O. Okinyo

The first biosynthetic studies revealing that both 1-methoxybrassinin (**2**) and sinalbin (**12**) are close precursors of the phytoalexins erucalexin (**5**) and 1-methoxyspirobrassinin (**6**).

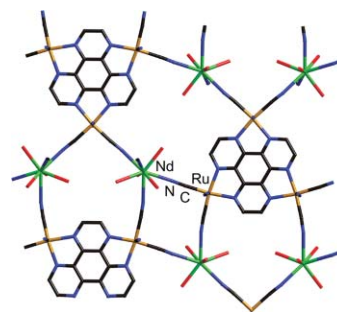


1851

Polynuclear cyanoruthenate chromophores based on hexaaza-triphenylene containing up to twelve cyanides: photophysical and structural properties

Juan-Manuel Herrera, Michael D. Ward,* Harry Adams, Simon J. A. Pope and Stephen Faulkner

The complex $[\{\text{Ru}(\text{CN})_4\}_3(\mu^3\text{-HAT})]^{6-}$ (HAT = hexaaza-triphenylene) has twelve externally-directed cyanide groups, which result in (i) remarkable solvatochromism in its absorption spectrum, and (ii) unusually high connectivity in its coordination networks with Ln(III) cations.

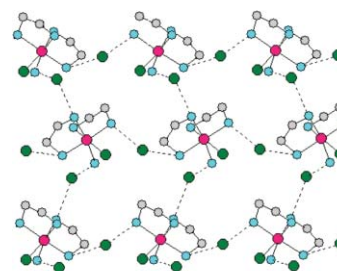


1854

On the spontaneous induction of chirality in the preparation of Werner's complex *cis*-[CoBr(NH₃)(en)₂Br]₂

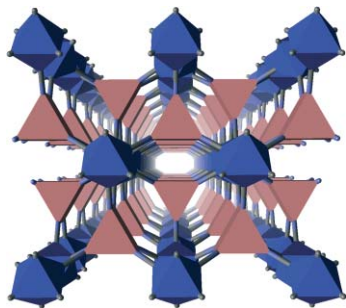
Fang Guo, Meritxell Casadesus, Eugene Y. Cheung, Michael P. Coogan* and Kenneth D. M. Harris*

The product obtained directly from the standard reaction to produce Werner's complex *cis*-[CoBr(NH₃)(en)₂Br]₂ is shown, *via* structure determination from powder X-ray diffraction data, to be a racemic crystalline phase.



Racemic Phase P2₁/n

1857

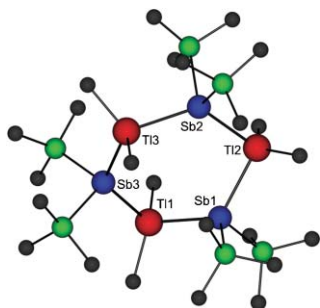


Dehydration of the nanoporous coordination framework $\text{Er}^{\text{III}}[\text{Co}^{\text{III}}(\text{CN})_6] \cdot 4(\text{H}_2\text{O})$: single crystal to single crystal transformation and negative thermal expansion in $\text{Er}^{\text{III}}[\text{Co}^{\text{III}}(\text{CN})_6]$

Thorsten Pretsch, Karena W. Chapman, Gregory J. Halder and Cameron J. Kepert*

Single crystallinity is retained in the topotactic conversion of $\text{Er}[\text{Co}(\text{CN})_6] \cdot 4(\text{H}_2\text{O})$ to $\text{Er}[\text{Co}(\text{CN})_6]$ with heating. The dehydrated phase is unusual in having a trigonal prismatic lanthanoid coordination geometry and exhibits pronounced negative thermal expansion (*i.e.*, contraction on heating).

1860

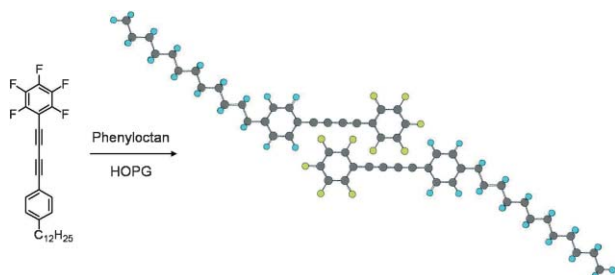


Synthesis and structural characterization of the first metal organic thallium antimonide

Stephan Schulz,* Florian Thomas and Martin Nieger

$[\text{Me}_2\text{TlSb}(\text{SiMe}_3)_2]_3$ **1** was obtained from a metathesis reaction between $[\text{Me}_2\text{AlSb}(\text{SiMe}_3)_2]_3$ and dmap-TlMe_3 ($\text{dmap} = 4$ -dimethylaminopyridine) whereas the corresponding TlBi heterocycle $[\text{Me}_2\text{TlBi}(\text{SiMe}_3)_2]_3$ **2** was found to decompose in solution even at -90°C .

1862

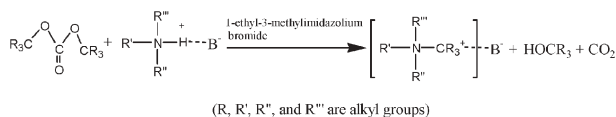


A self assembled molecular zipper based on a perfluorophenyl-phenyl diacetylene motif

Lijin Shu, Zhongcheng Mu, Harald Fuchs, Lifeng Chi* and Marcel Mayor*

The perfluorophenyl-phenyl diacetylene rod comprising a dodecyl chain self assembles in parallel rows on graphite. The large surface area structure is supported by an intermolecular fluor–diacetylene interaction.

1864



The synthesis of quaternary ammonium salts from ammonium salts and dialkyl carbonate

Zhuoqun Zheng, Tinghua Wu* and Xiaoping Zhou*

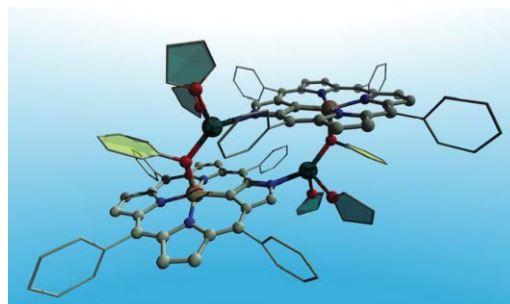
Quaternary ammonium salts were directly synthesized from ammonium salts and dialkyl carbonates over an ionic liquid catalyst 1-ethyl-3-methylimidazolium bromide.

1866

Molecular assembling using axial phenolate on an iron N-confused porphyrin complex

Chen-Hsiung Hung,* Chia-Hao Chang, Wei-Min Ching and Chuan-Hung Chuang

A dimeric iron N-confused porphyrin complex assembled using sodium ions to link the peripheral nitrogen and axial phenolate oxygen gives an ordered structure with an iron-to-iron distance of 8.864 Å and channel-like crystal packing.



1869

Enantioselective synthesis mediated by chiral crystal of achiral hippuric acid in conjunction with asymmetric autocatalysis

Tsuneomi Kawasaki, Kenta Suzuki, Kunihiko Hatase, Masanari Otsuka, Hideko Koshima and Kenso Soai*

Enantiomorphous crystals composed of achiral hippuric acid, *i.e.*, naturally occurring *N*-benzoylglycine, have been used successfully as chiral inducers in enantioselective synthesis in combination with asymmetric autocatalysis to afford the product with extremely high enantiomeric excess.

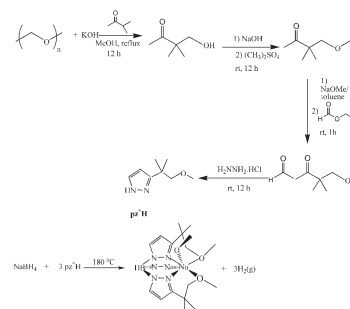


1872

A tris-pyrazolylborate ligand with hemilabile O-donor groups. Examples of η^3 , η^5 , η^6 and bridging modes of bonding to Li^+ , Na^+ , K^+ , Tl^+ and Ca^{2+} ions

Malcolm H. Chisholm,* Judith C. Gallucci and Gülşah Yaman

A tris-pyrazolylborate ligand bearing ether appendages is shown to be a potential hemilabile ligand based on NMR studies and structural characterization of its η^3 , η^5 , η^6 , and μ -binding modes in coordination with Li^+ , Na^+ , K^+ , Tl^+ , and Ca^{2+} ions.



1875

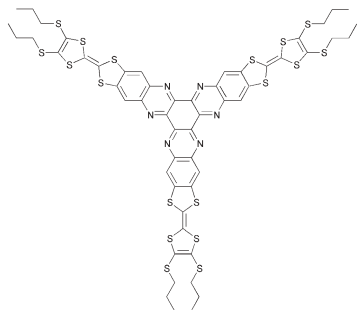
An unusual dimerization of primary unsaturated alcohols catalyzed by $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$

Takashi Doi, Takahide Fukuyama, Satoshi Minamino, Guillaume Husson and Ilhyong Ryu*

$\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ catalyzes the dimerization of primary unsaturated alcohols leading to the formation of α -hydroxymethyl ketones.



1878

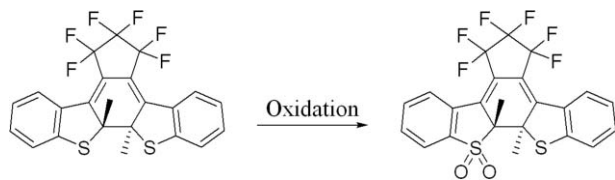


A redox-active tri-star molecule: merging of TTF and HAT chemistry

Chunyang Jia, Shi-Xia Liu,* Christian Tanner, Claudia Leiggner, Lionel Sanguinet, Eric Levillain, Samuel Leutwyler, Andreas Hauser and Silvio Decurtins

A highly π -conjugated molecule combining two characteristics; a charge-transfer transition originating from its inherent donor–acceptor nature in its neutral state and an intervalence charge-transfer transition in its dication mixed-valence state is reported.

1881

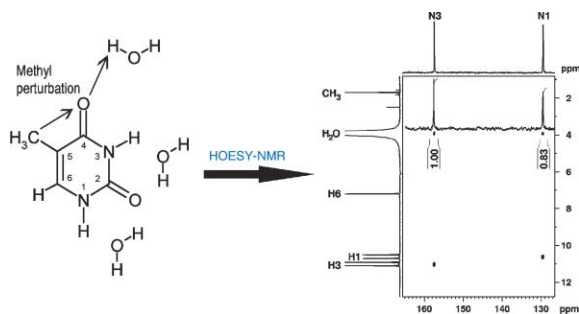


Fatigue-resistant photochromic dithienylethenes by controlling the oxidation state

Yong-Chul Jeong, Dae Gyu Park, Eunyoung Kim,* Kwang-Hyun Ahn* and Sung Ik Yang*

High fatigue-resistant photochromic dithienylethenes were synthesized by controlling the oxidation state of 1,2-bis(2-methyl-1-benzothiophene-3-yl)perfluorocyclopentene (BTF6) and 1,2-bis(2,5-dimethylthien-3-yl)perfluorocyclopentene (DMTF6).

1884

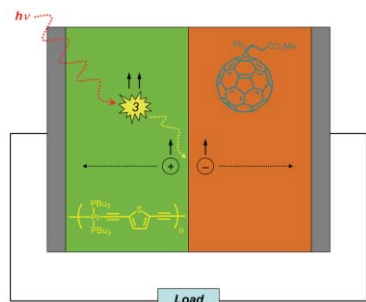


NMR diffusion and nuclear Overhauser investigation of the hydration properties of thymine: influence of the methyl group

Pierre Thureau,* Bernard Ancian, Stéphane Viel and André Thévand

The absence of preferential hydration in thymine and its lowest water accessibility with respect to uracil were evidenced by NMR diffusion and HOESY experiments.

1887



Platinum–acetylide polymer based solar cells: involvement of the triplet state for energy conversion

Fengqi Guo, Young-Gi Kim, John R. Reynolds* and Kirk S. Schanze*

Relatively efficient photovoltaic devices were fabricated using blends of a phosphorescent platinum–acetylide polymer and a fullerene (PCBM); involvement of the triplet excited state of the platinum–acetylide polymer in photoinduced charge transfer is believed to contribute to the device efficiency.

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