**Cover (far left)**

A porphyrin dodecamer and the lamellar arrays formed by self-assembly of the zinc derivative on addition of the bidentate ligand DABCO.

Inside cover (left)

The sequence of events in atomic pair distribution function analysis of X-ray and neutron powder diffracton data for the structural characterisation of disordered materials.



Chemical biology articles published in this journal also appear in the *Chemical Biology Virtual Journal*:
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contents

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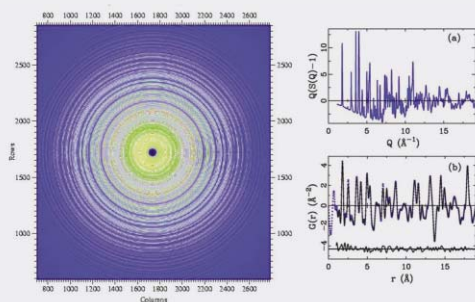
Chemical Science

April 2004/Volume 1/Issue 4
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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

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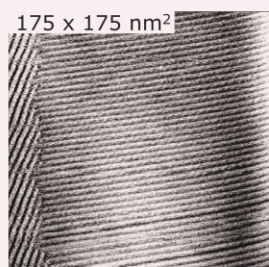
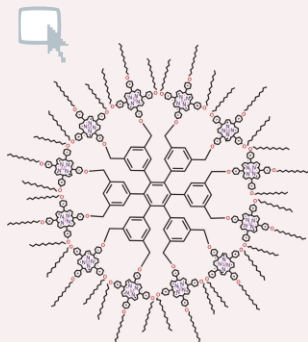
**Beyond crystallography: the study of disorder, nanocrystallinity and crystallographically challenged materials with pair distribution functions**

Simon J. L. Billinge and M. G. Kanatzidis

Some of the more spectacular successes of atomic pair distribution function (PDF) analysis of powder diffraction data in studying the structure of complex materials and compounds.

COMMUNICATIONS

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**Synthesis and self-assembly of giant porphyrin discs**

Marga C. Lensen, Sandra J. T. van Dingenen, Johannes A. A. W. Elemans,* Harm P. Dijkstra, Gerard P. M. van Klink, Gerard van Koten, Jan W. Gerritsen, Sylvia Speller, Roeland J. M. Nolte and Alan E. Rowan*

A giant porphyrin disc ($M_w = 15$ kDa) has been synthesized and its self-assembly behaviour at an interface studied by liquid STM which reveals the presence of huge domains of highly ordered and molecularly resolved columnar stacks.

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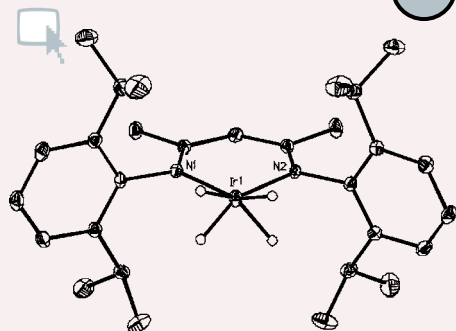
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Synthesis of a β -diimine iridium tetrahydride for arene C–H bond activation

Wesley H. Bernskoetter, Emil Lobkovsky and Paul J. Chirik*

Coordination of a sterically demanding β -diimine ligand to iridium allows facile synthesis of an iridium(V) tetrahydride that promotes catalytic arene activation at ambient temperature.

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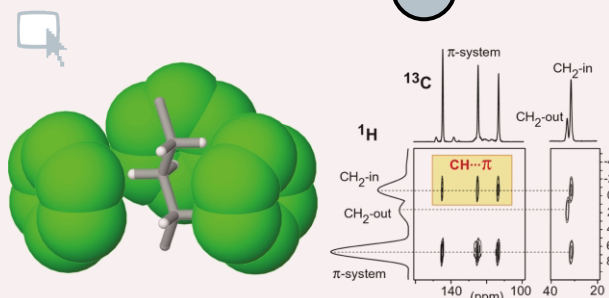


Molecular satellite dishes: attaching parabolic and planar arenes to heterofullerenes

Frank Hauke, Stefan Atalick, Dirk M. Guldi,* James Mack, Lawrence T. Scott* and Andreas Hirsch*

The first examples of molecular architectures that involve only a polycyclic aromatic hydrocarbon and a fullerene core connected by one single bond are presented. The polycyclic aromatic serves as a 'molecular satellite dish', collecting radiation and transmitting it unidirectionally to the fullerene body.

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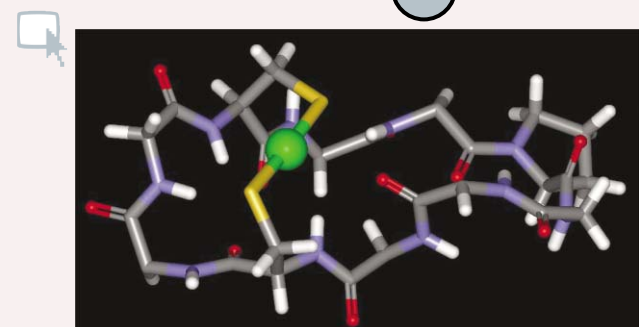


Cooperation of multiple $\text{CH}\cdots\pi$ interactions to stabilize polymers in aromatic nanochannels as indicated by 2D solid state NMR

Piero Sozzani,* Angiolina Comotti, Silvia Bracco and Roberto Simonutti

Polymers encased in aromatic supramolecular nanochannels are stabilized in the extended conformation by multiple $\text{CH}\cdots\pi$ interactions. Their protons undergo large NMR upfield shifts and close contacts with host carbons in the robust nanocomposites.

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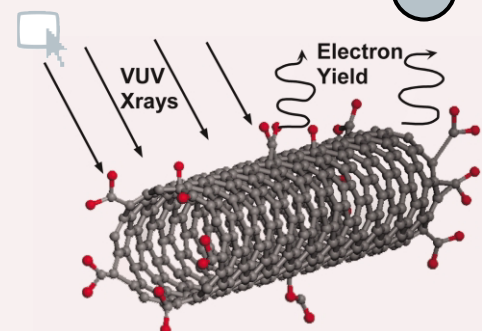


Novel model peptide for Atx1-like metallochaperones

Olivier S n que, Serge Crouzy, Didier Boturyn, Pascal Dumy, Michel Ferrand and Pascale Delangle*

The cyclodecapeptide $\text{c}(\text{GMTCSGCSR})$ binds selectively Hg^{2+} and Cu^+ over Pb^{2+} , Cd^{2+} and Zn^{2+} , and provides a promising structural model of the binding loop of the copper metallochaperone Atx1.

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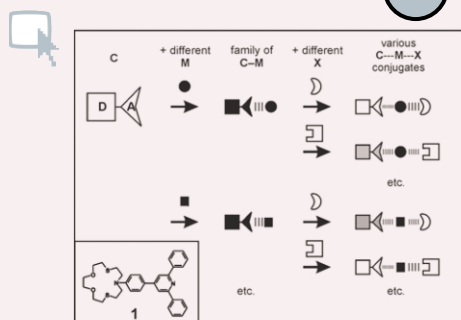


Ozonized single-walled carbon nanotubes investigated using NEXAFS spectroscopy

Sarbajit Banerjee, Tirandai Hemraj-Benny, Mahalingam Balasubramanian, Daniel A. Fischer, James A. Misewich and Stanislaus S. Wong*

Near Edge X-Ray Absorption Fine Structure (NEXAFS) spectroscopy is demonstrated as a useful tool to simultaneously gauge the level of oxidation and of structural modification made upon chemical functionalization of single-walled carbon nanotubes.

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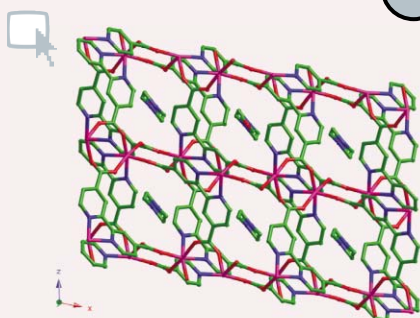


Coordinative and electrostatic forces in action: from the design of differential chromogenic anion sensors to selective carboxylate recognition

Beatriz García-Acosta, Xavier Albiach-Martí, Eduardo García, Luis Gil, Ramón Martínez-Mañez,* Knut Rurack,* Félix Sancenón and Juan Soto

A new family of differential chromogenic anion chemosensors is described based on anilinyridine–metal cation coordinative signalling ensembles.

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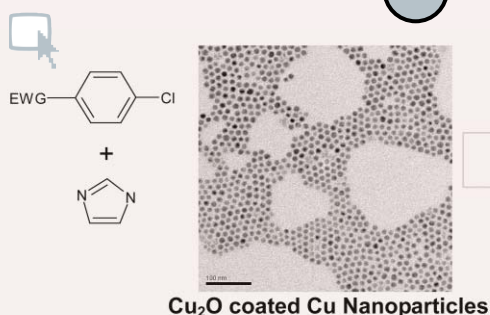


Solvent templated synthesis of metal–organic frameworks: structural characterisation and properties of the 3D network isomers {[Mn(dcbp)]·12DMF}_n and {[Mn(dcbp)]·2H₂O}_n

Eithne Tynan, Paul Jensen, Paul E. Kruger* and Anthea C. Lees

The reaction of MnCl₂ and 4,4'-dicarboxy-2,2'-bipyridine (H₂dcbp) under solvothermal conditions yields robust isomeric MOFs, the identity of which is directly dependent upon the solvent employed. Their disparate physical properties are described

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Synthesis of Cu₂O coated Cu nanoparticles and their successful applications to Ullmann-type amination coupling reactions of aryl chlorides

Seung Uk Son, In Kyu Park, Jongnam Park and Taeghwan Hyeon*

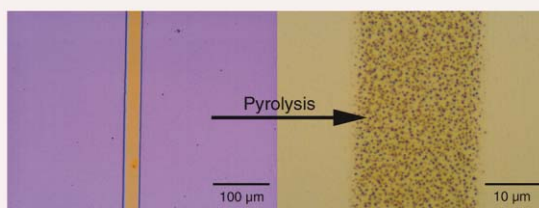
We synthesized uniform Cu₂O coated Cu nanoparticles from the thermal decomposition of copper acetylacetonate followed by air oxidation and used these nanoparticles as catalysts for Ullmann type amination coupling reactions of aryl chlorides.

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UV photopatterning of a highly metallized, cluster-containing poly(ferrocenylsilane)

Alison Y. Cheng, Scott B. Clendenning, Guocheng Yang, Zheng-Hong Lu, Christopher M. Yip and Ian Manners*

UV photolithography using thin films of a cobalt-clusterized poly(ferrocenylsilane) as a negative-tone resist provides a convenient route for the deposition of patterned polymer and magnetic ceramic onto flat substrates with excellent lateral shape retention.

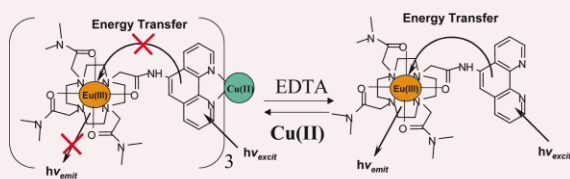


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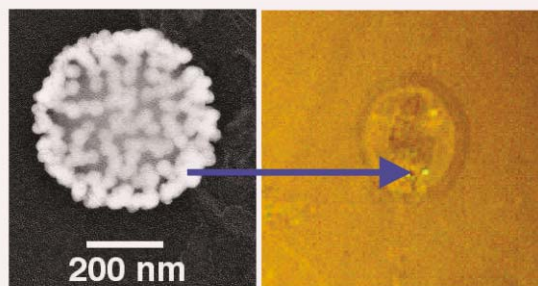
Eu(III)–cyclen–phen conjugate as a luminescent copper sensor: the formation of mixed polymetallic macrocyclic complexes in water

Thorfinnur Gunnlaugsson,* Joseph P. Leonard, Katell Sénéchal and Andrew J. Harte

The Eu(III) emission of the Eu(III)–cyclen–phen conjugate **1·Eu** is 'switched off' upon coordination to Cu(II) in pH 7.4 buffered water, signifying the recognition of Cu(II) by the phen ligand and the formation of a polymetallic macrocyclic supramolecular complex in solution. Upon addition of EDTA, the emission is 'switched back on' demonstrating the reversibility of this recognition event.



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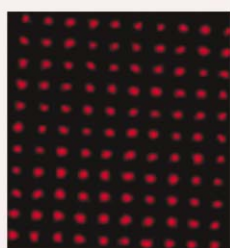


Nanoprobe implantation into mammalian cells by cationic transfection

Yan Zhao, Bryce Sadtler, Min Lin, Gregory H. Hockerman and Alexander Wei*

Submicron-sized gold particles and gold/silica nanocomposites can be introduced into mammalian cells by cationic liposomal transfection systems with minimal cell trauma. This mechanism is mild and should serve as a general intracellular delivery method for nano- and submicron-sized objects.

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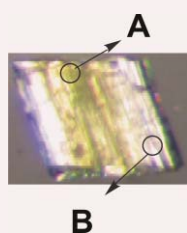


Patterning of DNA nanostructures on silicon surface by electron beam lithography of self-assembled monolayer

Guo-Jun Zhang,* Takashi Tanii, Takashi Funatsu and Iwao Ohdomari

Nanoscale patterns of modified oligonucleotides are produced on octadecyltrimethoxysilane self-assembled monolayers at a silicon surface by electron beam lithography. DNA structures with feature sizes on the order of 250 nm were detected by epi-fluorescence microscopy.

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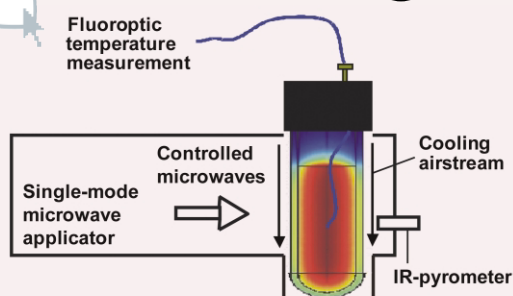


Crystalline molecular alloys

Sylvie Ferlay and Wais Hosseini*

The 3-D epitaxial growth of two almost identical crystalline systems composed of 2-D H-bonded networks generates crystalline molecular alloys.

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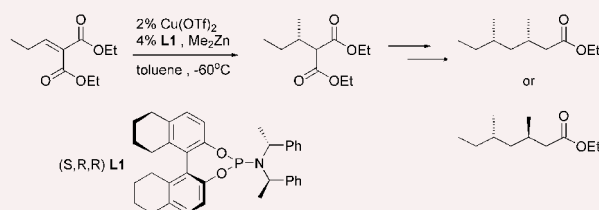


An efficient method to perform milliliter-scale PCR utilizing highly controlled microwave thermocycling

Kristina Orrling, Peter Nilsson, Mats Gullberg* and Mats Larhed*

The combination of controlled microwave thermocycling and air-jet cooling permits an amplifications efficiency of close to 100% in a 15 mL PCR reaction. Thus, it was concluded that correct microwave heating does not reduce the enzymatic function of the Taq polymerase.

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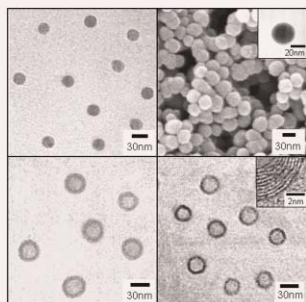


A catalytic and iterative route to β -substituted esters via highly enantioselective conjugate addition of dimethylzinc to unsaturated malonates

Julia Schuppan, Adriaan J. Minnaard and Ben L. Feringa*

Unprecedented enantioselectivities of up to 98% have been obtained using a chiral phosphoramidite ligand in the conjugate addition of dimethylzinc to acyclic unsaturated malonates. Based on this asymmetric catalysis, an iterative and stereodivergent route to 3,5-dimethyl esters has been developed.

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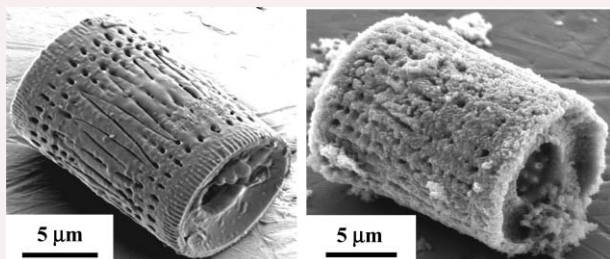


Facile fabrication of polymer and carbon nanocapsules using polypyrrole core/shell nanomaterials

Jyongsik Jang,* Xiang Li Li and Joon Hak Oh

Linear/crosslinked core/shell nanospheres composed of only polypyrroles (PPys) were synthesized by microemulsion polymerization using two oxidants with different chemical oxidation potentials, and used as a precursor for the fabrication of PPy and carbon nanocapsules.

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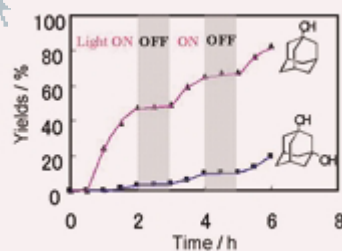


Anatase assemblies from algae: coupling biological self-assembly of 3-D nanoparticle structures with synthetic reaction chemistry

Raymond R. Unocic, Frank M. Zalar, Peter M. Sarosi, Ye Cai and Kenneth H. Sandhage*

The “fossilisation” of biologically self-assembled silica nanostructures by metathesis with TiF_4 to give titania replicas is reported. This approach could potentially be extended to other bioclastic or biomimetic preforms and, further, to synthetic micro/nanoassemblies.

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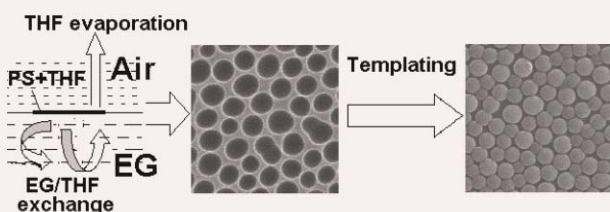


Photoassisted oxygenation of alkane catalyzed by ruthenium complexes using 2,6-dichloropyridine *N*-oxide under visible light irradiation

Motowo Yamaguchi,* Takashi Kumano, Dai Masui and Takamichi Yamagishi

The chloro(Me_2SO)ruthenium(II) complexes with tris(2-pyridylmethyl)amine or its derivative catalyse the selective, stereospecific, and photoregulative alkane oxidation in the presence of 2,6-dichloropyridine *N*-oxide under visible light irradiation.

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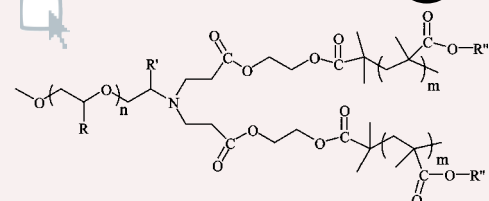


A simple route to micropatterned polymer surfaces

Yong Wang, Zhimin Liu,* Buxing Han,* Haixiang Gao, Jianling Zhang and Xun Kuang

Polymer surfaces with microscale concave arrays were fabricated by a simple route and they can be also used as templates to prepare corresponding convex-patterned polymer surfaces.

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$R, R' = \text{H or CH}_3$;

$R'' = -\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$; $-\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_3)_2$; $-\text{CH}_2\text{CH}(\text{CH}_2\text{OH})_2$

$-\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}$; $-\text{CH}_2\text{CH}_2\text{OH}$

Direct synthesis and aqueous solution properties of Y-shaped, stimulus-responsive block copolymer surfactants

Yuanli Cai, Carine Burguiere and Steven P. Armes*

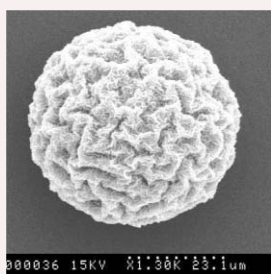
A wide range of well-defined, Y-shaped stimulus-responsive block copolymers are synthesized under mild conditions using Atom Transfer Radical Polymerisation; the reversible micellar self-assembly of these new polymeric surfactants in aqueous solution has been investigated.

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Preparation of metal sulfide–polymer composite microspheres with patterned surface structures

Yu Fang,* Chaoliang Bai and Ying Zhang

Minigels have been employed as templates to prepare metal sulfide–polymer composite microspheres with patterned surface structures.

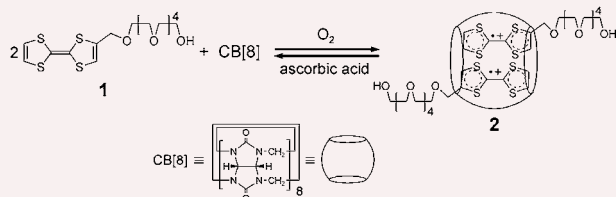


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Stable π -dimer of a tetrathiafulvalene cation radical encapsulated in the cavity of cucurbit[8]uril

Albina Y. Ziganshina, Young Ho Ko, Woo Sung Jeon and Kimoon Kim*

The first stable π -dimer of a tetrathiafulvalene (TTF) cation radical encapsulated in the cavity of cucurbit[8]uril has been isolated at room temperature and fully characterized; it shows absorption bands at 400, 540 and 760 nm, characteristic of the TTF cation radical dimer.

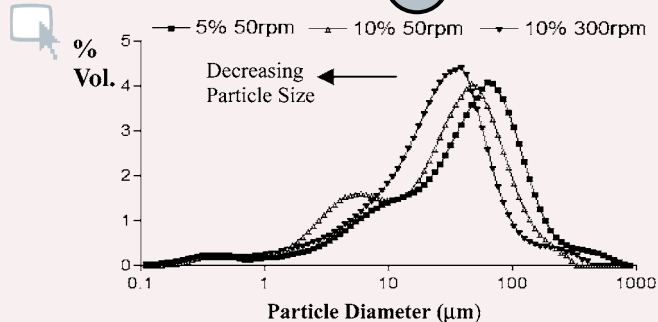


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Synthesis of poly(glycolide) in supercritical carbon dioxide in the presence of a hydrocarbon stabiliser

Daniel Bratton, Malcolm Brown and Steven M. Howdle*

The development of the first inexpensive, non-toxic hydrocarbon stabilisers that are effective for ring opening polymerisation in supercritical carbon dioxide is described.

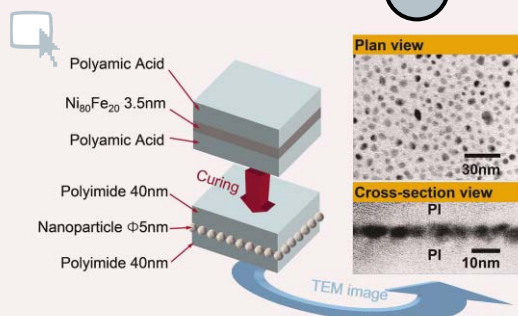


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Fabrication of Ni nanoparticles by selective oxidation of permalloy thin film during imidization of polyamic acid

Sung K. Lim, Chong S. Yoon* and Chang K. Kim

Nanoparticles were fabricated by inserting $\text{Ni}_{80}\text{Fe}_{20}$ thin film between two polyimide precursor layers. Ni nanoparticles were formed as a result of preferential oxidation of Fe in the alloy film during imidization.

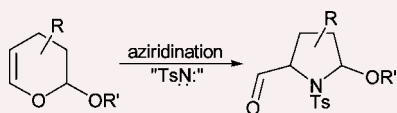


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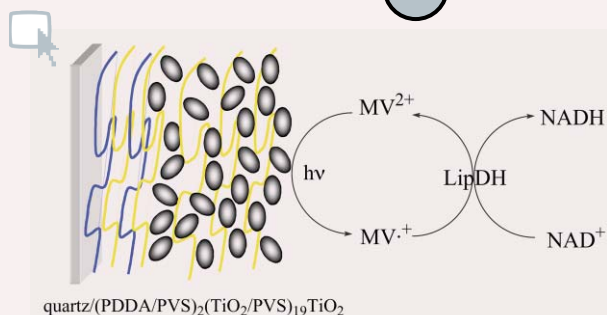
Aminative rearrangement of 2-alkoxy-3,4-dihydro-2H-pyrans: a novel stereocontrolled route to substituted pyrrolidines

Alan Armstrong,* Graham R. Cumming and Kurt Pike

Aziridination of 2-alkoxy-3,4-dihydro-2H-pyrans leads to rearrangement and stereocontrolled formation of 5-alkoxypyrrolidines which may be reduced to pyrrolidines or allylated stereoselectively.



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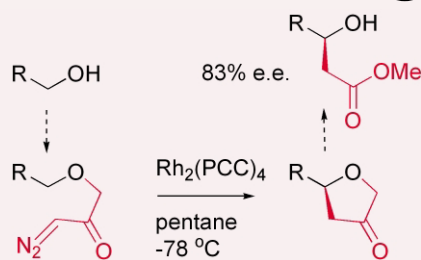


Photosensitized NADH formation system with multilayer TiO₂ film

Takashi Sagawa,* Ryota Sueyoshi, Mikako Kawaguchi, Mayu Kudo, Hiroataka Ihara and Katsutoshi Ohkubo*

In addition to the fabrication and characterization of a TiO₂/polymer film, photocatalysis by the film for the reduction of nicotinamide adenine dinucleotide in the presence of methyl viologen and lipoamide dehydrogenase was investigated.

816



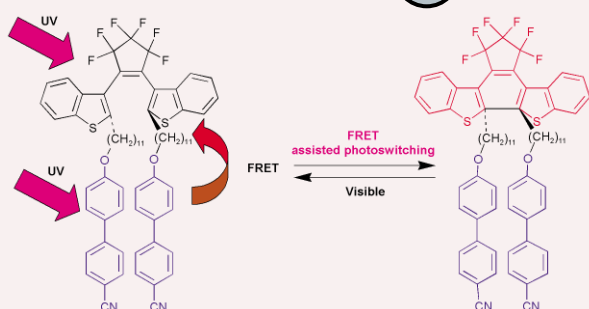
PCC=3-phenylcholestane-2-carboxylate

Asymmetric synthesis of secondary alcohols from primary alcohols via intramolecular carbenoid C–H insertion catalyzed by rhodium(II) 3-phenylcholestane-2-carboxylate

Cheol Hee Hwang, You Hoon Chong, Sue Yeon Song, Hyo Shin Kwak and Eun Lee*

Chiral secondary alcohols may be prepared from primary alcohols via asymmetric C–H insertion reactions of α' -alkoxy- α -diazoketones catalyzed by rhodium(II) (2*R*,3*R*)-3-phenylcholestane-2-carboxylate.

818

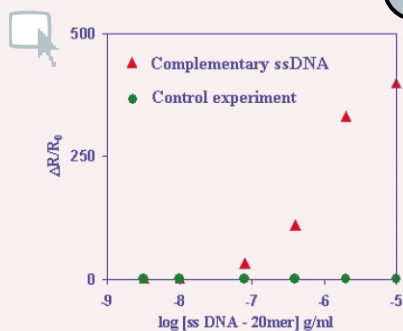


The enhancement of photoswitching in a diarylethene derivative by the incorporation of cyanobiphenyl groups

Michel Frigoli and Georg H. Mehl*

A photochromic liquid crystal system based on a diarylethene core linked to cyanobiphenyl groups was synthesised and the photochromic and mesomorphic behaviour was investigated. The mesogens assist in the photoconversion reaction.

820

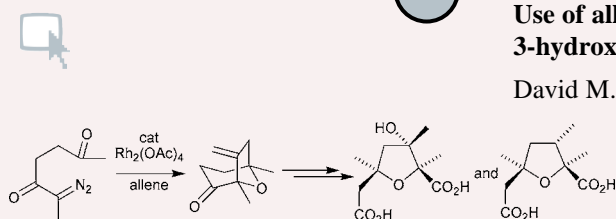


Novel label-free DNA sensors based on poly(3,4-ethylenedioxythiophene)

K. Krishnamoorthy, Rajesh S. Gokhale, Aliasgar Q. Contractor and Anil Kumar*

We report on the design and development of novel label-free DNA sensors based on conducting poly(3,4-ethylenedioxythiophene) for the direct detection and quantification of target ssDNA. These sensors can detect target DNA concentrations as low as 80 ng ml⁻¹ and also the smaller probe ssDNA can detect the longer target ssDNA containing complementary sequence.

822



Use of allene in 1,3-dipolar addition to a carbonyl ylide: syntheses of 3-hydroxy-*cis*-nemorensic acid and nemorensic acid

David M. Hodgson* and Frédéric Le Strat

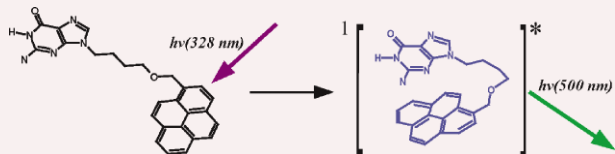
1,3-Dipolar addition of allene to the carbonyl ylide derived from 6-diazoheptane-2,5-dione is the key step in syntheses of 3-hydroxy-*cis*-nemorensic acid and nemorensic acid.

824

Exciplex formation between pyrene and guanine in highly polar solvents

Takahiro Kawai, Masashi Ikegami and Tatsuo Arai*

Guanine derivatives connected to pyrene with methylene spacers exhibited exciplex emission in highly polar solvents.

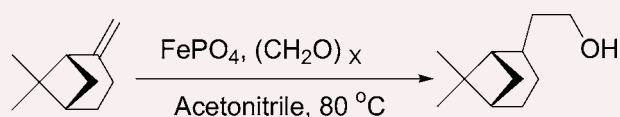


826

Mesoporous iron phosphate as an active, selective and recyclable catalyst for the synthesis of nopol by Prins condensation

Unnikrishnan R. Pillai and Endalkachew Sahle-Demessie*

Mesoporous iron phosphate is a highly active and recyclable heterogeneous catalyst for the selective synthesis of nopol by Prins condensation of β -pinene and paraformaldehyde.

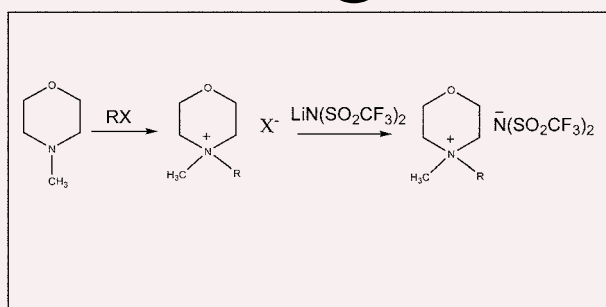


828

Ionic liquids based on *N*-alkyl-*N*-methylmorpholinium salts as potential electrolytes

Ki-Sub Kim, Sukjeong Choi, D. Demberenyamba, Huen Lee,* Jaeseung Oh, Byoung-Bae Lee and Su-Jin Mun

The first examples of a new family of ionic liquids based on *N*-alkyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide have been synthesized and investigated for use as potential electrolytes.

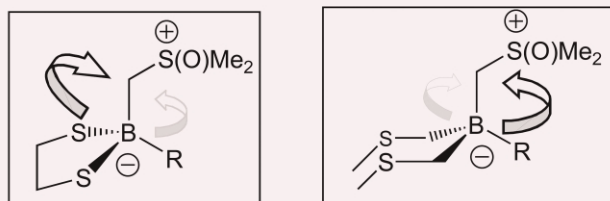


830

On the relative migratory aptitudes of carbon and heteroatoms in borate complexes. A surprising α -thia effect

Jonathan M. Stoddard and Kenneth J. Shea*

The relative migratory aptitudes of borate complexes of dimethylsulfoxonium methylide are $RS > R > RSCH_2$.

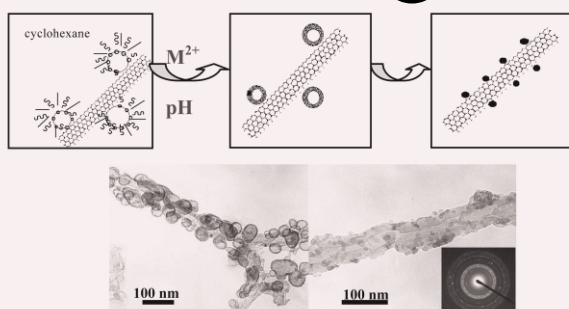


832

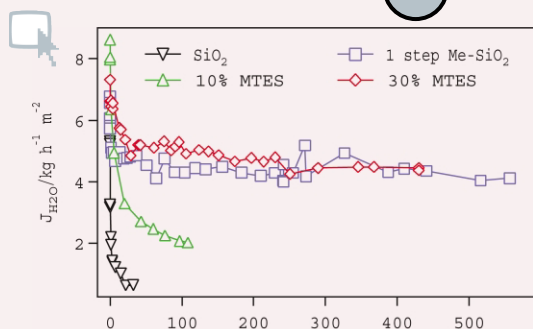
Noncovalent attachment of oxide nanoparticles onto carbon nanotubes using water-in-oil microemulsions

Jing Sun, Lian Gao* and Mikio Iwasa

We report a simple and general method of attaching ZnO and MgO nanoparticles noncovalently onto MWNTs using water-in-oil microemulsions. This approach provides a convenient way to anchor other metal oxides to carbon nanotubes.



834

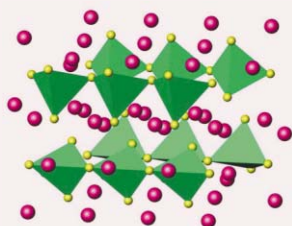


Long-term pervaporation performance of microporous methylated silica membranes

Jean Campaniello, Charles W. R. Engelen, Wim G. Haije, Paul P. A. C. Pex and Jaap F. Vente*

It has been proven for the first time that the incorporation of methyl groups in microporous silica membranes enhances the service time in the dehydration of a butanol–water mixture at 95 °C from a few weeks to more than 18 months. The observed water flux fluctuates between 4 and 5 kg h⁻¹ m⁻², and decreases by only ~7% per year, and the selectivity ranges between 500 and 20 000.

836

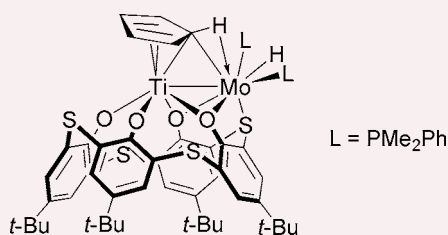


Linear antiferromagnetism in Ba₂CoS₃

T. Baikie, A. Maignan and M. G. Francesconi

Here we describe the preparation and the structural and magnetic properties of Ba₂CoS₃, the first inorganic solid showing one-dimensional corner connectivity between [Co²⁺–anion] tetrahedra. This structural arrangement favours one-dimensional antiferromagnetism. Research on low-dimensional antiferromagnets is related to the investigation of the mechanism of high *T_c* superconductivity.

838

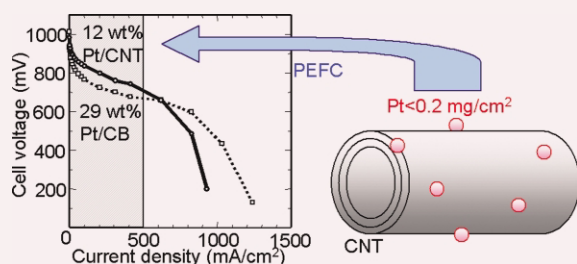


Ti–Mo heterobimetallic thiacalix[4]arene complex containing an unusual α -agostic μ_2 - η^5 : η^2 -cyclopentadienyl ligand

Shin Takemoto, Shinpei Tanaka, Yasushi Mizobe and Masanobu Hidai*

A new Ti–Mo heterobimetallic complex containing a thiacalix[4]arene ligand exhibits an unusual α -agostic μ_2 - η^5 : η^2 -coordination of a cyclopentadienyl ligand.

840



Reduction of Pt usage in fuel cell electrocatalysts with carbon nanotube electrodes

Taketoshi Matsumoto, Toshiki Komatsu, Kazuya Arai, Takahisa Yamazaki, Masashi Kijima, Harukazu Shimizu, Yosuke Takasawa and Junji Nakamura*

The 12 wt% Pt-deposited carbon nanotube electrode gives 10% higher voltages than 29 wt% Pt-deposited carbon black and reduces the Pt usage by 60% in polymer electrolyte fuel cells with hydrogen and oxygen.

842

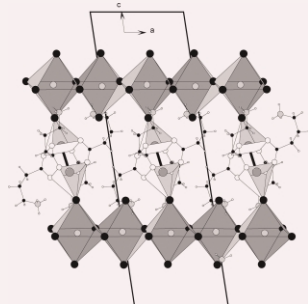


Novel heteroditopic chelate for self-assembled gadolinium(III) complex with high relaxivity

Robert Ruloff, Gerard van Koten and André E. Merbach*

[Fe(tpy-DTTA)₂Gd₂] is a self-assembled trinuclear complex based on a novel ligand in which a terpyridine and a poly(amino carboxylate) moiety are connected; it has a well-defined topology with favourable features to attain high relaxivities.

844

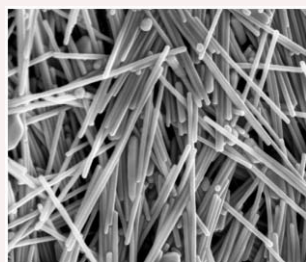


An organic–inorganic hybrid perovskite containing copper paddle-wheel clusters linking perovskite layers : $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$

Nicolas Mercier* and Amédée Riou

The incorporation of $\text{Cu}_2(\text{CO}_2)_4$ clusters, built up from amino carboxylic acid zwitterionic molecules, led both to the stabilization of a layered hybrid perovskite, and to the formation of a covalent bond pathway between adjacent perovskite layers.

846

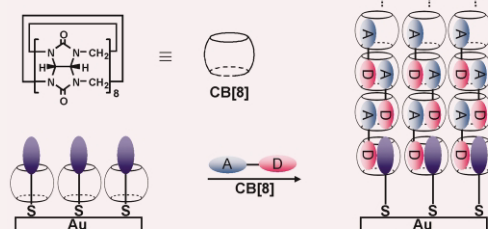


Different morphologies of silver nanoparticles as catalysts for the selective oxidation of styrene in the gas phase

R. J. Chimentão, I. Kirm, F. Medina,* X. Rodríguez, Y. Cesteros, P. Salagre and J. E. Sueiras

Silver nanoparticles with different morphologies obtained from the polyol process show potential application as catalysts for the selective oxidation of styrene in the gas phase.

848

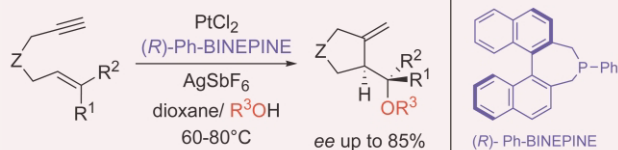


Growth of poly(pseudorotaxane) on gold using host-stabilized charge-transfer interaction

Kyungpil Kim, Dongwoo Kim, Jae Wook Lee, Young Ho Ko and Kimoon Kim*

A novel supramolecular polymer (poly(pseudorotaxane)) in which the repeating units are linked by host-stabilized charge-transfer interaction between the guest molecules is grown on gold and characterized.

850

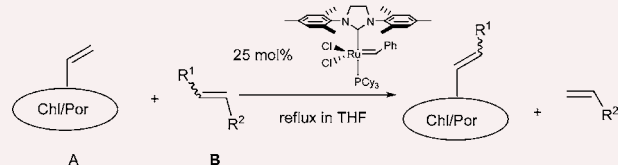


Functionalized carbo- and heterocycles via Pt-catalyzed asymmetric alkoxy cyclization of 1,6-enynes

Lise Charruault, Véronique Michelet,* Rossana Taras, Serafino Gladiali* and Jean-Pierre Genêt*

The combination of silver salts with the Pt(II)/(*R*)-Ph-BINEPINE system afforded high enantioselectivity in the first asymmetric version of the highly atom-economical hydroxycyclization of 1,6-enynes. Functionalized carbo- and heterocycles were efficiently prepared in enantio-enriched form.

852



Cross-metathesis reactions of vinyl-chlorins and -porphyrins catalyzed by a “second generation” Grubbs’ catalyst

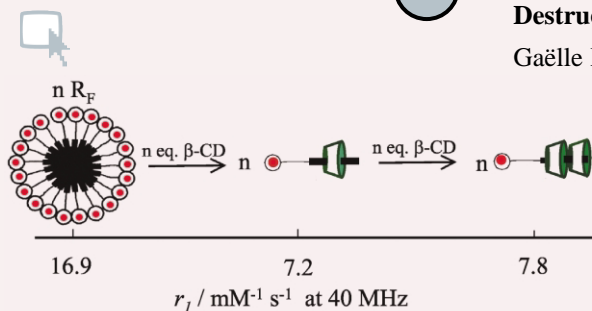
Xin Liu, Ethan Sternberg and David Dolphin*

The first application of olefin cross-metathesis with vinylchlorins and vinylporphyrins using a “second generation” Grubbs’ catalyst is reported. Cross-metathesis products were obtained in good yields with high *E*-stereoselectivity.

854

Destruction of perfluoroalkyl surfactant aggregates by β -cyclodextrin

Gaëlle M. Nicolle and André E. Merbach*

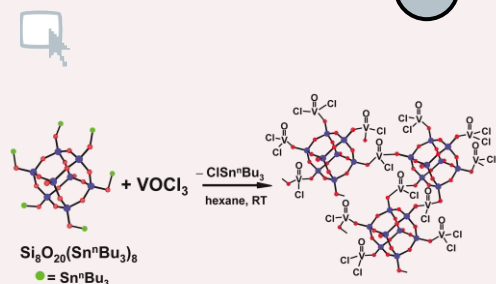


A ^1H NMR relaxivity (r_1) and ^{19}F NMR spectroscopy study reveals the rapid and complete destruction of perfluoroalkyl surfactant micelles upon addition of β -cyclodextrin to form successively 1:1 and 2:1 ($\beta\text{-CD}:\text{R}_\text{F}$) inclusion complexes.

856

Building block syntheses of site-isolated vanadyl groups in silicate oxides

Narendra N. Ghosh, Jason C. Clark, Geoffrey T. Eldridge and Craig E. Barnes*

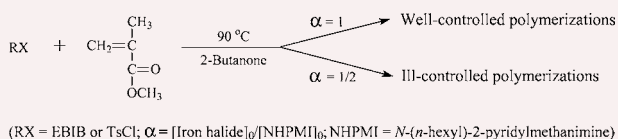


Three dimensional linking of spherosilicate building blocks with VOCl_3 yields nanostructured silicate matrices containing monodispersed vanadyl groups.

858

An efficient iron-based catalyst bearing *N*-alkyl-2-pyridylmethanimine ligand for atom transfer radical polymerisation

Huiqi Zhang and Ulrich S. Schubert*

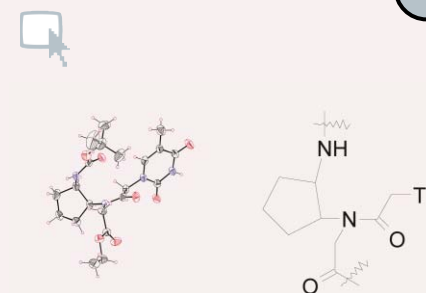


The combination of iron(II) bromide with one equivalent of *N*-(*n*-hexyl)-2-pyridylmethanimine is shown to be an efficient catalyst for the well-controlled atom transfer radical polymerisation of methyl methacrylate.

860

***cis*-Cyclopentyl PNA (*cp*PNA) as constrained chiral PNA analogues: stereochemical dependence of DNA/RNA hybridization**

T. Govindaraju, Vaijayanti A. Kumar* and Krishna N. Ganesh*

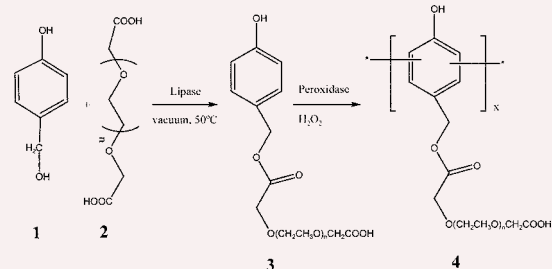


DNA/RNA hybridization studies of PNA-T oligomers with *cis*-(1*S*,2*R*) and (1*R*,2*S*)-cyclopentyl units in the backbone show stereochemistry dependent binding with RNA/DNA discrimination.

862

“Green”-enzymatic synthesis of pegylated phenolic macromer and polymer

Rajesh Kumar, Ferdinando Bruno, Virinder S. Parmar,* Jayant Kumar, Arthur C. Watterson, Kethinni G. Chittibabu and Lynne A. Samuelson*

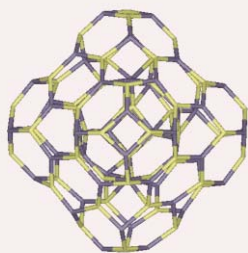


A novel biocatalytic route that incorporates a multi-enzymatic approach (combination of a lipase from *Candida antarctica* and an oxidase, from horseradish) for the synthesis of pegylated polyphenolics has been developed.

864

ZnS bubble clusters with onion-like structures

Eleonora Spanó, Said Hamad* and C. Richard A. Catlow

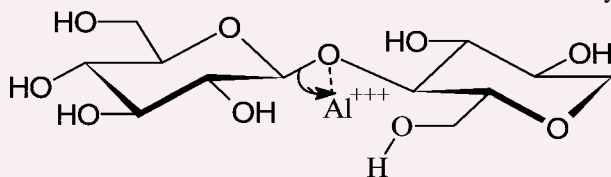


The structure of the $(\text{ZnS})_{60}$ cluster has been studied. The most stable configuration was found to be a “double bubble” or onion-like structure, with one small cluster enclosed inside a bigger one.

866

Efficient electrophilic catalysis of 1,5-anhydrocellobiitol hydrolysis by Al^{III} ; implications for the conservation of “rosin-alum” sized paper

John Baty and Michael L. Sinnott*

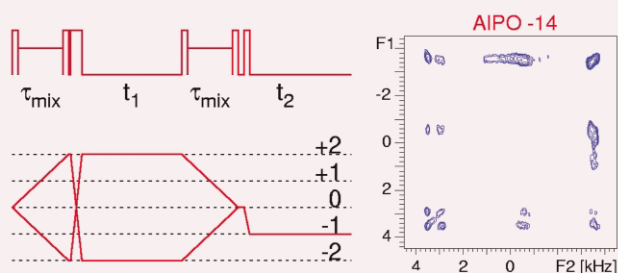


Al_2SO_4 greatly accelerates the hydrolysis of 1,5-anhydrocellobiitol, a model for the $\beta(1\rightarrow4)$ glucan link in cellulose, suggesting that the rapid ageing of “rosin-alum” sized paper arises from the direct action of Al^{III} as an electrophile, not hydrated Al as a source of protons, as previously supposed by paper conservators.

868

Detecting proximities between quadrupolar nuclei by double-quantum NMR

Gregor Mali* and Francis Taulelle

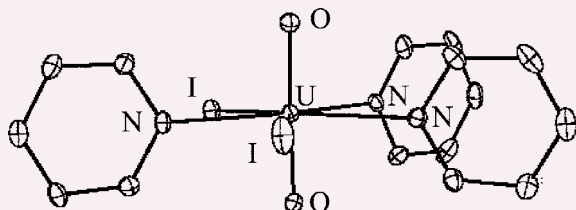


A robust, easy to optimise, and efficient homonuclear correlation NMR experiment for half-integer quadrupolar nuclei in solids is described and tested experimentally on Na_2HPO_4 and the aluminophosphate molecular sieve $\text{AIPO}_4\text{-14}$.

870

Synthesis of the stable UO_2I_2 , the last of the uranyl dihalides. X-Ray crystal structure of $[\text{UO}_2\text{I}_2(\text{py})_3]$

Jean-Claude Berthet,* Martine Nierlich and Michel Ephritikhine

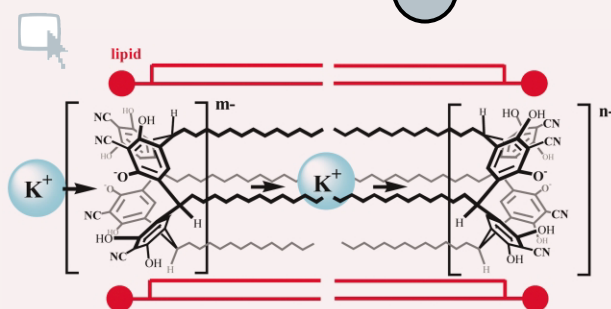


The last remaining dioxouranium dihalide not to have been isolated, UO_2I_2 , has been prepared from uranyl triflate and iodotrimethylsilane. The specific features of the U–I bond mean that UO_2I_2 and its adducts are potentially useful precursors for the synthesis of new uranium compounds.

872

Tetracyanoresorcin[4]arene ion channel shows pH dependent conductivity change

Wen-Hua Chen, Masanori Nishikawa, Song-De Tan, Mika Yamamura, Akiharu Satake and Yoshiaki Kobuke

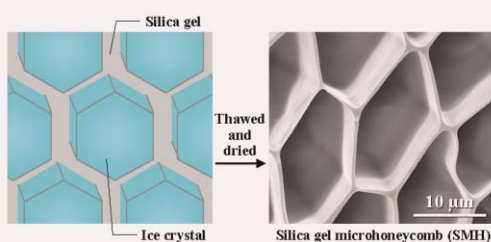


A pH sensitive artificial ion channel was synthesized. Conductivities for potassium ion were increased by the progress of dissociation at the channel mouth.

874

Formation of monolithic silica gel microhoneycombs (SMHs) using pseudosteady state growth of microstructural ice crystals

Shin R. Mukai,* Hirotomoto Nishihara and Hajime Tamon

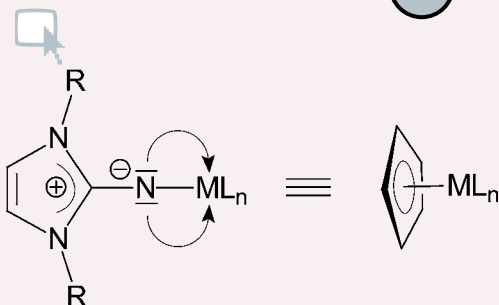


Monolithic silica gel microhoneycombs with unidirectionally aligned homogeneous channels inside them were prepared through pseudosteady state growth of ice crystals, which occurs during unidirectional freeze–gelation.

876

Titanium complexes with imidazolin-2-iminato ligands

Matthias Tamm,* Sören Randoll, Thomas Bannenberg and Eberhardt Herdtweck

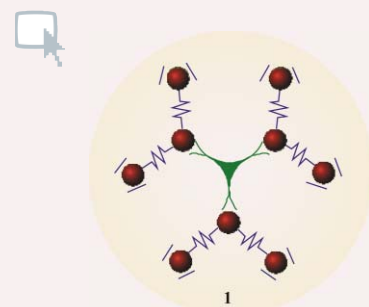


The reaction of the stable carbene 1,3-di-*tert*-butylimidazolin-2-ylidene with trimethylsilyl azide furnishes the corresponding *N*-silylated 2-iminoimidazoline. Treatment with titanium(IV) chlorides affords complexes with a monoanionic imidazolin-2-iminato ligand which can be regarded as a monodentate analogue to cyclopentadienyls.

878

A mixed-bridging ligand nonanuclear Ru(II) dendrimer containing a tris-chelating core. Synthesis and redox properties

Julien Leveque, Cécile Moucheron, Andrée Kirsch-De Mesmaeker, Frédérique Loiseau, Scolastica Serroni, Fausto Puntoriero, Sebastiano Campagna, Hélène Nierengarten and Alain Van Dorsselaer

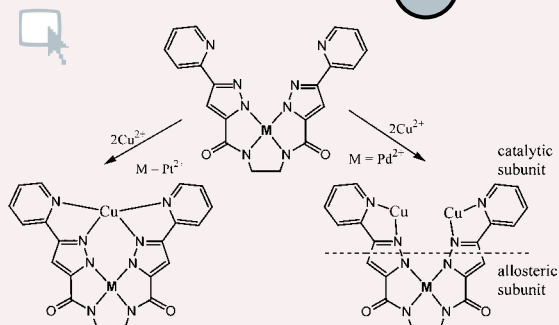


The first ligand-cored nonanuclear metallo-dendrimer containing mixed bridging ligands has been prepared and its redox behavior investigated. The redox-active core is not reduced at the expected potential, and this effect is attributed to the shielding induced by the rigid dendritic array.

880

On/off regulation of catalysis by allosteric control of metal complex nuclearity

Larisa Kovbasyuk, Hans Pritzkow, Roland Krämer* and Igor O. Fritsky

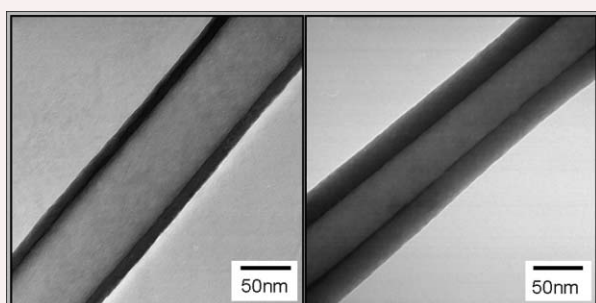


The nature of the allosteric metal ion M (Pd^{2+} or Pt^{2+}) in complexes ML of a polytopic ligand controls uptake of additional Cu^{2+} ions; while $[\text{Cu}_2\text{Pd}(\text{L-4H})]^{2+}$ is a highly active catalyst for phosphodiester cleavage, $[\text{CuPt}(\text{L-4H})]$ is inactive.

882

A facile synthesis of polypyrrole nanotubes using a template-mediated vapor deposition polymerization and the conversion to carbon nanotubes

Jyongsik Jang* and Joon Hak Oh

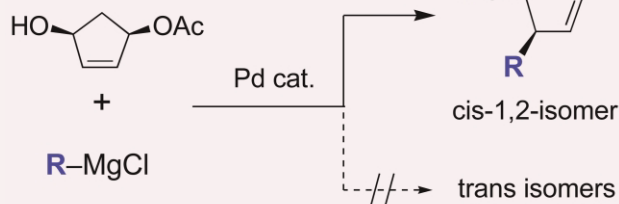


Polypyrrole (PPy) nanotubes with highly uniform surface and tunable wall thickness were fabricated by a template-mediated vapor deposition polymerization (VDP), and transformed into carbon nanotubes through a carbonization process.

884

Palladium-catalyzed reaction of 4-cyclopentene-1,3-diol monoacetate with Grignard reagents producing hitherto unreachable *cis*-1,2-isomers

Hatsuhiko Hattori, Ashraf A. Abbas and Yuichi Kobayashi*

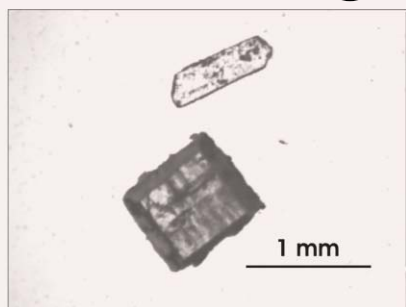


Among four possible products from the monoacetate and hard nucleophiles, *cis*-1,2-isomers were obtained by Pd-catalyzed reaction with $RMgCl$ (R = alkyl, aryl) stereo- and regio-selectively.

886

Diiminoisoindoline: tautomerism, conformations, and polymorphism

Zhi-Qin Zhang, Jeffrey M. Njus, Daniel J. Sandman,* Chengyun Guo, Bruce M. Foxman,* Peter Erk* and Richard van Gelder

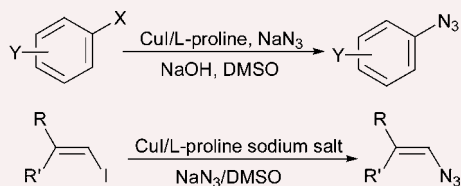


Two polymorphs of the industrially important compound diiminoisoindoline occur in the amino tautomeric form as a conformational isomorph with a 1 : 1 mixture of the *syn*- and *anti*-isomers, and a conformational polymorph containing only the *syn*-isomer.

888

Synthesis of aryl azides and vinyl azides via proline-promoted CuI-catalyzed coupling reactions

Wei Zhu and Dawei Ma*

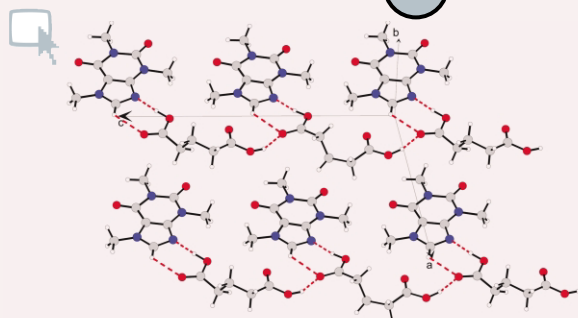


The coupling reaction of aryl halides or vinyl iodide with sodium azide was carried out in 40–95 °C under catalysis of CuI/L -proline (or L -proline sodium salt) to provide aryl azides or vinyl azides in 57–93% yields.

890

Solvent-drop grinding: green polymorph control of cocrystallisation

Andrew V. Trask, W. D. Samuel Motherwell and William Jones*

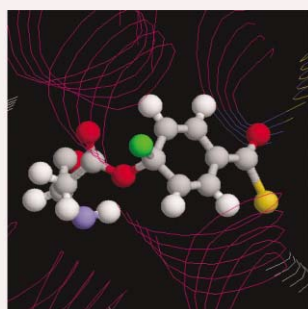


Concomitant polymorph formation of a caffeine : glutaric acid cocrystal is reported. The two polymorphs can be prepared in essentially pure form, however, by grinding in the presence of an appropriate solvent.

892

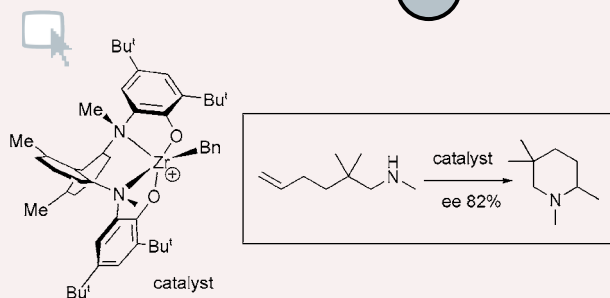
A QM/MM study of a nucleophilic aromatic substitution reaction catalyzed by 4-chlorobenzoyl-CoA dehalogenase

Dingguo Xu, Hua Guo,* Jiali Gao and Qiang Cui



Potential of mean force calculated using a QM/MM method indicates the existence of a stable Meisenheimer complex as a discrete intermediate in the dechlorination of 4-chlorobenzoate catalyzed by the 4-chlorobenzoyl-CoA dehalogenase.

894

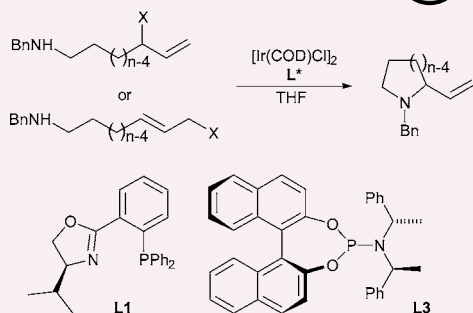


Zirconium catalysed enantioselective hydroamination/cyclisation

Paul D. Knight, Ian Munslow, Paul N. O'Shaughnessy and Peter Scott*

A chiral zirconium alkyl cation catalyses the cyclisation of certain aminoalkenes with enantioselectivity up to 82%, the highest thus far observed for such a process.

896

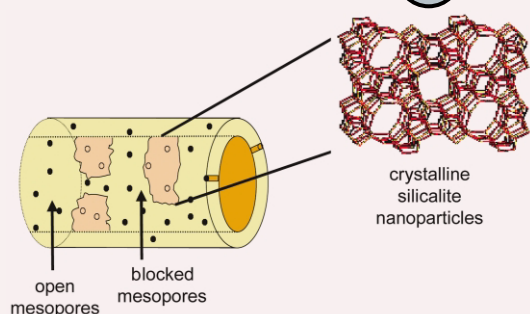


First intramolecular enantioselective iridium-catalysed allylic aminations

Carolin Welter, Oliver Koch, Gunter Lipowsky and Günter Helmchen*

Enantioselective iridium-catalysed intramolecular allylic aminations, using phosphinooxazolines or phosphorus amidites as ligands, provided ee values of >90% at a catalyst loading of <0.5 mol-%. Reactions catalysed by complexes of phosphorus amidite **L3** displayed a marked preference for intra- over corresponding intermolecular reactions.

998

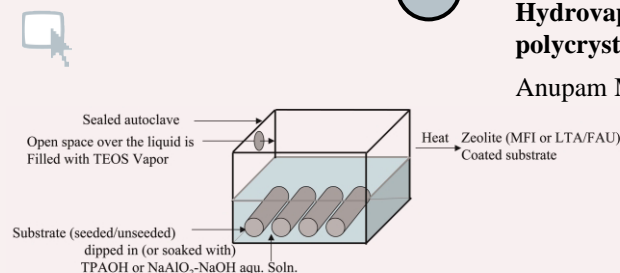


Post-synthesis deposition of V-zeolitic nanoparticles in SBA-15

V. Meynen,* E. Beyers, P. Cool, E. F. Vansant, M. Mertens, H. Weyten, O. I. Lebedev and G. Van Tendeloo

This paper shows the formation of a new type of zeolitic V-activated PHTS (plugged hexagonal templated silica) with open and blocked pores by post-synthesis deposition of vanadium silicalite zeolitic nanoparticles inside the mesopores of SBA-15.

900

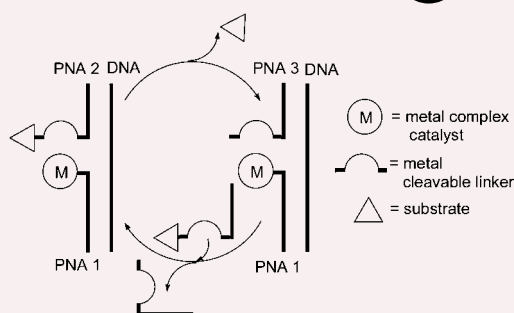


Hydrovapor thermal conversion of tetraethoxysilane vapor to polycrystalline zeolite layer by *in situ* gelation

Anupam Mitra, Shinichi Ichikawa, Eiichi Kikuchi and Masahiko Matsukata*

Alumina supported zeolite membranes were fabricated in a substrate-in-TPAOH (or NaAlO₂-NaOH)-aqueous-solution/tetraethoxysilane-vapor system; a novel approach towards continuous production of zeolite membranes.

902



DNA-templated catalysis using a metal-cleavable linker

Felix H. Zelder, Jens Brunner and Roland Krämer*

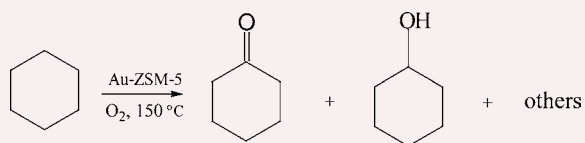
Catalytic hydrolysis of an ester substrate by a Cu(II) complex catalyst, both attached to oligopeptide nucleic acids, is triggered by complementary DNA. The use of a metal-cleavable hydroxyquinoline linker provides improved flexibility in the design of nucleic acid probes.

COMMUNICATIONS

904

A highly efficient oxidation of cyclohexane over Au/ZSM-5 molecular sieve catalyst with oxygen as oxidant

Rui Zhao, Dong Ji, Gaomeng Lv, Guang Qian, Liang Yan, Xiaolai Wang and Jishuan Suo*



A highly efficient oxidation of cyclohexane to cyclohexanol and cyclohexanone is accomplished over calcined Au/ZSM-5 molecular sieve catalyst with oxygen as oxidant.

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