

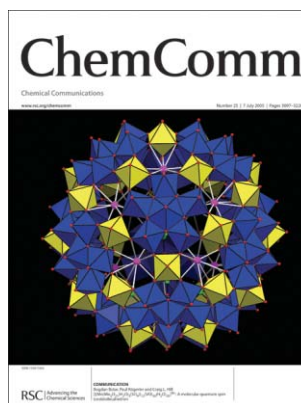
IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (25) 3097-3228 (2005)



Cover

See Neil J. Shirtcliffe, Glen McHale, Michael I. Newton, Carole C. Perry and Paul Roach, page 3135. Phenolphthalein in water on MTEOS sol-gel foams heated to 390 °C (left) and heated to 400 °C (right). Image reproduced by permission of Neil J. Shirtcliffe *et al.* from *Chem. Commun.*, 2005, 3135.



Inside cover

See Bogdan Botar, Paul Kögerler and Craig L. Hill, page 3138. An icosidodecahedral array of thirty vanadium(IV) centers embedded in a 2.5 nm polymolybdate spherical capsule. Image reproduced by permission of Craig L. Hill *et al.* from *Chem. Commun.*, 2005, 3138.

CHEMICAL SCIENCE

C49

Drawing together the research highlights and news from all RSC publications, *Chemical Science* provides a 'snapshot' of the latest developments across the chemical sciences showcasing newsworthy articles, as well as the most significant scientific advances.

Chemical Science

July 2005/Volume 2/Issue 7

www.rsc.org/chemicalscience

CONFERENCE REPORT

3111

Highlights from the 40th EUCHEM Conference on Stereochemistry, Bürgenstock, Switzerland, April 2005

Klemens Högenauer and Deborah Longbottom

'Where most see a wall, some see a door and a few go through to discover a rich, new world.....open sesame!'



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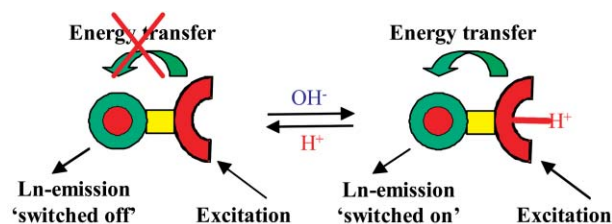
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3114

Responsive lanthanide luminescent cyclen complexes: from switching/sensing to supramolecular architectures

Thorfinnur Gunnlaugsson and Joseph P. Leonard

This article highlights some of the recent developments in the use of responsive cyclen based lanthanide luminescent devices, focusing on Eu(III), Tb(III), Nd(III) and Yb(III) complexes, where the photophysical properties, such as the excited state lifetimes, quantum yield/intensity and emission polarisation are modulated by the local chemical environment, *e.g.* ions and molecules, or through self-assembly of either f–f or mixed f–d cyclen complexes.



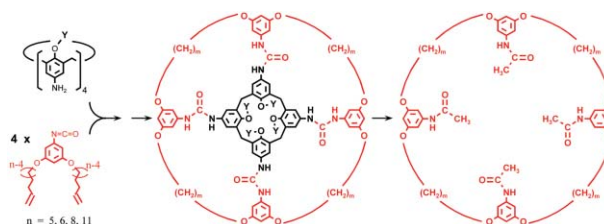
COMMUNICATIONS

3132

Synthesis of huge macrocycles using two calix[4]arenes as templates

Yudong Cao, Leyong Wang, Michael Bolte, Myroslav O. Vysotsky and Volker Böhmer*

Macrocycles with up to 100 atoms have been synthesised by metathesis reactions between alkenyl groups. Two calix[4]arenes as templates ensure the correct connection of the reactive fragments.



3135

Porous materials show superhydrophobic to superhydrophilic switching

Neil J. Shirtcliffe,* Glen McHale, Michael I. Newton, Carole C. Perry and Paul Roach

Switching between superhydrophobicity and superhydrophilicity in porous materials was predicted theoretically and demonstrated experimentally. This effect could be used in a new type of sensor.

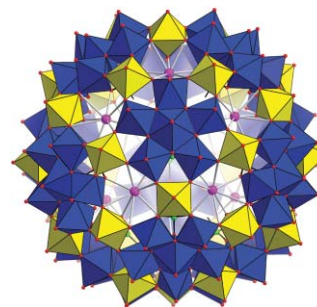


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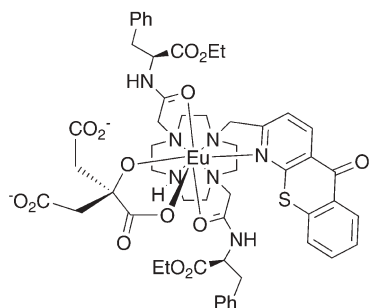
$[(\text{Mo})\text{Mo}_5\text{O}_{21}(\text{H}_2\text{O})_3(\text{SO}_4)_{12}(\text{VO})_{30}(\text{H}_2\text{O})_{20}]^{36-}$: A molecular quantum spin icosidodecahedron

Bogdan Botar,* Paul Kögerler* and Craig L. Hill*

A self-assembly reaction of molybdate and vanadate leads to a spherical polyoxomolybdate cluster-anion with a diameter of 2.5 nm which comprises an icosidodecahedral spin array of V(IV) centers.



3141

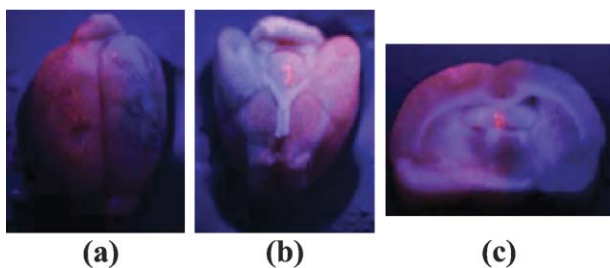


A pH-insensitive, ratiometric chemosensor for citrate using europium luminescence

David Parker* and Junhua Yu

Ratiometric analysis of europium emission bands allows the analysis of citrate in the presence of competing anions.

3144

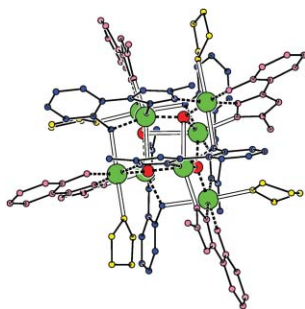


Rapid and effective labeling of brain tissue using TAT-conjugated CdS:Mn/ZnS quantum dots

Swadeshmukul Santra,* Heesun Yang, Jessie T. Stanley, Paul H. Holloway, Brij M. Moudgil, Glenn Walter and Robert A. Mericle

Gross views of a rat brain labeled with TAT-conjugated dots, clearly showing that Qdot-loaded brain tissue could be visualized grossly under handheld-UV lamp. (a) and (b) represent dorsal views and (c) represents coronal section.

3147

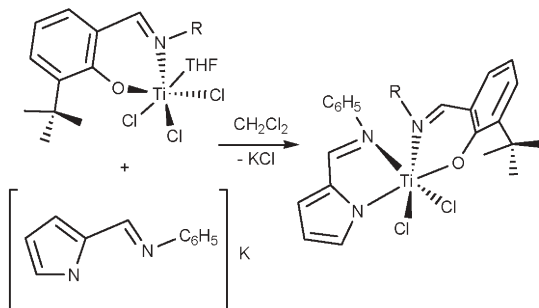


New routes to manganese higher-nuclearity topologies: synthesis of the cluster $[\text{Mn}_8(\mu_4\text{-O})_4(\text{phpz})_8(\text{thf})_4]$

Stefania Tanase, Guillem Aromí, Elisabeth Bouwman, Huub Kooijman, Anthony L. Spek and Jan Reedijk*

The synthesis of a high-nuclearity manganese cluster, $[\text{Mn}_8(\mu_4\text{-O})_4(\text{phpz})_8(\text{thf})_4]$ assembled in a one-pot reaction from the ligand 3(5)-methyl-5(3)-(2-hydroxyphenyl)pyrazole (H_2phpz) and different manganese(II) salts in basic medium is described.

3150



Hybrid catalysts: the synthesis, structure and ethene polymerisation activity of (salicylaldiminato)(pyrrolylaldiminato) titanium complexes

Dale A. Pennington, Simon J. Coles, Michael B. Hursthouse, Manfred Bochmann and Simon J. Lancaster*

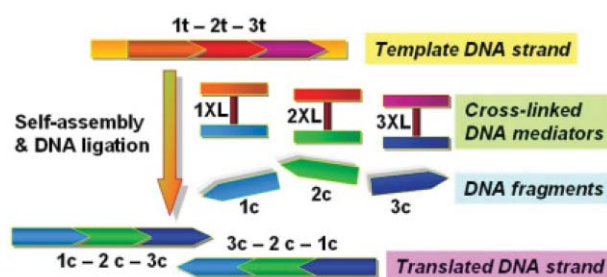
The first examples of hybrid octahedral complexes, with a combination of salicylaldiminato and pyrrolylaldiminato ligands, yield extremely high ethene polymerisation productivities.

3153

Programmable DNA translation system using cross-linked DNA mediators

Masayuki Endo,* Shinsuke Uegaki and Tetsuro Majima*

The information of template DNA strands was converted into the specific sequences in a programmable way by following the mediation of cross-linked DNAs.

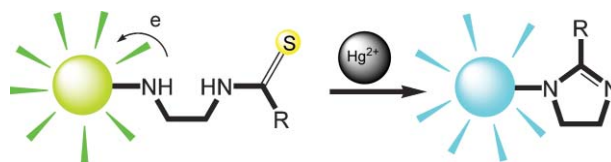


3156

A selective fluorescent ratiometric chemodosimeter for mercury ion

Bin Liu and He Tian*

A fluorescent naphthalimide chemodosimeter with high selectivity for Hg(II) in aqueous solution based upon the reactivity of thiourea derivatives toward Hg(II) utilized a different fluorescence signal for the detection.

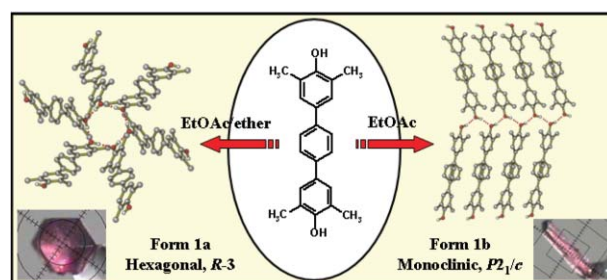


3159

Concomitant polymorphs of 2,2',6,6'-tetramethyl-4,4'-terphenyldiol: the β -quinol network reproduced in a metastable polymorph

Srinivasulu Aitipamula and Ashwini Nangia*

The fascinating rhombohedral network of β -hydroquinone is replicated in another diphenol after over 50 years by crystal engineering, leading to the idea of phenylogous polymorphic series.

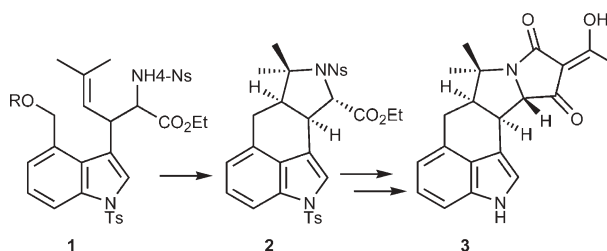


3162

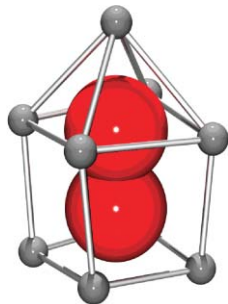
A total synthesis of (\pm)- α -cyclopiazonic acid using a cationic cascade

Charlotte M. Haskins and David W. Knight*

A total synthesis of (\pm)- α -cyclopiazonic acid **3** has been achieved in which the key step is a cationic cascade cyclisation in which the precursor **1**, derived from indole-4-methanol, is converted into the tetracyclic intermediate **2** in 74% isolated yield by exposure to triflic acid in chloroform.



3165

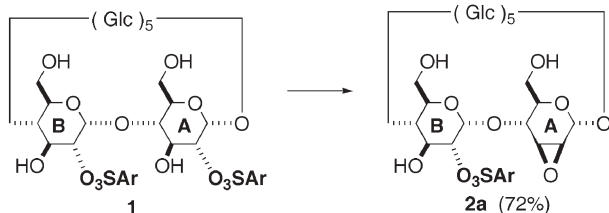


Spontaneous assembly of a nine-vertex lithium framework encapsulating the peroxide dianion

Martyn P. Coles* and Peter B. Hitchcock

A molecular house for peroxide. Investigation of the structure of the lithiated, bicyclic guanidine 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (hppH) has led to the reproducible isolation of the compound $\text{Li}_9(\text{hpp})_7(\text{O}_2)(\text{THF})_x$ ($x = 0, 1$), containing the peroxide dianion encapsulated within a mono-capped, cubic array of lithium ions.

3168

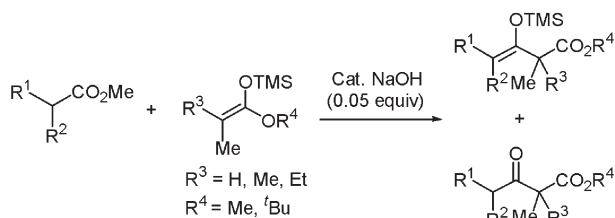


The first hetero-bifunctionalization of the secondary face of β -cyclodextrin: selective and efficient conversion of the A-ring of a 2^A,2^B-disulfonate to 2^A,3^A-epoxymannoside

Makoto Fukudome, Yuji Sugimoto, De-Qi Yuan and Kahee Fujita

The A-ring of **1** was converted to 2^A,3^A-epoxymannoside without affecting the other sulfonated residue, which affords the first approach to hetero-bifunctionalization at the secondary hydroxyl side of cyclodextrins.

3171

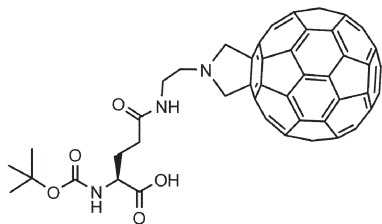


NaOH-catalyzed crossed Claisen condensation between ketene silyl acetals and methyl esters

Akira Iida, Kenta Takai, Tomohito Okabayashi, Tomonori Misaki and Yoo Tanabe*

We developed a mild and practical crossed Claisen condensation between ketene silyl acetals and methyl esters using catalytic NaOH to obtain α -monoalkylated β -keto esters and inaccessible α,α -dialkylated β -keto esters.

3174



Efficient solid-phase synthesis of fullero-peptides using Merrifield strategy

Alberto Bianco*

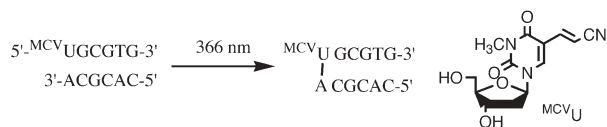
A new N-protected C₆₀-based amino acid, called Boc-L-fulleropyrrolidino-glutamic acid, was prepared and employed for the synthesis of fullero-peptides using the solid-phase Boc/Bzl chemistry developed by Merrifield.

3177

Photoinduced DNA end capping via *N*³-methyl-5-cyanovinyl-2'-deoxyuridine

Kenzo Fujimoto,* Yoshinaga Yoshimura, Tadayoshi Ikemoto, Akio Nakazawa, Masayuki Hayashi and Isao Saito

A modified oligodeoxynucleotide (ODN) containing *N*³-methyl-5-cyanovinyl-2'-deoxyuridine reacts by photoirradiation at 366 nm with an adenine residue of a complementary template ODN to yield an end-capped ODN in 87% yield.

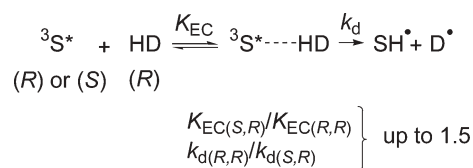


3180

Stereodifferentiation in the formation and decay of the encounter complex in bimolecular electron transfer with photoactivated acceptors

Julia Pérez-Prieto,* Raquel E. Galian, Maria C. Morant-Miñana and Miguel A. Miranda*

Experimental evidence has been obtained for the involvement of encounter complexes between both enantiomers of a π,π^* triplet excited ketone and a chiral phenol or indole. Kinetic evaluation indicates a significant stereodifferentiation in both steps of the quenching process.

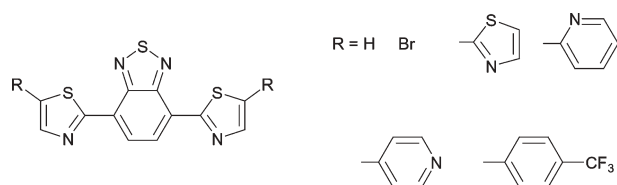


3183

Synthesis, characterization and FET properties of novel dithiazolylbenzothiadiazole derivatives

Md. Akhtaruzzaman, Naoto Kamata, Jun-ichi Nishida, Shinji Ando, Hirokazu Tada, Masaaki Tomura and Yoshiro Yamashita*

Dithiazolylbenzothiadiazoles have high electron affinity and the FET device of a trifluoromethylphenyl derivative exhibited good n-type performance with a high electron mobility.

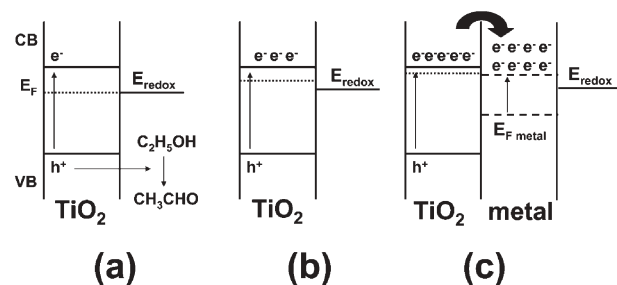


3186

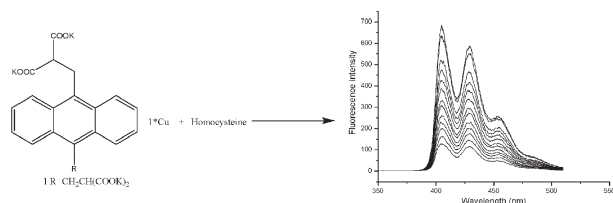
Efficient charge storage in photoexcited TiO₂ nanorod-noble metal nanoparticle composite systems

P. Davide Cozzoli,* M. Lucia Curri and Angela Agostiano

Following UV-illumination, TiO₂ nanorod-stabilized noble metal (Ag, Au) nanoparticles dispersed in deaerated organic mixtures can sustain a higher degree of conduction band electron accumulation than that achievable with pristine titania.



3189

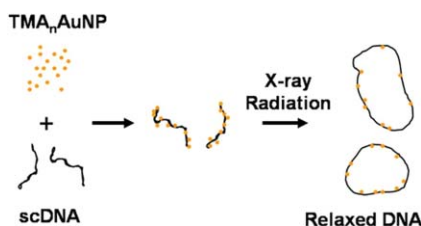


Fluorescence probes for thiol-containing amino acids and peptides in aqueous solution

Yanyan Fu, Hongxiang Li,* Wenping Hu* and Daoben Zhu*

A new fluorescence probe is described using the “chemosensing ensemble” method. The probe shows high selectivity and sensitivity for thiol-containing amino acids and peptides, and can detect cysteine and homocysteine from healthy to abnormal levels under physiologically-relevant conditions.

3192

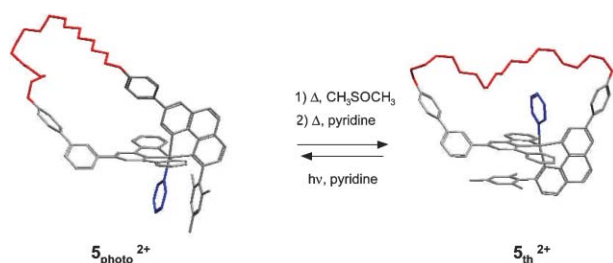


Enhanced relaxation of nanoparticle-bound supercoiled DNA in X-ray radiation

Erika A. Foley, Joshua D. Carter, Fang Shan and Ting Guo*

Supercoiled DNA is at least 100% more vulnerable in hard X-ray radiation when it is bound to 5 nm gold nanoparticles covered with positively charged trimethylammonium terminating alkanethiol ligands

3195

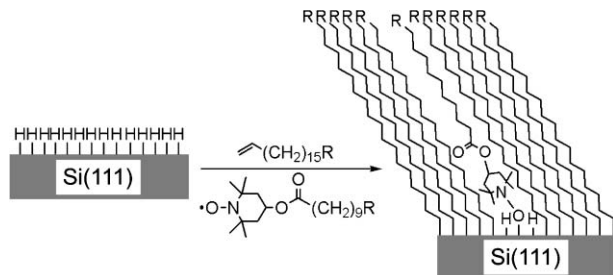


A Ru(terpy)(phen)-incorporating ring and its light-induced geometrical changes

Sylvestre Bonnet, Jean-Paul Collin* and Jean-Pierre Sauvage

A Ru(terpy)(phen) motif has been inscribed in a 39-membered ring. By visible light irradiation, a dramatic geometrical changeover of the cyclic complex takes place which can be reversed thermally.

3198



Mild methods to assemble and pattern organic monolayers on hydrogen-terminated Si(111)

Samer N. Arafat, Samrat Dutta, Mathew Perring, Michael Mitchell, Paul J. A. Kenis and Ned B. Bowden*

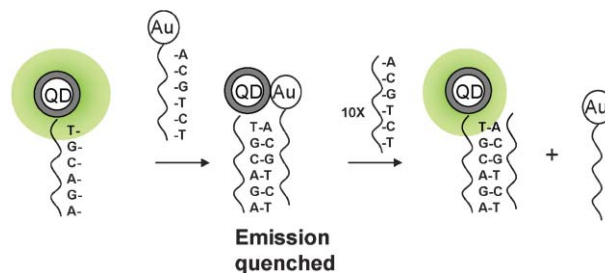
Mild methods to assemble well-ordered organic monolayers of olefins on Si(111) using 2,2,6,6-tetramethyl-1-piperidinyloxy and to pattern these monolayers on the micrometer-size scale using soft lithography are reported.

3201

Quenching of CdSe quantum dot emission, a new approach for biosensing

L. Dyadyusha, H. Yin, S. Jaiswal, T. Brown, J. J. Baumberg, F. P. Booy and T. Melvin*

The emission of CdSe quantum dots linked to the 5'-end of a DNA sequence is efficiently quenched by hybridisation with a complementary DNA strand with a gold nanoparticle attached at the 3'-end; contact of the quantum dot and gold nanoparticle occurs.

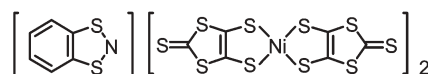


3204

A unique new multiband molecular conductor: [BDTA][Ni(dmit)₂]₂

Sarah S. Staniland, Wataru Fujita, Yoshikatsu Umezono, Kunio Awaga, Stewart J. Clark, HengBo Cui, Hayao Kobayashi and Neil Robertson*

[BDTA][Ni(dmit)₂]₂ has been prepared by simple mixing of precursor salts of the components. X-ray structure, conductivity, magnetic susceptibility and band calculations are consistent with a multiband electronic structure with fractional average charges on the components.

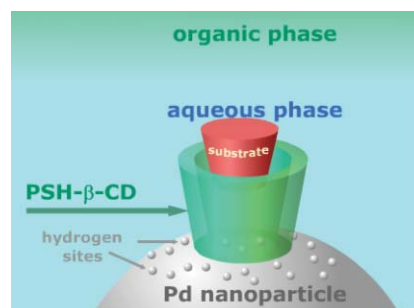


3207

A metal nanoparticle-based supramolecular approach for aqueous biphasic reactions

Shilpa C. Mhadgut, Kumaranand Palaniappan, Muralidhara Thimmaiah, Stephen A. Hackney, Béla Török* and Jian Liu*

β -cyclodextrin-modified Pd nanoparticles were successfully employed as a phase transfer/hydrogenation catalyst in aqueous biphasic systems.

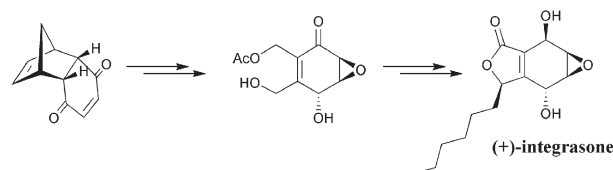


3210

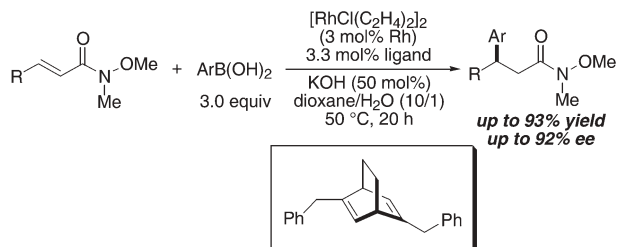
Enantioselective total synthesis of a novel polyketide natural product (+)-integrasone, an HIV-1 integrase inhibitor

Goverdhan Mehta* and Subhrangsu Roy

The first enantioselective total synthesis of (+)-integrasone, a novel HIV-1 integrase inhibitor, has been accomplished from the commercially available Diels–Alder adduct of cyclopentadiene and *p*-benzoquinone following a short, flexible strategy.



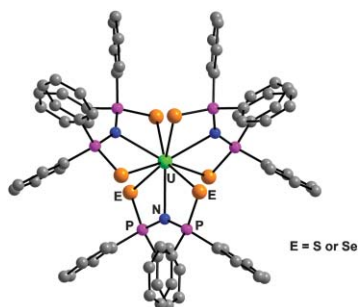
3213

**Rhodium/diene-catalyzed asymmetric 1,4-addition of arylboronic acids to α,β -unsaturated Weinreb amides**

Ryo Shintani, Takahiro Kimura and Tamio Hayashi*

A rhodium/chiral diene complex has been found to effectively catalyze the 1,4-addition of arylboronic acids to α,β -unsaturated Weinreb amides, furnishing useful β -chiral Weinreb amides in high enantioselectivity.

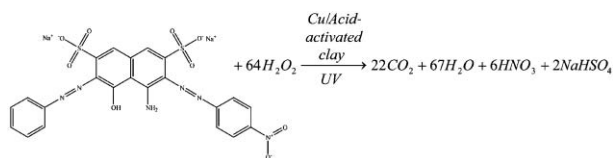
3215

**Homoleptic uranium(III) imidodiphosphinochalcogenides including the first structurally characterised molecular trivalent actinide–Se bond**

Andrew J. Gaunt, Brian L. Scott and Mary P. Neu*

The homoleptic, nine-coordinate, uranium(III) complexes, $U[N(E)PPh_2]_3$, have been prepared and characterised, including the first crystallographic determination of a molecular trivalent actinide–selenium bond.

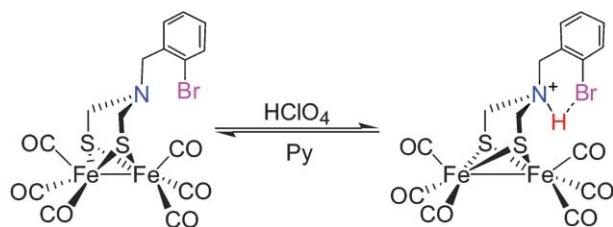
3218

**A novel heterogeneous acid-activated clay supported copper catalyst for the photobleaching and degradation of textile organic pollutant using photo-Fenton-like reaction**

Alex Chi-Kin Yip, Frank Leung-Yuk Lam and Xijun Hu*

Copper supported on acid-activated bentonite clay was found to be an effective catalyst for the photo degradation of Acid Black 1 at pH 3.0–8.0 without significant metal leaching.

3221

**Spectroscopic and crystallographic evidence for the N-protonated $Fe^I Fe^I$ azadithiolate complex related to the active site of Fe-only hydrogenases**

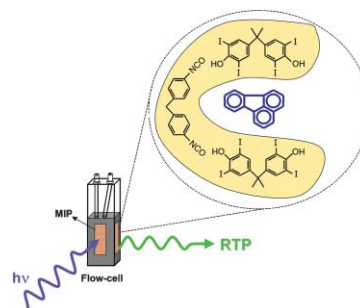
Fujun Wang, Mei Wang,* Xiaoyang Liu, Kun Jin, Weibing Dong, Guanghua Li, Björn Åkermark and Licheng Sun*

The spectroscopic evidence and the molecular structures of $[(\mu-SCH_2)_2N(CH_2C_6H_4-2-Br)]Fe_2(CO)_6$ and its N-protonated species, as structural models of the Fe-only hydrogenase active site, unambiguously reveal the rapid protonation and deprotonation processes between them.

Iodinated molecularly imprinted polymer for room temperature phosphorescence optosensing of fluoranthene

A. Salinas-Castillo, I. Sánchez-Barragán,
J. M. Costa-Fernández, R. Pereiro, A. Ballesteros,
J. M. González, A. Segura-Carretero,
A. Fernández-Gutiérrez and A. Sanz-Medel*

An approach is described for the design and synthesis of molecularly imprinted polymers (MIPs) with an internal heavy atom in their structure. The combination of the iodinated MIP with phosphorescence detection has demonstrated a great potential for fluoranthene monitoring in water.



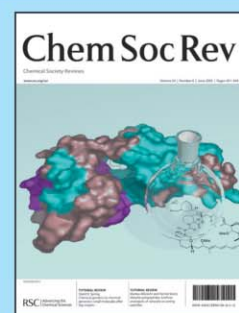
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