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ChemComm

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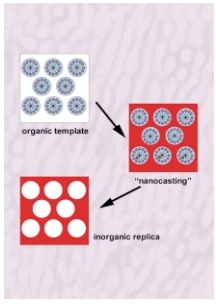
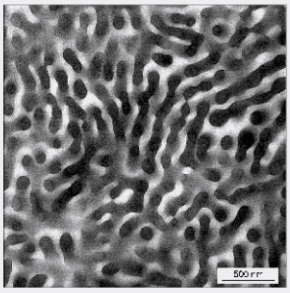


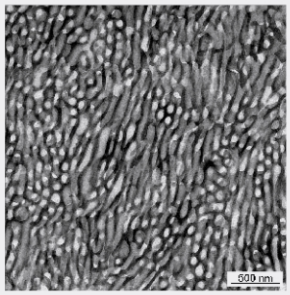
Cover
A schematic representation of the nanocasting concept, against a background TEM image of the silica replica of a bicontinuous sponge-like phase.

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

contents

FEATURE ARTICLE



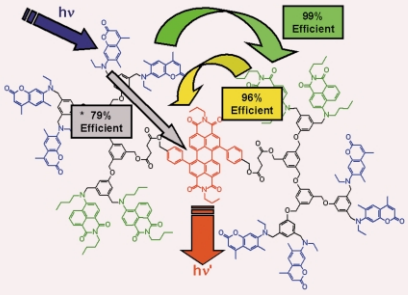


Porous materials *via* nanocasting procedures: innovative materials and learning about soft-matter organization

Sebastian Polarz and Markus Antonietti

Nanocasting, the 3D-transformation of self-assembled organic nanostructures into hollow inorganic replicas under preservation of fine structural details has recently turned out to be a versatile tool, both for the synthesis of porous media with new pore topology as well as for the characterization of the assembled structures themselves.

COMMUNICATIONS



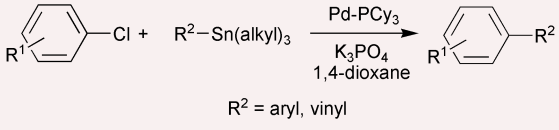
Cascade energy transfer in a conformationally mobile multichromophoric dendrimer

Jason M. Serin, Darryl W. Brousmiche and Jean M. J. Fréchet*

A novel dendritic system that favors cascade unidirectional FRET has been synthesized. This dendrimer illustrates the ability of a large light-harvesting antenna to concentrate absorbed light-energy both spectrally and spatially.

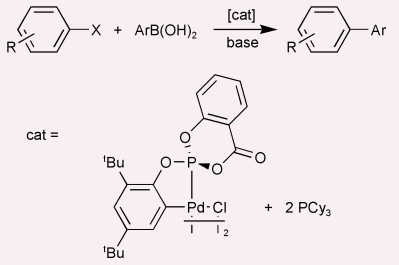
Simple tricyclohexylphosphine–palladium complexes as efficient catalysts for the Stille coupling of deactivated aryl chlorides

Robin B. Bedford,* Catherine S. J. Cazin and Samantha L. Hazelwood (née Welch)



The Stille coupling of a range of aryl chlorides is achieved by the use of simple palladium complexes with the inexpensive, easily handled ligand tricyclohexylphosphine.

2610

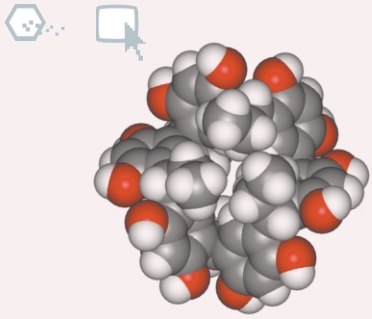


Extremely high activity catalysts for the Suzuki coupling of aryl chlorides: the importance of catalyst longevity

Robin B. Bedford,* Samantha L. Hazelwood (née Welch) and Michael E. Limmert

A ligand derived from salicylic acid gives greatly enhanced catalyst longevity and thus very high activity in the Suzuki coupling of aryl chlorides catalysed by Pd–PCy_3 systems.

2612

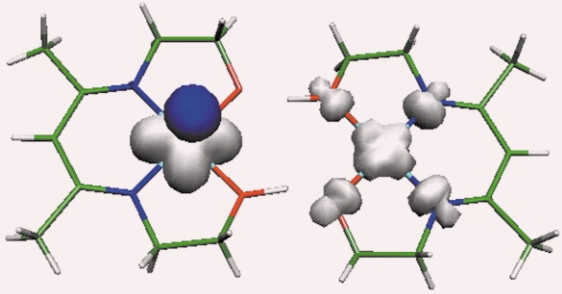


Resorcin[6]arene as a building block for tubular crystalline state architectures

Byron W. Purse, Alexander Shivanyuk and Julius Rebek Jr.*

Acid catalyzed condensation of resorcinol with propionaldehyde gives a resorcin[6]arene with *r-trans-cis-trans-cis-trans* configuration of the pendant ethyl groups. This compound was shown to form novel types of tubular crystal structures.

2614

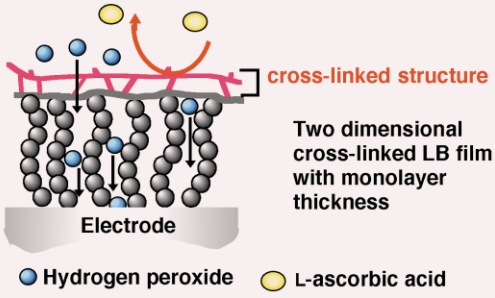


Early-late transition metal ferromagnetic coupling mediated by hydrogen bonding

Cédric Desplanches, Eliseo Ruiz and Santiago Alvarez*

Hydrogen bonding between early and late transition metal complexes is proposed as a strategy to obtain ferromagnetic interactions based on a theoretical study using density functional calculations.

2616

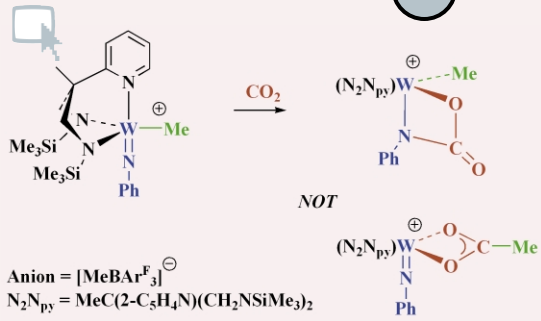


Permselective monolayer membrane based on two-dimensional cross-linked polysiloxane LB films for hydrogen peroxide detecting glucose sensors

Dai Kato, Mio Masaike, Takahito Majima, Yoshiki Hirata, Fumio Mizutani, Masayo Sakata, Chuichi Hirayama and Masashi Kunitake*

Novel two-dimensional cross-linked polysiloxane LB films have been applied as H_2O_2-permselective glucose sensors and found to be remarkably effective at eliminating interfering responses, even though the films were only a monolayer thick.

2618



Synthesis and reactivity of the imidotungsten methyl cation $[W(N_2N_{py})(NPh)Me]^+$: CO_2 adds to the W=NPh bond and does not insert into the W–Me bond

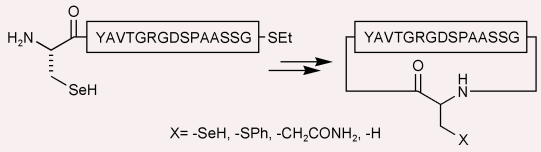
Benjamin D. Ward, Eric Clot, Stuart R. Dubberley, Lutz H. Gade and Philip Mountford*

Reactions of $[W(N_2NPy)(NPh)Me]^+$ with CO_2 and PhNCO give unexpected products.

2620

Selenocysteine-mediated backbone cyclization of unprotected peptides followed by alkylation, oxidative elimination or reduction of the selenol

Richard Quaderer and Donald Hilvert*

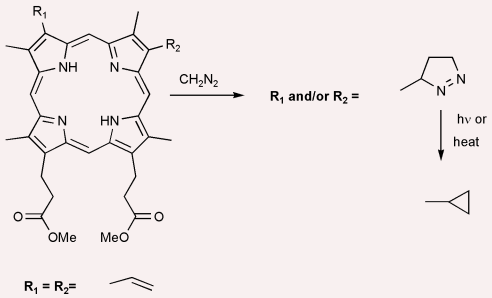


An unprotected 16 residue peptide containing a C-terminal thioester and an N-terminal selenocysteine residue efficiently cyclizes in the presence of thiophenol; subsequent reduction, elimination or alkylation of the selenol yields modified cyclic peptides with alanine, dehydroalanine or a non-natural amino acid at the site of ligation.

2622

Nitrogen extrusion from pyrazoline-substituted porphyrins and chlorins using long wavelength visible light

Angela Desjardins, Jeffery Flemming, Ethan D. Sternberg and David Dolphin*

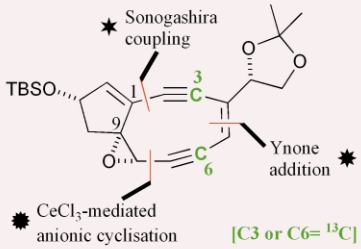


Protoporphyrin dimethyl ester reacts with diazomethane to give pyrazolines which upon heating or irradiation with long wavelengths extrude dinitrogen to give the corresponding cyclopropyl derivatives.

2624

Synthesis of ^{13}C-labelled, bicyclic mimetics of natural enediynes

Parthasarathi Das, Takashi Mita, Martin J. Lear and Masahiro Hirama*

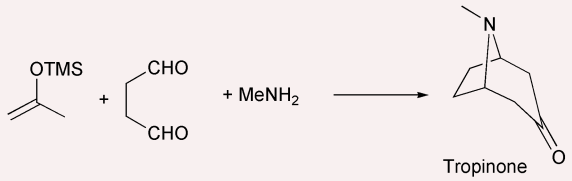


Using a new reliable and practical synthetic approach (see illustration), the fully-functionalized bicyclic core of natural nine-membered chromophores has been ^{13}C-labelled for the first time.

2626

One-pot synthesis of tropinone by tandem (domino) ene-type reactions of acetone silyl enol ethers

Koichi Mikami* and Hirofumi Ohmura

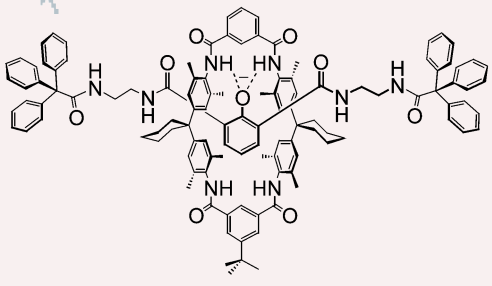


A synthetic approach for tropane alkaloids is shown on the basis of tandem (domino) ene-type reactions of acetone silyl enol ethers with iminium ions.

2628

Novel template effect for the preparation of [2]rotaxanes with functionalised centre pieces

Pradyut Ghosh, Oliver Mermagen and Christoph A. Schalley*

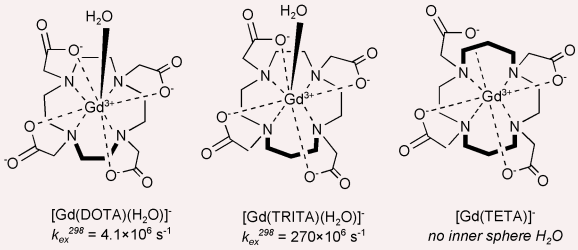


A new template effect has been designed for the preparation of rotaxanes with functionalised axle centre pieces. The phenolic OH group is efficiently protected against chemical modification by the wheel.

2630

Accelerating water exchange for Gd^{III} chelates by steric compression around the water binding site

Robert Ruloff, Éva Tóth, Rosario Scopelliti, Raphaël Tripier, Henri Handel and André E. Merbach*

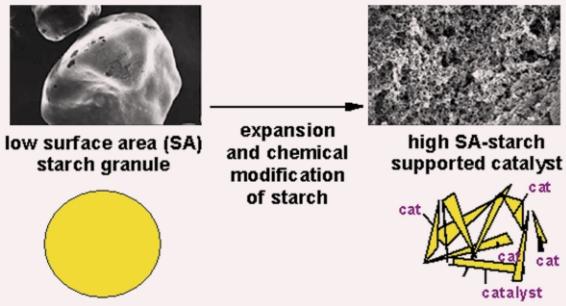


As the result of a rational design, steric compression was increased around the water binding site in $[Gd(TRITA)(H_2O)]^-$. This leads to a high water exchange rate which is optimal to attain maximum proton relaxivities.

2632

New materials based on renewable resources: chemically modified expanded corn starches as catalysts for liquid phase organic reactions

Shinichi Doi, James H. Clark,* Duncan J. Macquarrie and Krzysztof Milkowski

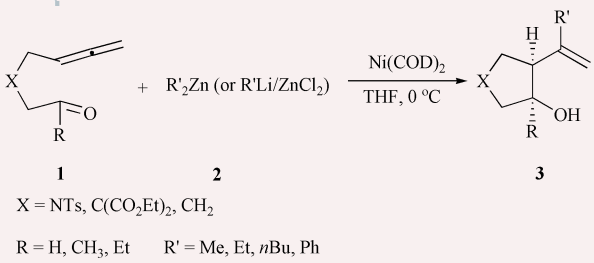


Catalytically active chemically modified expanded corn starches have been developed with site loadings and activities comparable or superior to traditional materials.

2634

cis-Stereoselective nickel-catalyzed cyclization/alkylation and arylation reactions of allenyl-aldehydes and -ketones with organozinc reagents

Suk-Ku Kang* and Seok-Keun Yoon

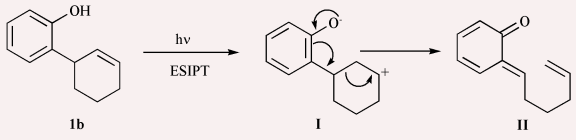


Highly stereoselective alkylative and arylative cyclization reactions of allenyl-aldehydes and -ketones with organozinc reagents occur efficiently in the presence of catalytic $Ni(COD)_2$ to afford *cis*-fused homoallylic cyclopentanols.

2636

Novel generation of an *o*-quinone methide from 2-(2′-cyclohexenyl)phenol by excited state intramolecular proton transfer and subsequent C–C fragmentation

Julio Delgado, Amparo Espinós, M. Consuelo Jiménez and Miguel A. Miranda*

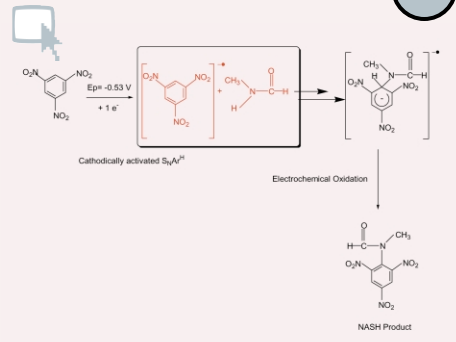


Formation of an *o*-quinone methide *via* C–C fragmentation of a zwitterion formed by intramolecular excited state proton transfer from an *o*-allylphenol derivative is reported for the first time.

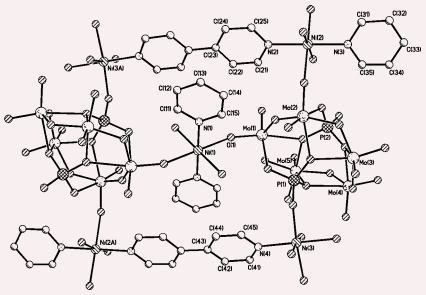
2638

Cathodically activated nucleophilic aromatic substitution of hydrogen: a novel electrochemical mechanism

Iluminada Gallardo,* Gonzalo Guirado and Jordi Marquet



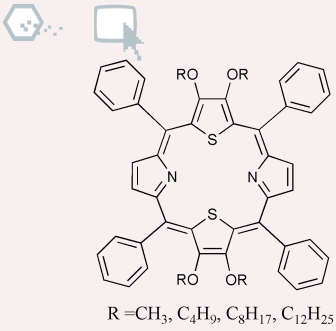
Cathodically activated nucleophilic aromatic substitution of hydrogen (S_NAr^H) is reported; furthermore the first example of an $S_{RN}2$ mechanism, which have been searched for more than 20 years, is also reported.



A novel compound with an interpenetrating 2D network structure constructed by $[Mo_5P_2O_{23}]$ and Ni–4,4′-bipyridine components: its synthesis, characterization and magnetic behaviour

Jin Chen, Shaofang Lu,* Rongmin Yu, Zhongning Chen, Zixiang Huang and Canzhong Lu

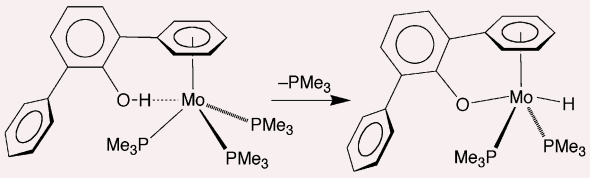
A novel compound $(Hbpy)_2\{[(H_2O)_3Ni(bpy)_{0.5}Ni(bpy)(H_2O)_4]_2[Mo_5P_2O_{23}]$-$[Ni((bpy)_{0.5})_2(H_2O)_2][Mo_5P_2O_{23}]\}\cdot 8H_2O$ with a unique 2D network structure has been synthesized. The five Ni(II) ions in the five-Ni(II) segment are in non-interacting single-ion triplet states with a high-spin Ni(II) configuration.



Synthesis and crystal structure of 2,3,12,13-tetraalkoxy-21,23-dithiaporphyrins

Neeraj Agarwal, Sarada P. Mishra, Anil Kumar, C.-H. Hung and M. Ravikanth*

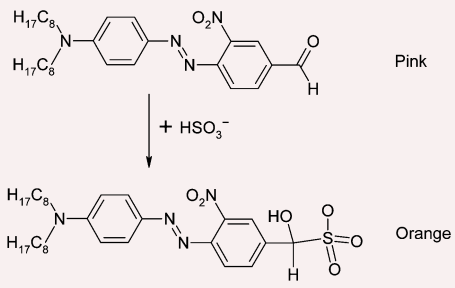
The first novel synthesis of four 2,3,12,13-tetraalkoxy-21,23-dithiaporphyrins is reported.



A non-classical hydrogen bond in the molybdenum arene complex $[\eta^6$-$C_6H_5C_6H_3(Ph)OH]Mo(PMe_3)_3$: evidence that hydrogen bonding facilitates oxidative addition of the O–H bond

Tony Hascall, Mu-Hyun Baik, Brian M. Bridgewater, Jun Ho Shin, David G. Churchill, Richard A. Friesner* and Gerard Parkin*

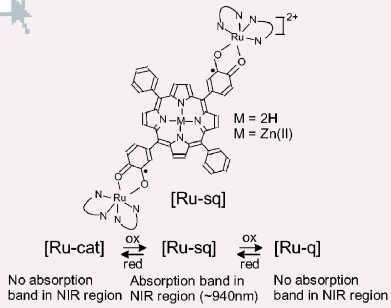
The η^6-arene complex $[\eta^6$-$C_6H_5C_6H_3(Ph)OH]Mo(PMe_3)_3$ exhibits a non-classical Mo···H–OAr hydrogen bond that facilitates oxidative addition of the O–H bond to give $[\eta^6,\eta^1$-$C_6H_5C_6H_3(Ph)O]Mo(PMe_3)_2H$.



A chromoreactand for the selective detection of HSO_3^- based on the reversible bisulfite addition reaction in polymer membranes

Gerhard J. Mohr

A new chromoreactand for the reversible optical detection of bisulfite anion is presented with a sensitivity in the range from 0.1 to 10 mM while no absorbance changes are observed for anions such as sulfate, chloride, phosphate or hydroxide.



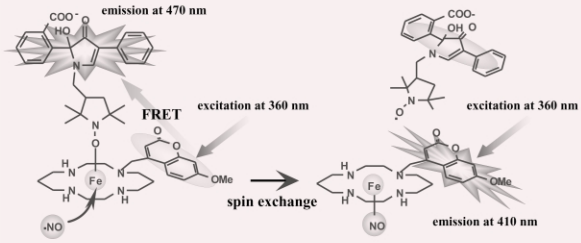
Redox switchable NIR dye derived from ruthenium–dioxolene–porphyrin systems

Atindra D. Shukla, Bishwajit Ganguly, Paresh C. Dave, Anunay Samanta* and Amitava Das*

Newly synthesized $Ru(bpy)_2(sq)$-derivatives show fast switching between on/off states for an intense near-IR band.

Ratiometric direct detection of nitric oxide based on a novel signal-switching mechanism

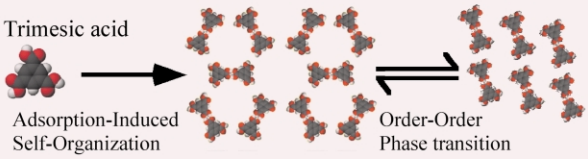
Nobuaki Soh,* Toshihiko Imato, Kenji Kawamura, Mizuo Maeda and Yoshiki Katayama



A novel fluorescent probe, which could be the first example of a ratiometric molecular probe for direct monitoring of NO production, has been developed using a 'spin-exchange' mechanism.

A two-dimensional molecular network structure of trimesic acid prepared by adsorption-induced self-organization

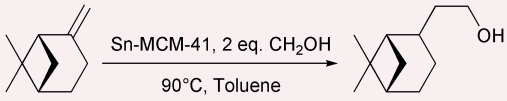
Yudai Ishikawa, Akihiro Ohira, Masayo Sakata, Chuichi Hirayama and Masashi Kunitake*



The supramolecular structures of trimesic acid on Au(111) were constructed by precise potential-controlled adsorption based on adsorption-induced self-organization and visualized by *in situ* STM with submolecular resolution.

Synthesis of nopol over MCM-41 catalysts

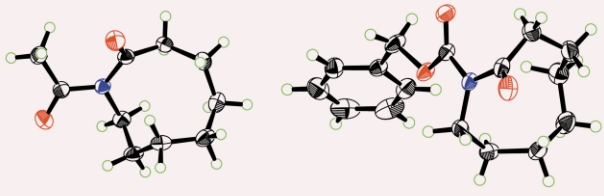
Aída Luz Villa de P., Edwin Alarcón and Consuelo Montes de Correa



A simplified CVD method was used to create efficient Sn(IV) sites in MCM-41 for the Prins condensation of β-pinene and paraformaldehyde. The highly selective and recyclable catalyst does not need a chlorinated solvent to obtain nopol.

N-Substituent effect on the *cis–trans* geometry of nine-membered lactams

Shinji Yamada* and Akie Homma

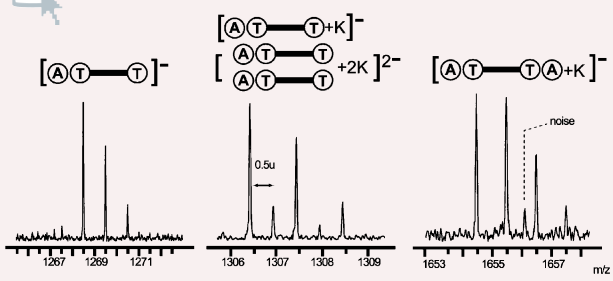


cis-**1a** *trans*-**1d**

An unusual *cis* to *trans* ring geometrical change was observed in nine-membered lactams by replacing an *N*-acyl substituent with *N*-benzyloxycarbonyl.

Detection of complementary hydrogen bond complexes in water by electrospray ionization-Fourier-transform ion cyclotron resonance mass spectrometry

Rika Iwaura, Mayumi Ohnishi-Kameyama, Mitsuru Yoshida and Toshimi Shimizu*

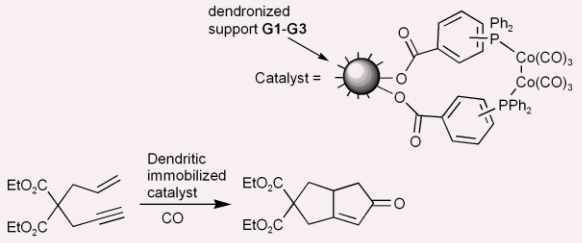


Complementary base paired complex formation of a thymidine-appended bolaamphiphile with adenosine derivatives was able to be detected with high resolution and high sensitivity in aqueous solutions by ESI-FTICR MS.

2700

Dendritic effect in polymer-supported catalysis of the intramolecular Pauson–Khand reaction

Adi Dahan and Moshe Portnoy*

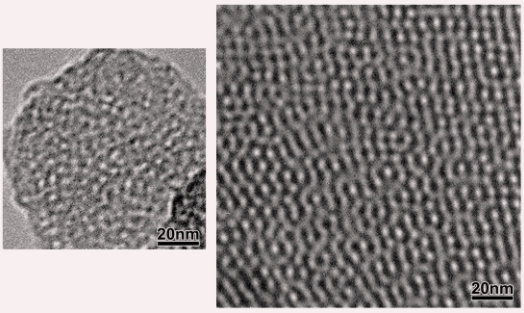


Supported dendritic catalysts for the Pauson–Khand reaction were prepared using dendronized polystyrene support; a significant positive dendritic effect was observed in the intramolecular reaction.

2702

Synthesis of hexagonal and cubic super-microporous niobium phosphates with anion exchange capacity and catalytic properties

Nawal Kishor Mal and Masahiro Fujiwara*

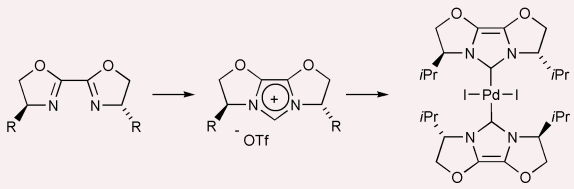


Super-microporous hexagonal niobium phosphate synthesized using neutral surfactant (S^0I^0 mechanism) and cubic structure with cationic surfactant ($S^+X^-I^+$); the hexagonal niobium phosphate possesses an anion exchange capacity of 6.3 mmol g^{-1}.

2704

Oxazolines as chiral building blocks for imidazolium salts and N-heterocyclic carbene ligands

Frank Glorius,* Gereon Altenhoff, Richard Goddard and Christian Lehmann

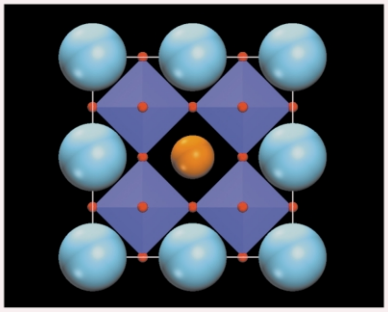


Enantiomerically pure imidazolium triflates can be readily prepared from bioxazolines and oxazolineimines; deprotonation of the *i*Pr-bioxazoline derived imidazolium triflate gives a chiral N-heterocyclic carbene that can act as a ligand in a catalytically active palladium complex.

2706

Solubility of cerium in $LaCoO_3$–influence on catalytic activity

S. A. French,* C. R. A. Catlow, R. J. Oldman, S. C. Rogers and S. A. Axon

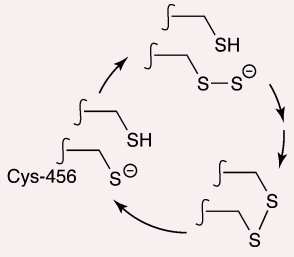


The calculations describe in detail the theoretical study of the mechanisms for incorporating dopants in non-stoichiometric perovskite lattices. Comparison with a stoichiometric lattice shows a large increase in dopant solubility, which in turn leads to an increase in the catalytic activity of lanthanum cobaltate.

2708

A paradigm for biological sulfur transfers *via* persulfide groups: a persulfide–disulfide–thiol cycle in 4-thiouridine biosynthesis

Chapman M. Wright, Peter M. Palenchar and Eugene G. Mueller*



The enzyme ThiI turns over only once in the absence of reductants, and Cys-456 receives sulfur from the sulfurtransferase IscS, confirming a persulfide–disulfide–thiol cycle in 4-thiouridine biosynthesis and providing a paradigm for other sulfur transfer systems.

2710

Dialkyl aluminium amides: new reagents for the conversion of C=O into C=NR functionalities

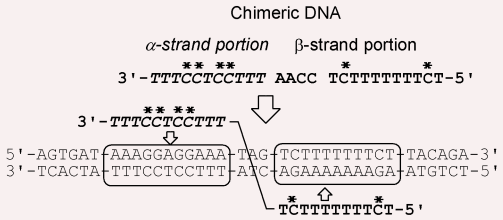
John C. Gordon,* Piyush Shukla, Alan H. Cowley, Jamie N. Jones, D. Webster Keogh and Brian L. Scott

A new synthetic approach for the preparation of α-diimines and β-aminoenones is described. In particular, this methodology provides a convenient alternative route to these classes of ligands bearing highly electronegative substituents.

2712

Alternate stranded triplex formation of chimeric DNA composed of tandem α- and β-anomeric strands

Kazuo Shinozuka,* Noritake Matsumoto, Hideo Suzuki, Tomohisa Moriguchi and Hiroaki Sawai

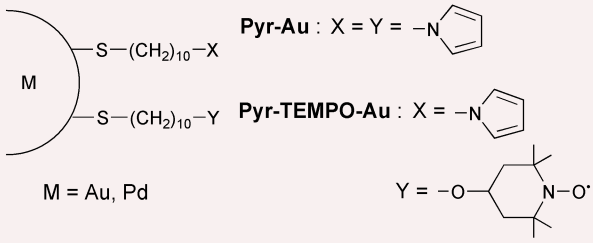


A chimeric oligoDNA composed of tandem α- and β-anomeric oligonucleotide strands forms stable alternate stranded triplex upon binding with double helical DNA.

2714

Preparation and electrochemical polymerization of new multifunctional pyrrolethiolate-stabilized gold and palladium nanoparticles

Kisato Hata and Hisashi Fujihara*

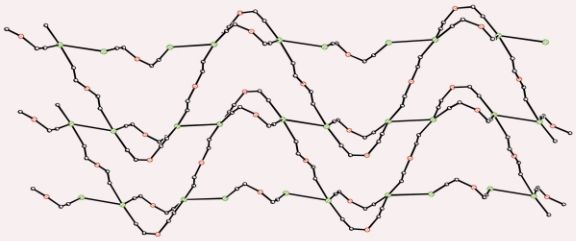


New pyrrolylalkanethiolate-stabilized gold and palladium nanoparticles have been prepared: electrochemical polymerization of their metal nanoparticles and their TEMPO-derivatized metal nanoparticles gave the remarkably stable poly(pyrrole metal nanoparticle) films on metal electrodes.

2716

A novel 2-D interlinking zigzag-chain d–f mixed-metal coordination polymer generated from an organometallic ligand

Yang-Yi Yang and Wing-Tak Wong*

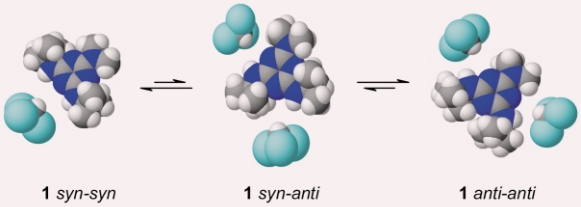


A flexible organometallic ligand, 1,1′-ferrocenedicarboxylic acid, was incorporated in the self-assembly of a d–f mixed-metal coordination polymer featuring a 2-D interlinking zigzag-chain network and bearing two types of bridging conformations.

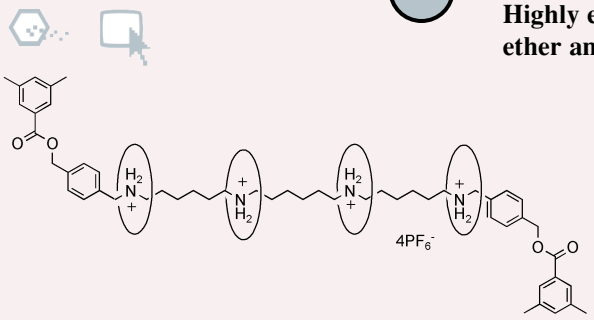
2718

Steric hindrance to the solvation of melamines and consequences for non-covalent synthesis

Ion Ghiviriga* and Daniela C. Oniciu



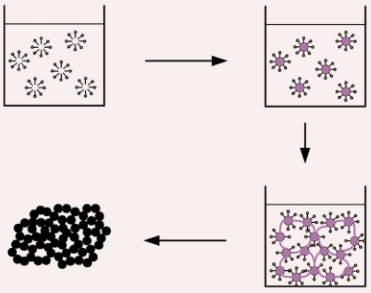
Steric hindrance to solvation affects the stability and dynamics of supramolecular assemblies containing melamines. Solvents which bind the triazine nitrogen disfavor structures like **1** *syn–anti* in which the melamine exposes to the solvent faces, such as *t*Bu–H, for whom binding to the ring nitrogen is hindered but not blocked. These solvents also display the fastest rates for assembling/disassembling processes.



Highly efficient synthesis of [3]- and [5]-rotaxanes consisting of crown ether and a *sec*-ammonium salt

Nobuhiro Watanabe, Takaya Yagi, Nobuhiro Kihara and Toshikazu Takata*

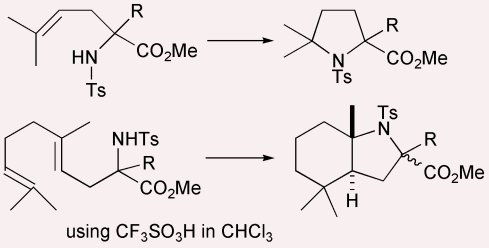
[3]- and [5]-rotaxanes consisting of a crown ether and ammonium salts were synthesized in high yields by a tributylphosphine-catalyzed end-capping method which provides a simple and practical means of obtaining higher-order rotaxanes.



Novel synthesis of porous carbons with tunable pore size by surfactant-templated sol–gel process and carbonisation

Kyu Tae Lee and Seung M. Oh*

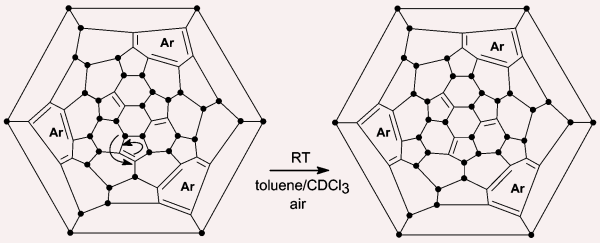
Surfactant-templated sol–gel polymerisation was explored to synthesize resorcinol–formaldehyde (RF) gels without supercritical drying step, which were further carbonised to obtain porous carbons of a tunable pore size.



Sulfonamides as novel terminators of cationic cyclisations

Charlotte M. Haskins and David W. Knight*

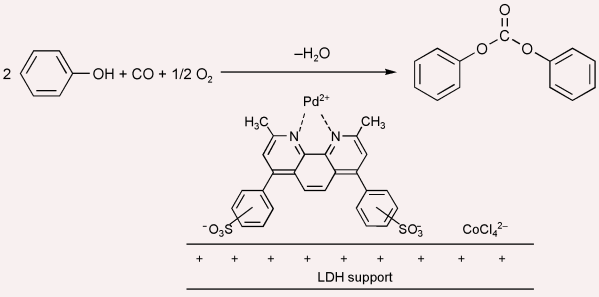
Triflic acid is an excellent catalyst for inducing the overall 5-*endo*-trig cyclisation of homoallylic sulfonamides leading to pyrrolidines. The method is also applicable to the formation of polycyclic derivatives by cationic cyclisation cascades in which the sulfonamide nitrogen acts as a terminator.



Fluorine takes a hike: remarkable room-temperature rearrangement of the C_1 isomer of $C_{60}F_{36}$ into the C_3 isomer *via* a 1,3-fluorine shift

Anthony G. Avent and Roger Taylor*

In toluene/$CDCl_3$ at room temperature, the C_1 isomer of $C_{60}F_{36}$ rearranges during four days into the C_3 isomer, *via* a unique 1,3-shift of fluorine; this rare example of addend migration across a fullerene cage surface is accelerated by air.



A new heterogeneous catalyst for the oxidative carbonylation of phenol to diphenyl carbonate

Koen J. L. Linsen, Jo Libens and Pierre A. Jacobs*

Using LDH as support, anionic species of both the Pd catalyst and the Co co-catalyst are successfully heterogenised and evaluated in the oxidative carbonylation of phenol to diphenyl carbonate.

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