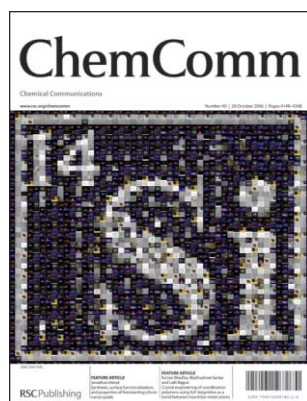


IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (40) 4149–4248 (2006)



Cover

See Jonathan Veinot,
page 4160.

The mosaic forming the familiar periodic table symbol for silicon consists of images highlighting the optical and microscopic properties of freestanding Si nanocrystals. Design by Joel Kelly and Colin Hessel, University of Alberta. Image reproduced by permission of Jonathan Veinot, *Chem. Commun.*, 2006, 4160.

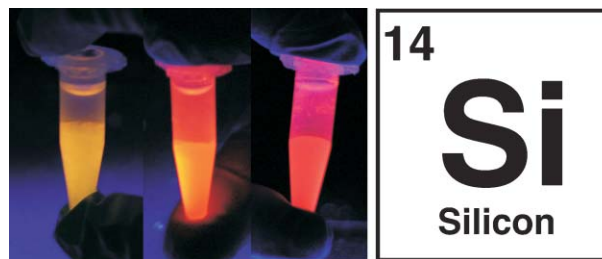
FEATURE ARTICLES

4160

Synthesis, surface functionalization, and properties of freestanding silicon nanocrystals

Jonathan G. C. Veinot*

This feature article outlines state-of-the-art methods for synthesizing and tailoring the surface chemistry of freestanding Si nanoparticles (FS-*nc*-Si), current opinion on FS-*nc*-Si optical properties, and a brief discussion of possible future research directions is presented.

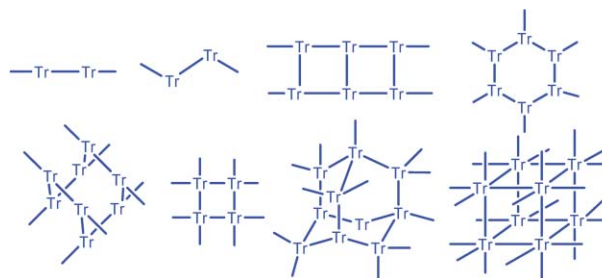


4169

Crystal engineering of coordination polymers using 4,4'-bipyridine as a bond between transition metal atoms

Kumar Biradha,* Madhushree Sarkar and Lalit Rajput

In recent years, the crystal engineering of coordination polymers has attracted the enormous interest of chemists due to the potential applications. This review covers the coordination networks of prototypical bridging ligand 4,4'-bipyridine with various transition metals.



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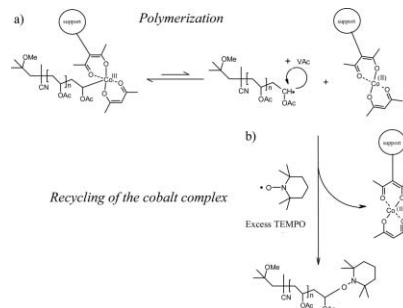
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4180

Supported cobalt mediated radical polymerization (SCMRP) of vinyl acetate and recycling of the cobalt complex

Valérie Sciannamea, Antoine Debuigne, Yasmine Piette, Robert Jerome* and Christophe Detrembleur

This communication aims at reporting for the first time on the preparation, use and recycling of supported cobalt complexes for the controlled radical polymerization of vinyl acetate.

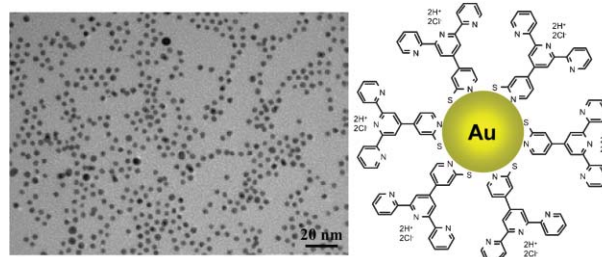


4183

Gold nanocomposites with rigid fully conjugated heteroditopic ligands shell as nanobuilding blocks for coordination chemistry

Cédric R. Mayer,* Eddy Dumas, Aude Michel and Francis Sécheresse

We report the facile direct synthesis of gold nanoparticles stabilized by fully conjugated easily tunable organic ligands; these nanocomposites have been efficiently used as monodisperse and solvent adaptable platforms to functionalize gold nanoparticles by metallic complexes.

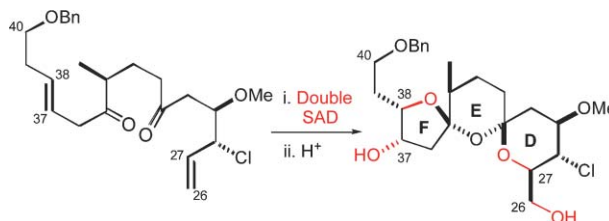


4186

Synthesis of the DEF-*bis*-spiroacetal of spirastrellolide A exploiting a double asymmetric dihydroxylation/spiroacetalisation strategy

Ian Paterson,* Edward A. Anderson, Stephen M. Dalby, Jong Ho Lim, Philip Maltas and Christian Moessner

An efficient synthesis of the C₂₆–C₄₀ tricyclic [5,6,6]-*bis*-spiroacetal segment of the marine macrolide spirastrellolide A has been developed, exploiting a novel double Sharpless asymmetric dihydroxylation/spiroacetalisation sequence.

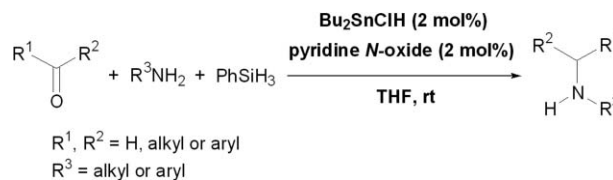


4189

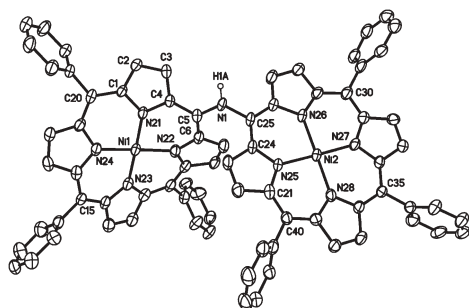
The reductive amination of aldehydes and ketones by catalytic use of dibutylchlorotin hydride complex

Hirofumi Kato, Ikuya Shibata,* Yuta Yasaka, Shinji Tsunoi, Makoto Yasuda and Akio Baba*

Silyl hydrides, such as Ph₂SiH₂ and PhSiH₃, promoted the reductive amination of aldehydes and ketones in the presence of a catalytic amount of Bu₂SnClH–pyridine *N*-oxide. This method has advantages in terms of its mild conditions and wide application to various carbonyls and amines.



4192

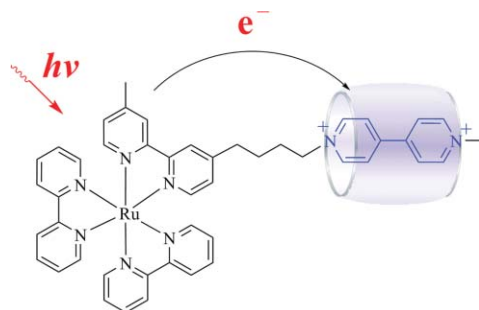


New palladium catalysed reactions of bromoporphyrins: synthesis and crystal structures of nickel(II) complexes of primary 5-aminoporphyrin, 5,5'-bis(porphyrinyl) secondary amine, and 5-hydroxy porphyrin

Louisa J. Esdaile, Mathias O. Senge and Dennis P. Arnold*

A unique bis(porphyrinyl)amine is one of three new porphyrin complexes formed from the coupling of nickel(II) bromoporphyrin with hydrazine under palladium catalysis.

4195

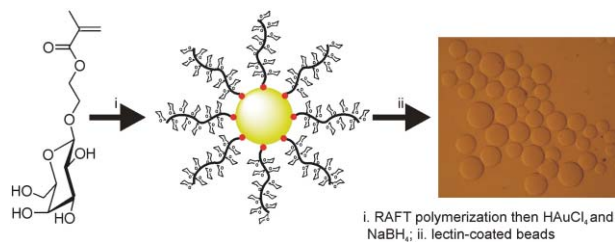


The photoinduced long-lived charge-separated state of Ru(bpy)₃-methylviologen with cucurbit[8]uril in aqueous solution

Shiguo Sun, Rong Zhang, Samir Andersson, Jingxi Pan, Björn Åkermark and Licheng Sun*

A stable 1 : 1 inclusion complex of Ru(bpy)₃-MV²⁺ with cucurbit[8]uril (CB[8]) is formed in aqueous solution; upon light irradiation, a long lived ($\tau \sim 2 \mu\text{s}$) charge-separated state Ru³⁺-MV^{•+}-CB[8] is observed.

4198

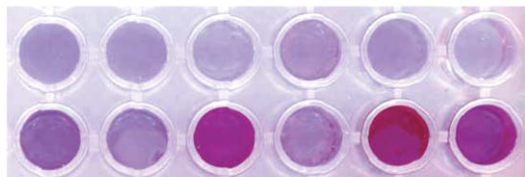
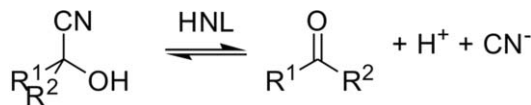


Facile *in situ* preparation of biologically active multivalent glyconanoparticles

Sebastian G. Spain, Luca Albertin and Neil R. Cameron*

Biologically active multivalent glyconanoparticles are prepared in an extremely simple method by reduction of well-defined glycopolymers, prepared by RAFT polymerisation, in an aqueous solution of HAuCl₄.

4201



A high-throughput screening assay for hydroxynitrile lyase activity

Jennifer Andexer, Jan-Karl Guterl, Martina Pohl and Thorsten Eggert*

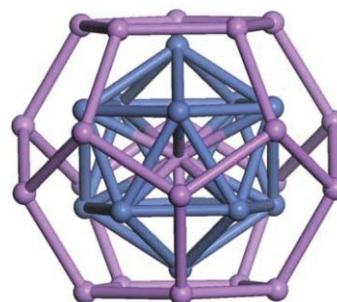
A high-throughput screening assay for hydroxynitrile lyase (HNL) activity is presented, which is useful to detect activity and enantioselectivity of HNLs for enzyme fingerprinting and screening of large variant libraries generated in metagenome or directed evolution approaches.

4204

The isolable matryoshka nesting doll icosahedral cluster $[\text{As}@\text{Ni}_{12}@\text{As}_{20}]^{3-}$ as a “superatom”: analogy with the jellium cluster Al_{13}^- generated in the gas phase by laser vaporization

R. Bruce King* and Jijun Zhao*

The valence electrons in the icosahedral cluster $[\text{As}@\text{Ni}_{12}@\text{As}_{20}]^{3-}$ can be partitioned so that the central As atom is As^{3-} and the intermediate Ni_{12} icosahedron receives 40 electrons from the lone pairs of the outer As_{20} dodecahedron to be isoelectronic with the Al_{13}^- jellium cluster.

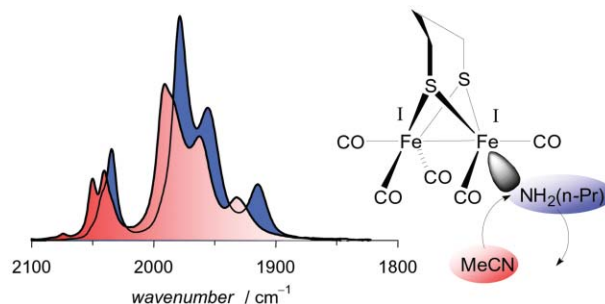


4206

Dynamic ligation at the first amine-coordinated iron hydrogenase active site mimic

Lennart Schwartz, Jesper Ekström, Reiner Lomoth* and Sascha Ott*

An amine ligand that is loosely coordinated to a novel iron hydrogenase active site model can be replaced by a solvent molecule; irrespective of the ligand set, the one electron reduction is chemically reversible and is shown to produce the same species.

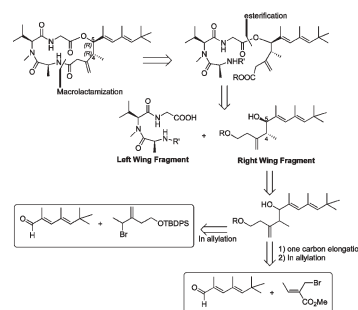


4209

Total synthesis of antillatoxin

Kiew-Ching Lee and Teck-Peng Loh*

The total synthesis of natural (4*R*,5*R*)-antillatoxin and its analog (4*S*,5*S*)-antillatoxin has been achieved in short steps. The optically pure key intermediates were prepared from indium mediated allylation of either primary or secondary allylic bromide with aldehyde in aqueous media, followed by highly selective Luche's reduction and chiral resolution. Our strategy provides a practical and easy entry to these key intermediates and analogs.

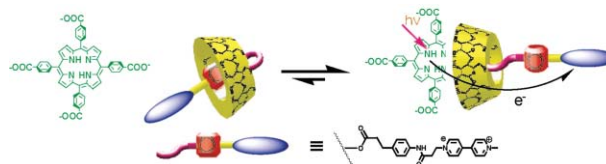


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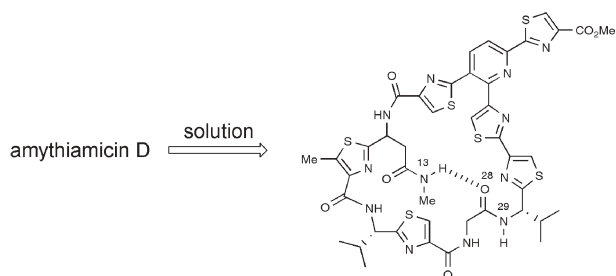
Competitive photoinduced electron transfer by the complex formation of porphyrin with cyclodextrin bearing viologen

Wei Deng, Takeshi Onji, Hiroyasu Yamaguchi, Noriaki Ikeda and Akira Harada*

Photoinduced electron transfer between a porphyrin and a new guest cyclodextrin bearing viologen occurs by a supramolecular formation with conformational change of a guest molecule.



4215

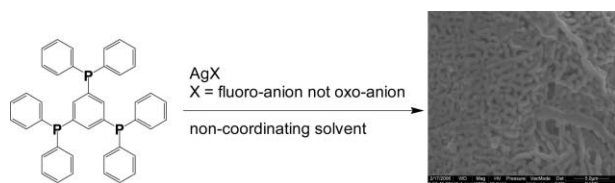


Solution structures of thiopeptide antibiotics

Richard J. Lewis, Rachael A. Hughes, Lilian Alcaraz, Stewart P. Thompson and Christopher J. Moody*

An NMR study of amythiamicin D establishes its solution conformation and the presence of a single intramolecular hydrogen bond, and provides the first evidence for self-association of thiopeptides in solution.

4218

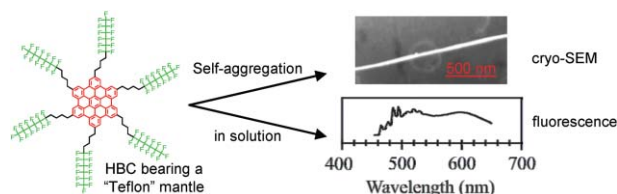


Solution state coordination polymers featuring wormlike macroscopic structures and cage-polymer interconversions

Jianyong Zhang, Xingling Xu and Stuart L. James*

In the absence of coordinating solvents and anions, silver salts and triphosphines form viscous, thixotropic coordination polymers in solution, which aggregate into unusual wormlike macroscopic structures and undergo cage-polymer interconversions depending on the stoichiometry and presence of templating anions.

4221



Self-aggregated perfluoroalkylated hexa-*peri*-hexabenzocoronene fibers observed by cryo-SEM and fluorescence spectroscopy

Olivier F. Aebischer, Annina Aebischer, Patrick Tondo, Bassam Alameddine, Massoud Dadras, Hans-Ulrich Güdel and Titus A. Jenny*

The characterization of a new HBC derivative bearing alkyl/perfluoroalkylated side chains is described. The self-aggregation behavior of this HBC was investigated by optical luminescence spectroscopy and correlated to cryo-SEM investigations.

4224



Selective detection of cesium by a water-soluble fluorescent molecular sensor based on a calix[4]arene-bis(crown-6-ether)

Vincent Souchon, Isabelle Leray* and Bernard Valeur*

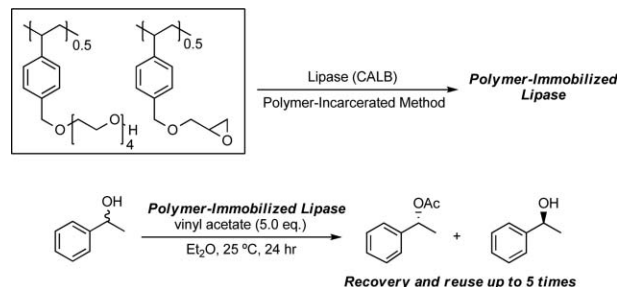
A tetrasulfonated calixarene with two appended crowns, each including a dioxycoumarin fluorophore, is highly soluble in water and shows excellent selectivity for cesium ions.

4227

Novel immobilization method of enzymes using a hydrophilic polymer support

Juta Kobayashi, Yuichiro Mori and Shū Kobayashi*

A novel immobilization of an enzyme with a hydrophilic polymer support in organic solvents has been developed utilizing the “polymer-incarcerated (PI) method”, which has been used to immobilize metal catalysts.

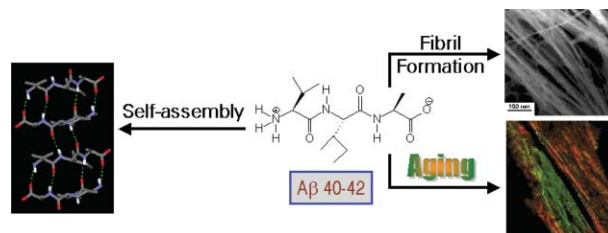


4230

A short water-soluble self-assembling peptide forms amyloid-like fibrils

Sudipta Ray, Apurba K. Das, Michael G. B. Drew and Arindam Banerjee*

A water-soluble tripeptide Val-Ile-Ala (VIA)—the C-terminus of the Alzheimer A β -peptide (A β ₄₀₋₄₂)—self-assembles, in crystalline form, to produce a β -sheet structure and unbranched nanofibrils which exhibit amyloid-like behavior.

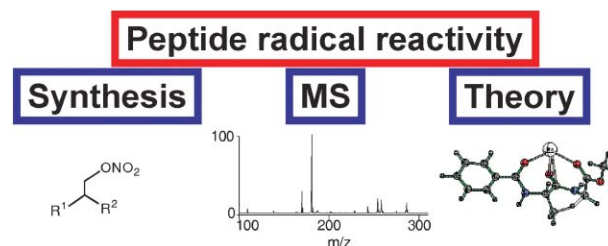


4233

Gas-phase regiocontrolled generation of charged amino acid and peptide radicals

Sheena Wee, Adam Mortimer, Damian Moran, Adam Wright, Christopher K. Barlow, Richard A. J. O'Hair,* Leo Radom* and Christopher J. Easton*

The combined use of advanced mass spectrometry experiments, condensed-phase synthesis of serine and homoserine nitrate ester radical precursors, and high-level *ab initio* calculations provides a powerful way of examining the fundamental reactivity of radicals derived from peptides.

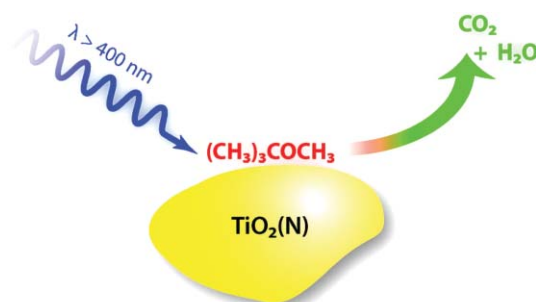


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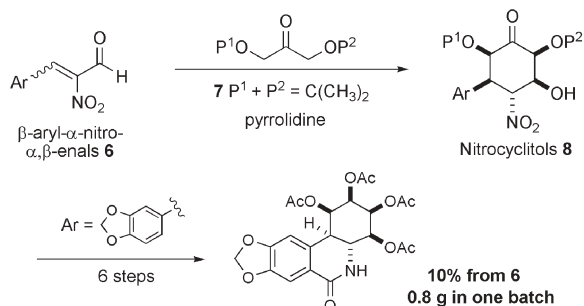
Efficient visible light-active N-doped TiO₂ photocatalysts by a reproducible and controllable synthetic route

Suil In, Alexander Orlov, Felipe García, Mintcho Tikhov, Dominic S. Wright and Richard M. Lambert*

A reproducible and controllable method allows the synthesis of practical quantities of efficient, visible light active TiO₂(N) photocatalysts in which the nitrogen content may be varied to achieve optimum performance.



4239

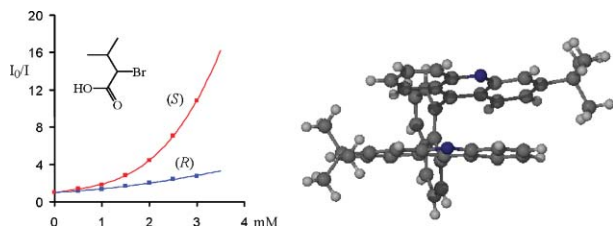


Annulation of β -aryl- α -nitro- α,β -enals and 2,2-dimethyl-1,3-dioxan-5-one: a one-step assembly of nitrocyclitols. Application to a short practical synthesis of (\pm)-7-deoxy-2-*epi*-pancratistatin tetraacetate

Juan Carlos Ortiz, Lidia Ozores, Fernando Cagide-Fagín and Ricardo Alonso*

Fully substituted six-membered nitrocyclitols **8** with five newly created carbon stereocentres are prepared in one step through a novel pyrrolidine-promoted annulation.

4242

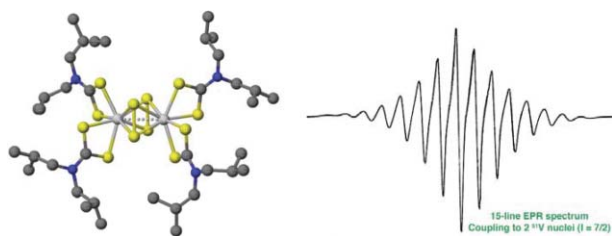


An enantioselective fluorescence sensing assay for quantitative analysis of chiral carboxylic acids and amino acid derivatives

Christian Wolf,* Shuanglong Liu and Brian C. Reinhardt

A chiral 1,8-diacridylnaphthalene-derived fluorosensor exhibiting a C_2 -symmetric cleft designed for stereoselective interactions with hydrogen bond donors has been used for the determination of both concentration and enantiomeric composition of carboxylic acids and amino acid derivatives.

4245



Highly-oxidised, sulfur-rich, mixed-valence vanadium(IV/V) complexes

Michelle K. Taylor, David J. Evans and Charles G. Young*

A new type of highly-oxidised, sulfur-rich, mixed-valence complex, exemplified by $[V_2(\mu-S_2)_2(S_2CN^iBu_2)]^+$, has been discovered. The complexes exhibit striking 15-line EPR spectra and symmetrical structures consistent with a Class III mixed-valence formulation at room temperature. All previously reported V(IV/V) complexes are supported by hard ligation and structure-dependent mixed-valence properties.

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