

Cover

Ionic liquids are demonstrating considerable potential as alternative reaction media for enantioselective chemo- and bio-catalysis (pp. 1033–1043).



Chemical biology articles published in this journal also appear in the *Chemical Biology Virtual Journal*: www.rsc.org/chembiol

contents

C33

Chemical Science

May 2004/Volume 1/Issue 5

www.rsc.org/chemicalscience

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.

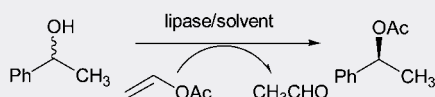
FEATURE ARTICLE

1033

Enantioselective chemo- and bio-catalysis in ionic liquids

Choong Eui Song

Recent developments in the enantioselective chemo- and bio-catalysis in ionic liquids are reviewed. In many cases, the use of ionic liquids provides many advantages over reactions in conventional organic solvents in terms of activity, enantioselectivity, stability and the reusability of the solvent–catalyst systems.

in [bmim][NTf₂]*E* = ~200 at 20 °C*E* = 150 at 70–90 °C

in MTBE

E = ~200 at 20 °C*E* = ~4 at 55 °C

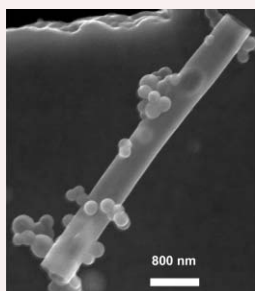
COMMUNICATIONS

1044

Synthesis of peptide-nanotube platinum-nanoparticle composites

Yujiang Song, Sivakumar R. Challa, Craig J. Medforth, Yan Qiu, Richard K. Watt, Donovan Peña, James E. Miller, Frank van Swol and John A. Shelnett*

Nanotubes prepared by the self-assembly of D-Phe-D-Phe molecules are investigated by electron microscopy and Monte Carlo simulations; the nanotubes appear to be porous and can form novel peptide–nanotube platinum–nanoparticle composites.



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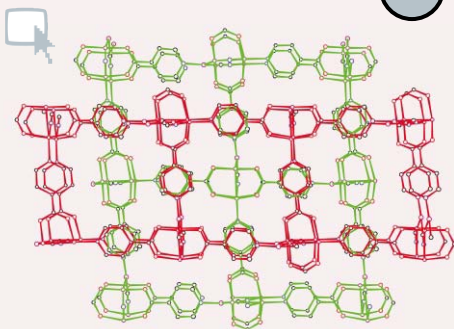
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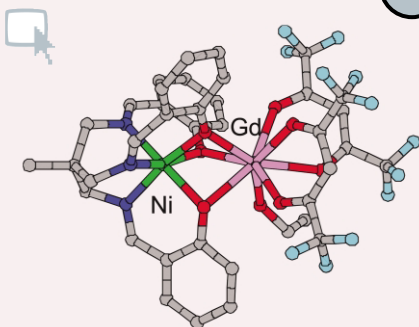


A novel ligand-unsupported 3D framework polymer of trimeric copper(I) and its NLO property

Yao Kang, Yuan-Gen Yao,* Ye-Yan Qin, Jian Zhang, Yu-Biao Chen, Zhao-Ji Li, Yi-Hang Wen, Jian-Kai Cheng and Rui-Feng Hu

A novel 3-D interpenetrated trimeric copper(I) polymer $[\text{Cu}_3(\text{CN})(\text{IN})_2]_n$ (IN = isonicotinate) in which a two-coordinated copper(I) was established has been synthesized and structurally determined.

1048

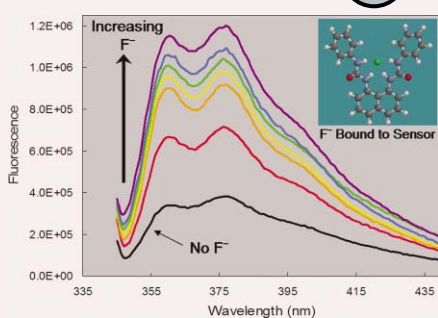


Ferromagnetic Ni^{II}-Gd^{III} interactions in complexes with NiGd, NiGdNi, and NiGdGdNi cores supported by tripodal ligands

Tomoka Yamaguchi, Yukinari Sunatsuki, Masaaki Kojima,* Haruo Akashi, Masanobu Tsuchimoto, Nazzareno Re, Shutaro Osa and Naohide Matsumoto

By using $[\text{NiL}]^-$ ($\text{H}_3\text{L} = 1,1,1\text{-tris}(N\text{-salicylideneaminomethyl})\text{ethane}$) as a complex ligand, di-, tri-, and tetranuclear mixed Ni^{II} and Gd^{III} complexes with ferromagnetic interactions were prepared. Selection of the additional ligand on the Gd^{III} ion plays an important role in controlling the nuclearity of the complex.

1050

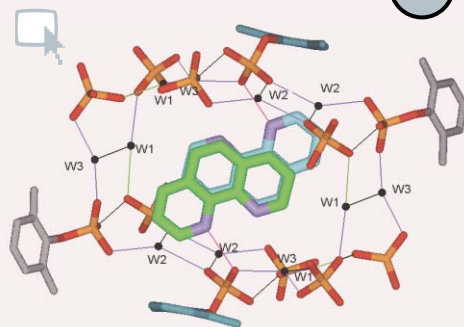


A novel fluoride sensor based on fluorescence enhancement

Guoxiang Xu and Matthew A. Tarr*

A novel halide sensor, which yields greater fluorescence upon binding to fluoride, has been synthesized and characterized. The new sensor is selective for fluoride over other halides.

1052

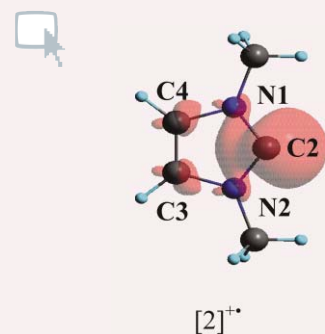


Solid-state caging of 1,10-phenanthroline π - π stacked dimers by calix[4]arene dihydroxyphosphonic acid

Adina N. Lazar, Alda Navaza and Anthony W. Coleman*

The calix[4]arene dihydroxyphosphonic acid-1,10-phenanthroline complex shows caging of the guest molecules as a π - π stacked dimer in a cavity formed by intermolecular hydrogen bonds and aromatic walls formed by the calixarene.

1054

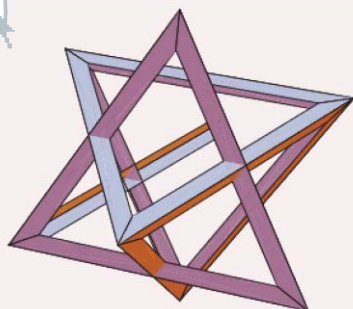


Reactions of *N*-heterocyclic carbenes (NHCs) with one-electron oxidants: possible formation of a carbene cation radical

Taramatee Ramnial, Iain McKenzie, Brian Gorodetsky, Emily M. W. Tsang and Jason A. C. Clyburne*

The radical cation $[\mathbf{2}]^{+\bullet}$ is postulated as an intermediate in the one-electron oxidation of *N*-heterocyclic carbenes.

1056

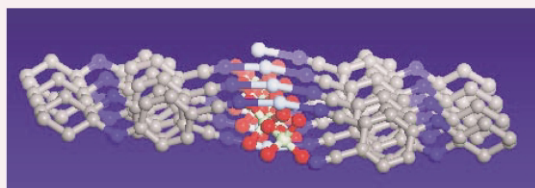


Self-assembly of a novel pentanuclear centred-tetrahedral silver species

Edwin C. Constable,* Catherine E. Housecroft, Markus Neuburger, Sebastien Reymann and Sylvia Schaffner

The sterically hindered ligand 3,6-di(2-pyridyl)-4-trimethylsilylpyridazine forms an unusual pentanuclear complex with silver(I) in which the five silver atoms define a metal-centred tetrahedron that is interstellaed with the tetrahedron defined by the four silicon atoms.

1058

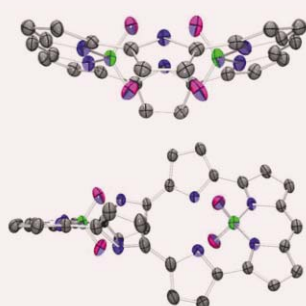


Helical and network coordination polymers based on a novel C₂-symmetric ligand : SHG enhancement through specific metal coordination

S. Philip Anthony and T. P. Radhakrishnan*

Network and helical coordination polymers of Cu(I) and Ag(I) based on a new chiral ligand show solid state SHG sensitive to the coordination mode and polymer structure.

1060

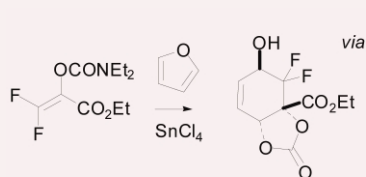


Octaethylporphyrin and expanded porphyrin complexes containing coordinated BF₂ groups

Thomas Köhler, Michael C. Hodgson, Daniel Seidel, Jacqueline M. Veauthier, Sylvie Meyer, Vincent Lynch, Peter D. W. Boyd,* Penelope J. Brothers* and Jonathan L. Sessler*

Whereas octaethylporphyrin forms a very labile bis-BF₂ complex, treatment of hexa- and octapyrrolic expanded porphyrins with BF₃·OEt₂ under standard conditions gives rise to stable, non-labile mono- and bis-BF₂ complexes.

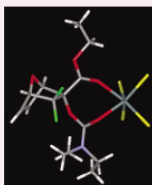
1062



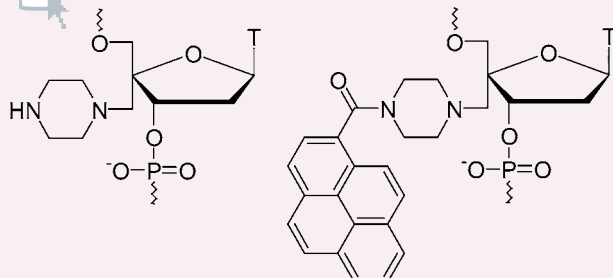
A surprising steric effect on a tandem cycloaddition/ring-opening reaction: rapid syntheses of difluorinated analogues of (hydroxymethyl)conduritols

John Fawcett, Andrew C. Moralee, Jonathan M. Percy,* Vittoria Salafia, Mark A. Vincent and Ian H. Hillier

A difluorinated dienophile and furan react in the presence of stoichiometric stannic chloride to form a cyclic carbonate directly *via* a tandem cycloaddition/ring-opening reaction.



1064

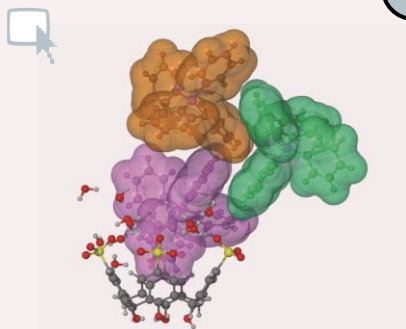


DNA-selective hybridization and dual strand invasion of short double-stranded DNA using pyren-1-ylcarbonyl-functionalized 4'-C-piperazinomethyl-DNA

Torsten Bryld, Torben Højland and Jesper Wengel*

DNA-selective hybridization and recognition of double-stranded DNA by a novel dual strand invasion approach have been accomplished using pyren-1-ylcarbonyl-functionalized 4'-C-piperazinomethyl-DNA.

1066

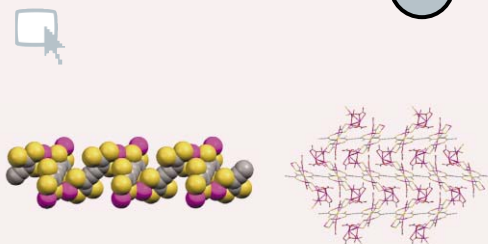


Exploiting phenyl embraces and π -stacking in the assembly of arrays of tetraphenylphosphonium *p*-sulfonatocalix[4]arene

Mohamed Makha, Colin L. Raston,* Alexandre N. Sobolev and Allan H. White

Pseudo-polymorphic supramolecular arrays of tetraphenylphosphonium cations and *p*-sulfonatocalix[4]arene anions can be constructed using interactions other than the electrostatic attraction between ions, providing myriad possibilities for new materials composed of these and similar components.

1068

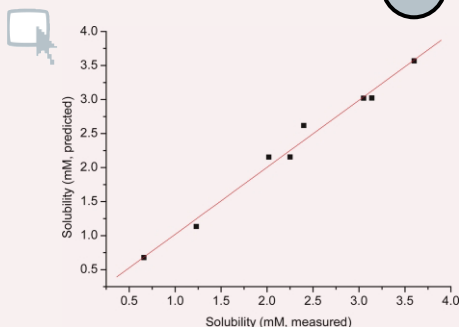


Hexakis(isopropylthio)-1,5-hexadien-3-yne and its fluorescent Ag(I) coordination polymers: assembly of helicates with thioether sites

Yuan-Te Fu, Vincent M. Lynch and Richard J. Lagow*

A new thioether-rich ligand with a conjugated backbone has been used to support fluorescent Ag(I) coordination polymers with interesting architectures.

1070



Carbon monoxide solubility in ionic liquids: determination, prediction and relevance to hydroformylation

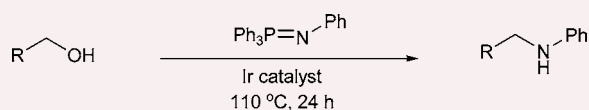
C. André Ohlin, Paul J. Dyson and Gábor Laurenczy*

The solubility of CO in ionic liquids has been determined using medium-pressure NMR techniques, and a method that allows solubility to be predicted is reported.

1072

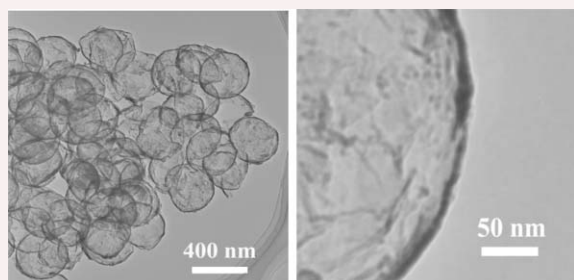
Conversion of alcohols into *N*-alkyl anilines via an indirect aza-Wittig reaction

Gerta Cami-Kobeci and Jonathan M. J. Williams*



Temporary oxidation of alcohols provides the aldehydes required for aza-Wittig reactions. The so-formed imines are reduced to amines under the catalytic reaction conditions.

1074



Ultrathin hollow nanoshells of manganese oxide

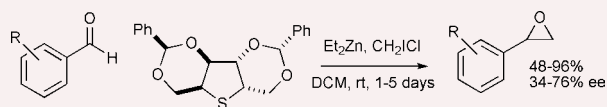
Lianzhou Wang, Yasuo Ebina, Kazunori Takada and Takayoshi Sasaki*

Hollow nanoshells of Mn_2O_3 with controllable thickness in the range 10–15 nm have been fabricated *via* layer-by-layer assembly of exfoliated MnO_2 nanosheets and polyelectrolytes on sacrificial polymer beads and subsequent calcination. These nanoshells may find applications in the fields of catalysis and electrochemistry.

1076

Sulfonium ylide epoxidation reactions: methylene transfer

Benjamin R. Bellenie and Jonathan M. Goodman*

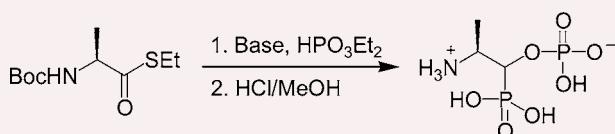


Using a D-mannitol derived chiral sulfide, terminal epoxides are formed in up to 76% ee; the first example of double asymmetric induction in a sulfonium methylene epoxidation is reported and an improved method of generating sulfonium ylides is detailed.

1078

Straightforward synthesis of *gem*-phosphonate-phosphate containing compounds via one-pot reaction of thioesters with diethyl phosphite

Kandasamy Pachamuthu and Richard R. Schmidt*

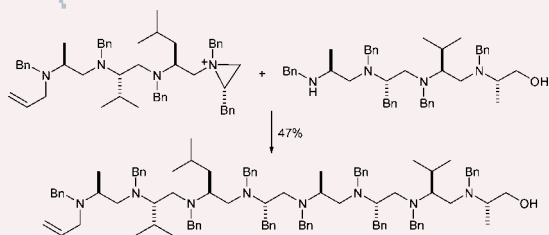


For the title compounds important biological functions have previously been found. Therefore, their efficient one-pot synthesis from thioesters and diethyl phosphite is of great interest.

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An iterative approach to novel polyamines via nucleophilic ring-opening of aziridinium ions with β -amino alcohols

Christopher McKay, Robert J. Wilson and Christopher M. Rayner*

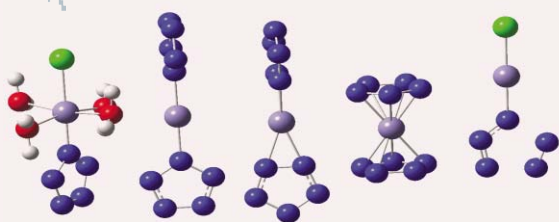


An iterative procedure for the synthesis of a novel class of synthetic polyamines has been developed, utilising the regioselective ring-opening of aziridinium ion intermediates. Facile *N*-allyl deprotection of intermediate polyamines allows the rapid construction of high molecular weight, stereochemically defined compounds in a convergent manner, with potential use in a diverse range of applications.

1082

Consideration of spin states in determining the structure and decomposition of the transition metal pentazoles FeClN_5 , $\text{Fe}(\text{N}_5)_2$, $\text{Fe}(\text{H}_2\text{O})_4\text{ClN}_5$, and $\text{Fe}(\text{NH}_3)_4\text{ClN}_5$

Luke A. Burke* and Paul J. Fazen

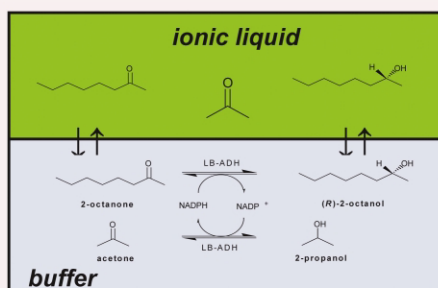


Optimised structures have been calculated for the unidentate, bidentate and ferrocene-like structures of the Fe(II) pentazoles FeClN_5 and $\text{Fe}(\text{N}_5)_2$ in order to study the effect of an unfilled d shell on the stability of the singlet, triplet and quintet states; the ground state is a quintet and has a lower barrier to decomposition than the singlet.

1084

Use of an ionic liquid in a two-phase system to improve an alcohol dehydrogenase catalysed reduction

Marrit Eckstein, Murillo Villela Filho, Andreas Liese and Udo Kragl*



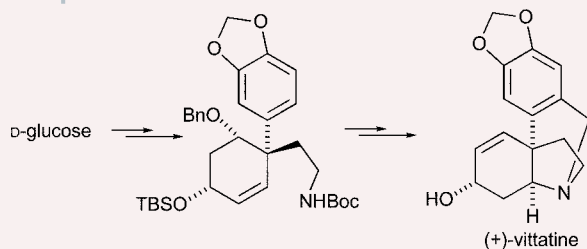
Due to favourable partition coefficients the highly enantioselective reduction of 2-octanone, catalysed by an alcohol dehydrogenase from *Lactobacillus brevis*, is faster in a biphasic system containing buffer and the ionic liquid [BMIM][$(\text{CF}_3\text{SO}_2)_2\text{N}$] compared to the reduction in a biphasic system containing buffer and methyl *tert*-butyl ether.

1086

A new entry to *Amaryllidaceae* alkaloids from carbohydrates: total synthesis of (+)-vittatine

Masahiro Bohno, Hidetomo Imase and Noritaka Chida*

The stereoselective and chiral synthesis of the *Amaryllidaceae* alkaloid, (+)-vittatine, starting from D-glucose is described.

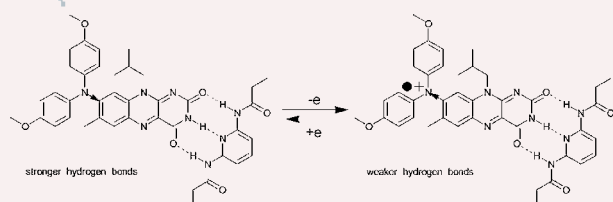


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Model systems for flavoenzyme activity: an electrochemically tuneable model of roseoflavin

Graeme Cooke,* Yves-Marie Legrand and Vincent M. Rotello

The electrochemically tuneable hydrogen bonding interactions between a roseoflavin analogue and an apoenzyme mimic are described.

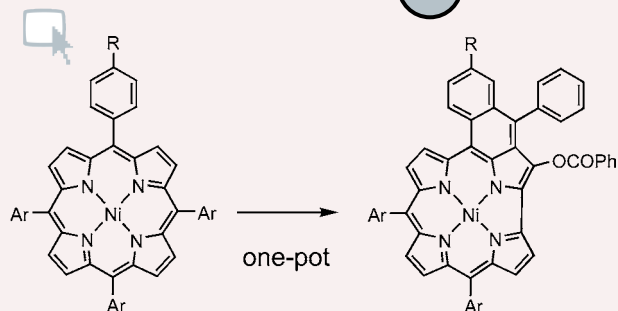


1090

Porphyrin ring contraction: a one-pot reaction leading to divalent corroles

Christophe Jeandon, Romain Ruppert and Henry J. Callot*

On reaction with benzoic anhydride and tin tetrachloride, followed by air oxidation under basic conditions, *meso*-tetraarylporphyrins ring contract to give novel non-aromatic divalent corroles.

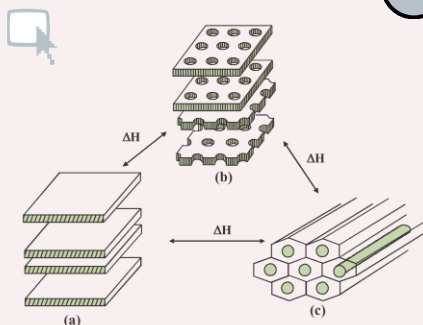


1092

Organization of branched rod-coil molecules into a 3-D tetragonally perforated lamellar mesophase

Nam-Keun Oh, Wang-Cheol Zin,* Jun-Hwan Im, Ja-Hyoung Ryu and Myongssoo Lee*

Tetramerization of coil-rod-coil ABC triblock copolymers to a tetrabranch molecule induces an unusual 3-D tetragonally perforated layered liquid crystalline phase (b) as an intermediate structure between 1-D lamellar (a) and 2-D hexagonal columnar (c) phases.

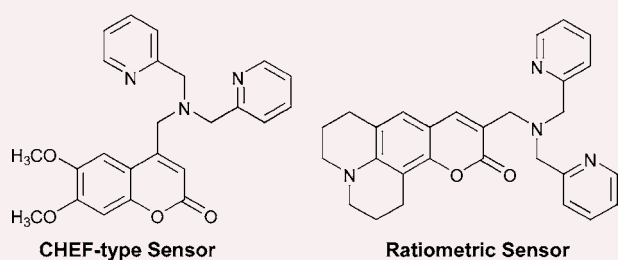


1094

DPA-substituted coumarins as chemosensors for zinc(II): modulation of the chemosensory characteristics by variation of the position of the chelate on the coumarin

Nathaniel C. Lim and Christian Brückner*

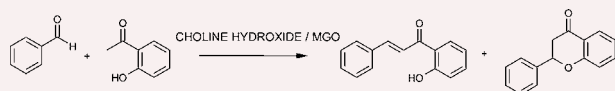
The sensory capabilities of two DPA-substituted coumarins are described; variation of the point of attachment of the DPA group to the coumarin framework switches a chelation-enhanced fluorescence-type sensor to a ratiometric sensor.



1096

Supported choline hydroxide (ionic liquid) as heterogeneous catalyst for aldol condensation reactions

Sònia Abelló, Francisco Medina,* Xavier Rodríguez, Yolanda Cesteros, Pilar Salagre, Jesús E. Sueiras, Didier Tichit and Bernard Coq

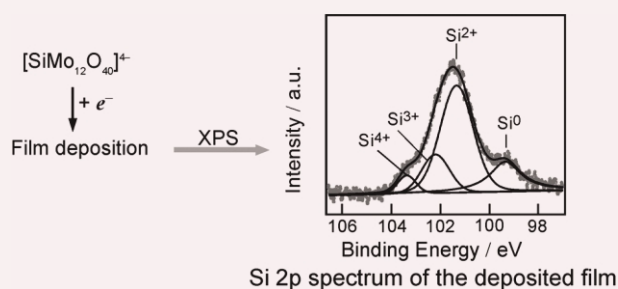


A new heterogeneous catalyst based on an ionic liquid (choline hydroxide) supported on MgO has been developed and applied with high performance to several aldol condensations between aldehydes and ketones.

1098

Involvement of heteroatoms in charge transfer of Keggin-type heteropolyanion

Masaharu Nakayama,* Takahiro Ii, Hiroyuki Komatsu and Kotaro Ogura

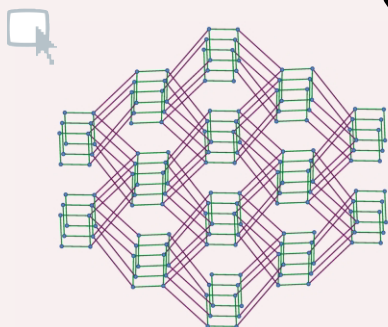


Spectroscopic properties of an electrochemically deposited film from a Keggin-type $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$ solution indicate that electron transfer takes place not only on polyatoms but also on heteroatoms of silicon.

1100

Two mixed-valence copper(I,II) imidazolate coordination polymers: metal-valence tuning approach for new topological structures

Xiao-Chun Huang, Jie-Peng Zhang, Yan-Yong Lin, Xiao-Lan Yu and Xiao-Ming Chen*

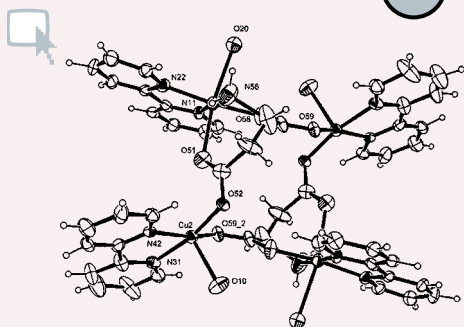


The two new mixed-valence Cu(I,II) coordination polymers $\text{Cu}_2(\text{im})_3$ and $\text{Cu}_3(\text{im})_4$ (Him = imidazole) were obtained by different hydrothermal conditions, which exhibit different Cu(I) and Cu(II) ratios, and an unprecedented uninodal 4-connected 4.8^5 net (see below) and a 4-connected (4,4) net, respectively.

1102

A new tetrameric Cu^{II} cluster with square topology exhibiting ferro- and antiferromagnetic magnetic pathways : which is which?

Mau Sinha Ray, Ashutosh Ghosh,* Ansuman Das, Michael G. B. Drew, Jordi Ribas-Ariño, Juan Novoa and Joan Ribas*

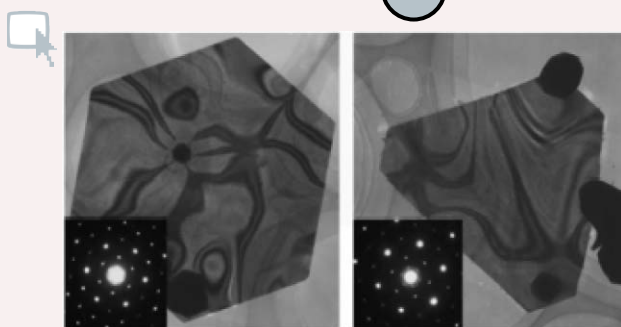


The new tetranuclear Cu^{II} cluster, $[\text{Cu}_4\text{L}_2(\text{bpy})_4(\text{H}_2\text{O})_3](\text{ClO}_4)_4 \cdot 2.5\text{H}_2\text{O}$ shows a peculiar magnetic behavior: one side is ferromagnetic and the other antiferromagnetic. But which is which? DFT calculations are necessary to assign each part.

1104

Synthesis of gold nanoplates by aspartate reduction of gold chloride

Yong Shao, Yongdong Jin and Shaojun Dong*



Gold crystal morphology is regulated by L-amino acids. Gold nanoplates with hexagonal and truncated triangular shapes can be induced in large quantities by aspartate. This is the first report on the production of large planar gold nanocrystals by biologically related small molecules.

1106

Synthesis of silver nanotubes by electroless deposition in porous anodic aluminium oxide templates

Shu-Hong Zhang, Zhao-Xiong Xie,* Zhi-Yuan Jiang, Xin Xu, Juan Xiang, Rong-Bin Huang and Lan-Sun Zheng

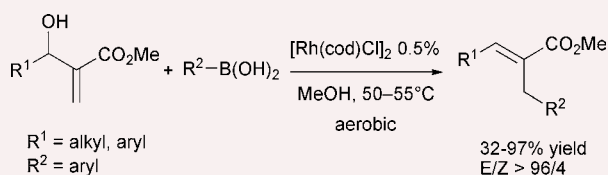


An electroless deposition method has been employed for the synthesis of silver nanotubes using porous anodic aluminium oxide as templates, by which high-yield silver nanotubes have been synthesized.

1108

Baylis–Hillman adducts in rhodium-catalyzed 1,4-additions: unusual reactivity

Laure Navarre, Sylvain Darses* and Jean-Pierre Genet*

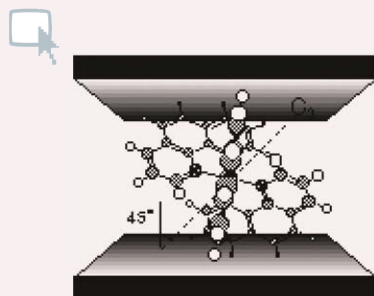


In the presence of a rhodium catalyst, unactivated Baylis–Hillman adducts reacted with arylboronic acids to afford trisubstituted alkenes with good yields. This highly efficient reaction (aerobic conditions, low temperature) is believed to proceed via an unexpected mechanism involving 1,4-addition/ β -hydroxy elimination steps and not π -allyl type rhodium intermediates.

1110

Two-dimensional molecular ordering of Os(II) complexes in organo-clay hybrid ultrathin films

Yasushi Umemura* and Emi Shinohara

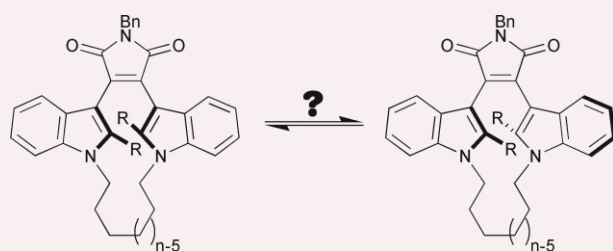


This communication describes the first example of a hybrid thin film of Os(II) complex, clay and alkylammonium cation which gives diffraction peaks arising from the monomolecular layer of the complex in the in-plane XRD pattern. Together with polarized electronic spectral data, the packing structure of the complex in the film is discussed.

1112

Towards configurationally stable bisindolylmaleimide cyclophanes: potential tools for investigating protein kinase function

Stephen Bartlett and Adam Nelson*

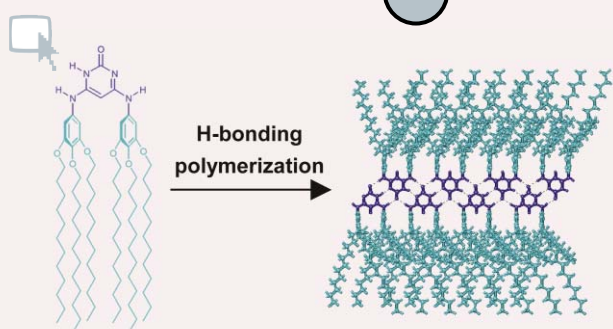


The effect of macrocycle size and substitution on the configurational stability of some bisindolylmaleimide cyclophanes was determined.

1114

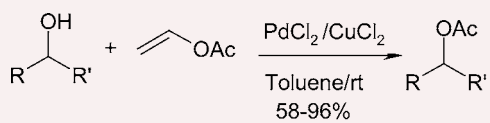
Synthesis and noncovalent polymerization of self-complementary hydrogen-bonding supramolecular synthons: *N,N'*-disubstituted 4,6-diamino-pyrimidin-2(1*H*)-ones

Shiki Yagai,* Tomoyuki Iwashima, Takashi Karatsu and Akihide Kitamura



Facile synthesis and solution-state self-assembling properties of diaminopyrimidinone derivatives are described. The supramolecular synthons self-assembled in nonpolar solvents by self-complementary DDA·AAD hydrogen-bonding, affording linear, rigid and robust molecular arrays.

1116



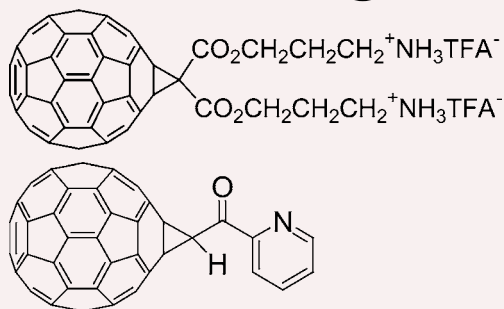
where R=R'= H, alkyl, aryl

Palladium(II) chloride catalyzed selective acetylation of alcohols with vinyl acetate

J. W. J. Bosco and Anil K. Saikia*

Palladium-catalysed acetylation of alcohols is described, which selectively converts primary and secondary alcohols into acetates with high yields under mild conditions.

1118

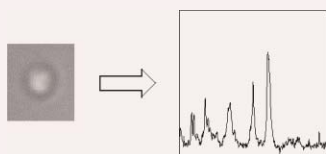


Ligand effects on the electrochemical and spectroscopic behaviors of methano[60]fullerene derivatives

Fengjun Deng, Guan-Wu Wang, Ting-Hu Zhang, Li-Juan Jiao and Shaowei Chen*

Quite drastic effects of the ligand chemical structures on the electronic energy properties of two methano[60]fullerene derivatives were observed voltammetrically and spectroscopically.

1120

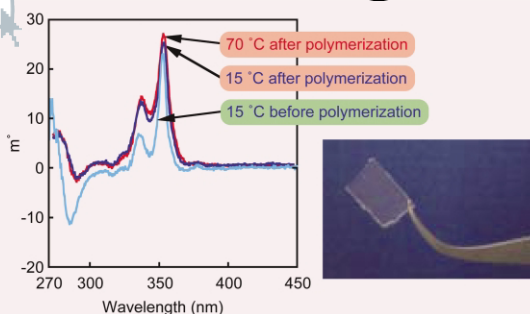


Analysis of liposomal membrane composition using Raman tweezers

John M. Sanderson* and Andrew D. Ward*

A method is described for analysing the membrane of a single liposome using Raman microscopy combined with optical tweezers. Using the method, we are able to identify solutes that partition into the membrane and determine bilayer lipid composition.

1122



Stabilization of enhanced chirality from pyrene-containing L-glutamide lipid in methyl methacrylate by photo-induced polymerization

Makoto Takafuji,* Arata Ishiodori, Taisuke Yamada, Toshihiko Sakurai and Hirotaka Ihara*

Enhanced CD spectra based on chirally-oriented structures of pyrene-containing L-glutamic acid-derived lipid were observed in polymerizable monomers. The transparent solid sheet was obtained by photo-induced polymerization of the monomer solvents and the CD strength was maintained after photo-induced polymerization.

1124

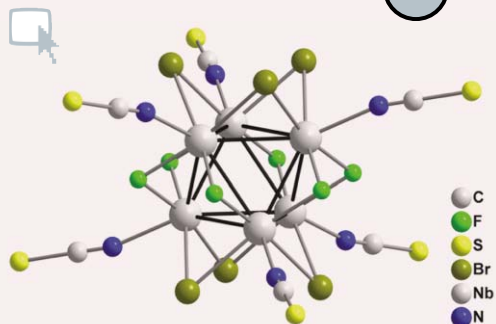


Palladium-catalysed coupling reaction of allenic alcohols with aryl- and alkenylboronic acids

Masahiro Yoshida,* Takahiro Gotou and Masataka Ihara*

The direct coupling of aryl- and alkenylboronic acids with allenic alcohols has been achieved using a palladium catalyst.

1126



Soluble μ -Fⁱ bridged niobium clusters: synthesis and crystal structures of (Et₄N)₆[Nb₆Fⁱ₆Brⁱ₆(NCS)^a]₆Br₂ and Cs_{1,6}K_{2,4}[Nb₆Fⁱ₆Iⁱ₆(NCS)^a]

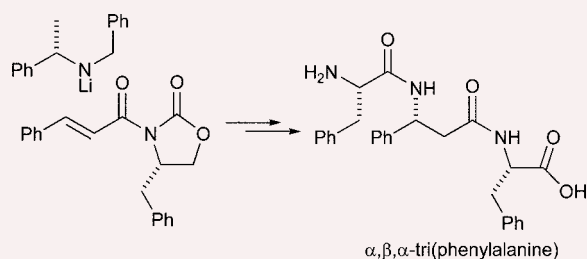
Nikolaï G. Naumov, Stéphane Cordier* and Christiane Perrin

Two new anions [Nb₆Fⁱ₆Xⁱ₆(NCS)^a]₆⁴⁻ (X = Br, I) based on octahedral niobium clusters with edge-bridging F ligands have been prepared by reaction of Cs₃Nb₆F₆Br₁₂ and Cs₄Nb₆F_{8.5}I_{9.5} with aqueous solution of KSCN.

1128

Double asymmetric induction as a mechanistic probe: conjugate addition for the asymmetric synthesis of a pseudotriptide

Stephen G. Davies,* Gesine J. Hermann, Miles J. Sweet and Andrew D. Smith

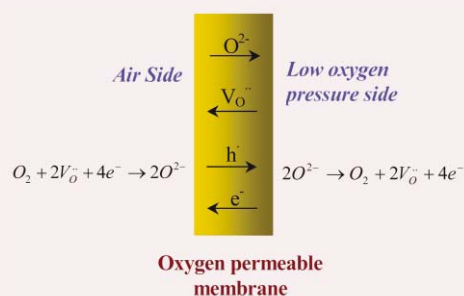


Double asymmetric induction as a mechanistic probe establishes that, for the conjugate addition of (*R*)- and (*S*)-lithium *N*-benzyl-*N*-α-methylbenzylamide to (*S*)-3'-phenylprop-2'-enoyl-4-benzyloxazolidinone, the reactive conformation of the *N*-acyl oxazolidinone is the *anti-s-cis* form.

1130

Novel cobalt-free oxygen permeable membrane

Xuefeng Zhu, Haihui Wang and Weishen Yang*

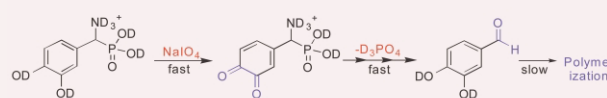


Membranes of the series BaCe_xFe_{1-x}O_{3-δ} avoid the use of expensive metals and cobalt, but possess high oxygen permeation fluxes and high stability under reducing environments.

1132

First example of the chemical, oxidative cleavage of the C–P bond in aminophosphonate chemistry. The oxidation of 1-amino-1-(3,4-dihydroxyphenyl)methylphosphonic acid by NaIO₄

Marcin Drąg, Adam Jezierski and Pawel Kafarski*

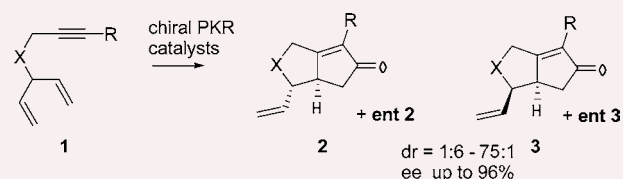


The first example of the chemical, oxidative cleavage of the C–P bond in aminophosphonate chemistry is reported, where the behavior of 1-amino-1-(3,4-dihydroxyphenyl)methylphosphonic acid upon the action of NaIO₄ have been investigated by NMR, EPR and UV-Vis spectroscopy in acidic and basic conditions.

1134

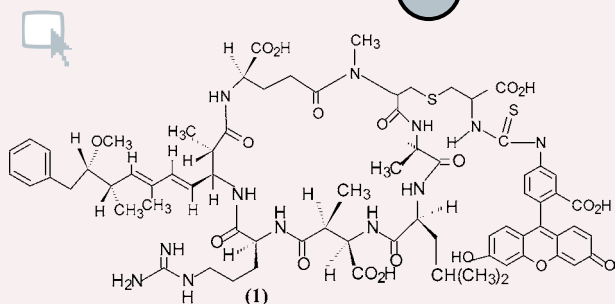
Desymmetrization of *meso*-dienyne by asymmetric Pauson–Khand type reaction catalysts

Nakcheol Jeong,* Dong Hoon Kim and Jun Hun Choi



Desymmetrization of the *meso* dienyne (**1**) by asymmetric Pauson–Khand type reaction catalysts provided the corresponding vinyl substituted bicyclic pentenones (**2** and **3**) in high enantioselectivity as well as diastereoselectivity.

1136

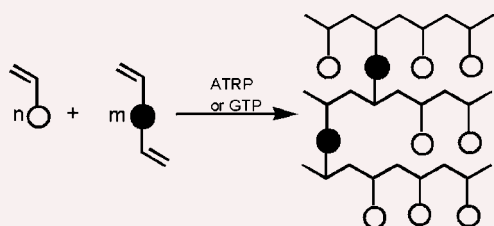


Novel fluorescent biosensor for pathogenic toxins using cyclic polypeptide conjugates

Omowunmi A. Sadik* and Fei Yan

Synthesis of a new fluorescent analog of microcystin-LR and its utilization for the development of an optical biosensor for cyanobacteria toxins.

1138

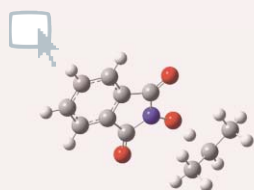


Synthesis of branched poly(methyl methacrylate)s via controlled/living polymerisations exploiting ethylene glycol dimethacrylate as branching agent

Francoise Isaure, Peter A. G. Cormack, Susan Graham, David C. Sherrington,* Steven P. Armes and Vural Bütün

Currently there is enormous scientific and technological interest in branched macromolecules but there remains a desperate need for novel, generic and cost-effective routes to branched vinyl polymers. The use of controlled/living polymerisations to synthesise branched polymers simply by exploiting appropriate levels of divinyl comonomers represents an important advance in methodology.

1140



TS for
 $\text{PINO}^\bullet + \text{RH} \rightarrow \text{NHPI} + \text{R}^\bullet$ (1)
 $E_{act} \approx 80 \text{ kJ/mol}$



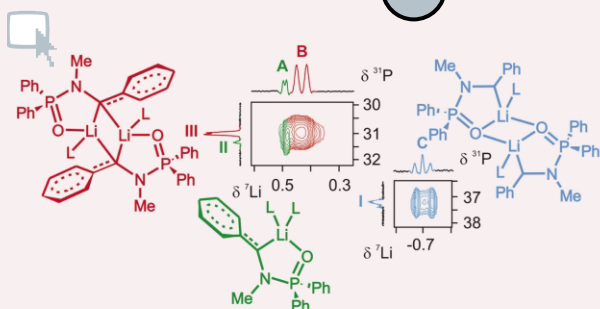
TS for
 $\text{NHPI} + \text{ROO}^\bullet \rightleftharpoons \text{PINO}^\bullet + \text{ROOH}$ (2)
 $E_{act} \leq 20 \text{ kJ/mol}$

Mechanism of the catalytic oxidation of hydrocarbons by N-hydroxyphthalimide: a theoretical study

Ive Hermans,* Luc Vereecken, Pierre A. Jacobs and Jozef Peeters

Quantum chemical calculations shine new light on the catalytic mechanism, revealing that reaction (2) is a fast equilibrium, shifted towards PINO[•], which is a highly efficient chain-propagating radical.

1142

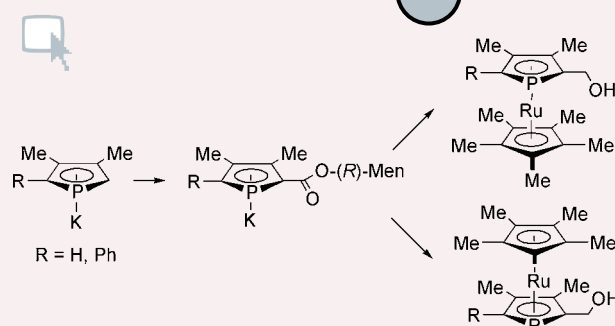


⁷Li, ³¹P Shift correlation. Application to the structural assignment of benzyl lithium complexes of N-methyl-N-benzylphosphinamide

Ignacio Fernández and Fernando López Ortiz*

⁷Li, ³¹P Shift correlation through scalar coupling is reported as a new tool for the structural elucidation of non-labelled lithium organophosphorus compounds in solution. Its applicability is shown with the identification of the benzylic anions resulting from the lithiation of Ph₂P(O)N(Me)CH₂Ph in diethyl ether.

1144



Synthesis and resolution of the planar chirality of ester-functionalised phospharuthenocenes

Duncan Carmichael,* Jürgen Klankermayer, Louis Ricard and Nicolas Seeboth

A base-induced [1,5] sigmatropic shift-coordination sequence transforms simple phospholides into unencumbered phospharuthenocenoyl menthyl esters. Separation and reduction provide multigram quantities of enantiopure phospharuthenocenemethanols.

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