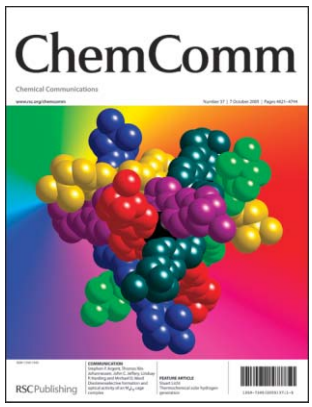
IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (37) 4621–4744 (2005)

In this issue...

Stockman *et al.* present a "tandem reaction" which turns a symmetrical acyclic precursor into a non-symmetrical complex alkaloid. See pp. 4661 – 4662.



Cover

See Stephen P. Argent, Thomas Riis-Johannessen, John C. Jeffery, Lindsay P. Harding and Michael D. Ward, page 4647. The cover shows the structure of the cage complex $[Zn_4(L^2)_6][BF_4]_8$. Image reproduced by permission of Michael D. Ward *et al.* from *Chem. Commun.*, 2005, 4647.

CHEMICAL SCIENCE

C73

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Chemical Science

October 2005/Volume 2/Issue 10

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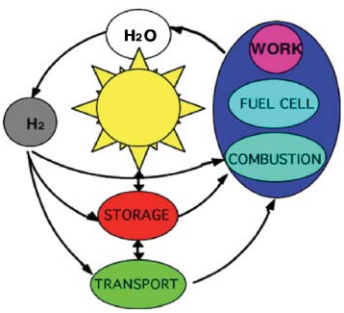
FEATURE ARTICLE

4635

Thermochemical solar hydrogen generation

Stuart Licht*

This review compares, solar direct, indirect and hybrid thermochemical processes to alternate solar/hydrogen generation processes; a hybrid solar thermal/electrochemical process can convert solar energy to hydrogen fuel at 50% efficiencies.



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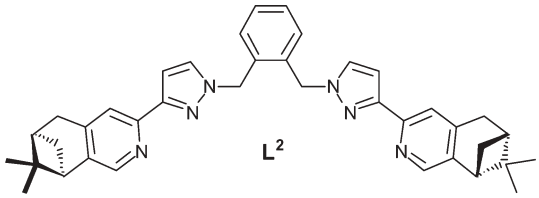
4647

Diastereoselective formation and optical activity of an M_4L_6 cage complex

Stephen P. Argent, Thomas Riis-Johannessen, John C. Jeffery, Lindsay P. Harding and Michael D. Ward*

The chiral ligand L^2 reacts with $M(BF_4)_2$ (M = Co, Zn) to afford tetrahedral cages $[M_4(L^2)_6][BF_4]_8$, in which the ligands each span one edge of the M_4 tetrahedron, with high diastereoselectivity; the helical twist induced in all ligands on coordination results in an increase in the optical rotation of the coordinated ligands compared to the same number of free ligands by a factor of 5.

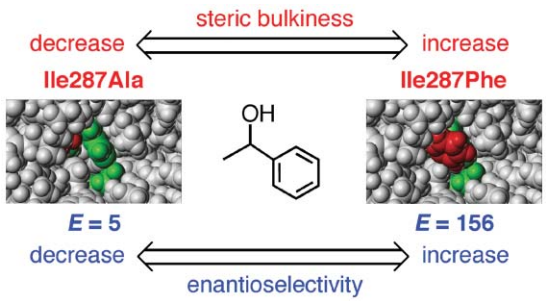


4650

Rational control of enantioselectivity of lipase by site-directed mutagenesis based on the mechanism

Tadashi Ema,* Toshiyuki Fujii, Misa Ozaki, Toshinobu Korenaga and Takashi Sakai*

The enantioselectivity of a *Burkholderia cepacia* lipase toward secondary alcohols could be both increased and decreased rationally by introducing only a single mutation on the basis of the mechanism proposed previously.

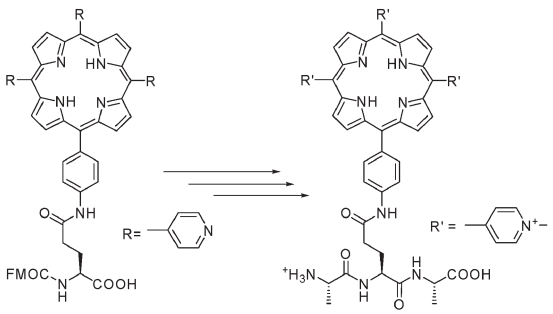


4652

Synthesis of cationic porphyrin modified amino acids

Eric Biron and Normand Voyer*

Amino acid derivatives bearing a porphyrin moiety on a side chain were synthesized. These modified amino acids can be used to develop novel supramolecular devices exploiting peptidic architectures.

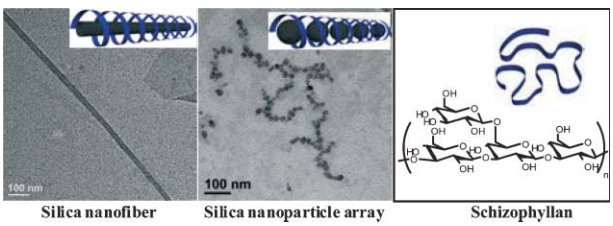


4655

β-1,3-Glucan polysaccharide can act as a one-dimensional host to create novel silica nanofiber structures

Munenori Numata, Chun Li, Ah-Hyun Bae, Kenji Kaneko, Kazuo Sakurai and Seiji Shinkai*

We have demonstrated that the creation of water-soluble silica nanostructures is possible by utilizing the SPG cavity as a one-dimensional host. The finding clearly shows that SPG has a potential ability to act not only as a one-dimensional host for TMPS but also as a vessel for a sol-gel polycondensation reaction.



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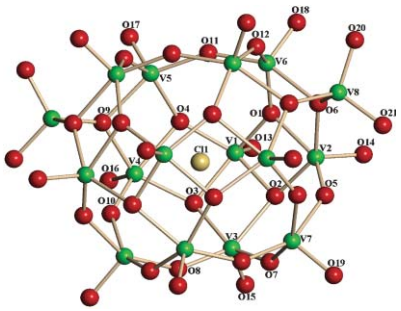
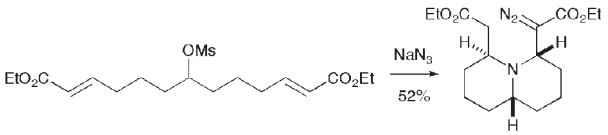


Synthesis and characterization of a polyoxovanadate cluster representing a new topology

M. Ishaque Khan,* Samar Ayesh, Robert J. Doedens,* Minghui Yu and Charles J. O'Connor

The polyoxoanionic cluster, $[V^{V}_{13}V^{IV}_{3}O_{42}(Cl)]^{8-}$, represents a novel topology in the family of polyoxovanadate clusters. The new mixed-valence species exhibits Curie paramagnetism.

4661

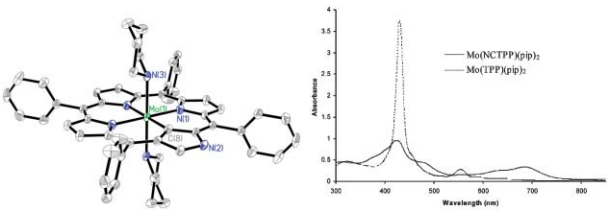


Combining two-directional synthesis and tandem reactions: desymmetrisation by intramolecular cycloaddition/triazoline fragmentation

Martin Rejzek, Robert A. Stockman,* Jan H. van Maarseveen and David L. Hughes

A tandem azide formation/cycloaddition/fragmentation/ Michael addition reaction of a symmetrical acyclic mesylate results in the formation of a non-symmetrical bicyclic quinolizidine derivative in one step.

4663



The synthesis of isostructural Mo^{2+} porphyrin and *N*-confused porphyrin complexes

John D. Harvey, Janet L. Shaw, Richard S. Herrick and Christopher J. Ziegler*

The synthesis and characterization of the first early transition metal complex of *N*-confused porphyrin is presented; $Mo(NCTPP)(pip)_2$ forms an identical structure to that of its normal porphyrin analogue, however this species shows striking electronic and magnetic differences.

4666

Intramolecular charge-transfer fluorescence of 1-phenyltridecamethylbicyclo[2.2.2]octasilane

Wataru Setaka, Natsuki Hamada, Chizuko Kabuto and Mitsuo Kira*

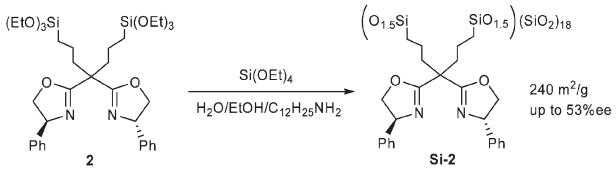
Compound **1** with three-fold symmetric Si–Si bonds shows dual fluorescence operated by a new mechanism in a non-polar solvent.

4669

The first synthesis of organic–inorganic hybrid materials with chiral bis(oxazoline) ligands

José M. Fraile, José I. García, Clara I. Herrerías and José A. Mayoral*

The first immobilization of hydrolysis-sensitive chiral bis(oxazoline) ligands through a sol–gel methodology is described. The highly porous materials lead to complexes which are able to catalyze enantioselective reactions.

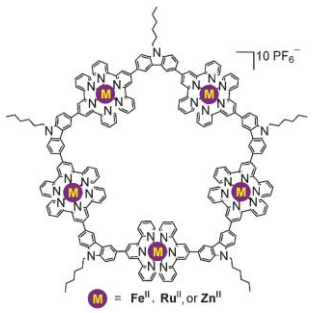


4672

Design, self-assembly, and photophysical properties of pentameric metallomacrocycles: [M_5(*N*-hexyl[1,2-bis(2,2′:6′,2″-terpyridin-4-yl)]carbazole)$_5$][M = Fe(II), Ru(II), and Zn(II)]

Seok-Ho Hwang, Pingshan Wang, Charles N. Moorefield, Luis A. Godínez, Juan Manríquez, Erika Bustos and George R. Newkome*

Pentameric metallocycles, obtained by self-assembly of carbazole-modified bis(terpyridine) building blocks, have been shown to be effective sensitizers in solar cell devices.

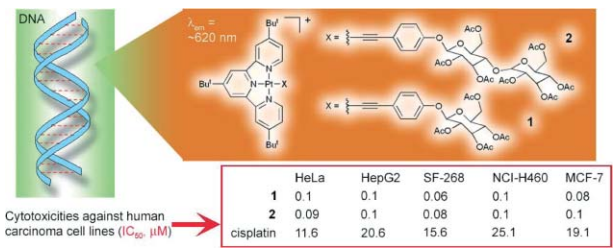


4675

Water soluble luminescent platinum terpyridine complexes with glycosylated acetylide and arylacetylide ligands: photoluminescent properties and cytotoxicities

Dik-Lung Ma, Tina Yuen-Ting Shum, Fuyi Zhang, Chi-Ming Che* and Mengsu Yang

Platinum(II) terpyridine complexes with glycosylated acetylide and arylacetylide ligands were prepared; the glycosylated arylacetylide complexes exhibit emission at $\lambda_{max} \approx 620$ nm in water and are up to ~100-times higher in potency than clinical cisplatin drug in killing cancer cells.



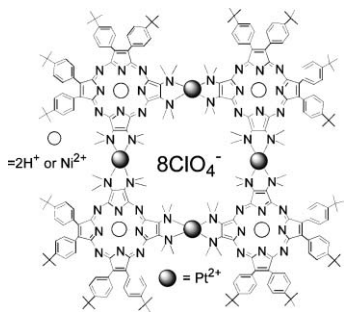
	HeLa	HepG2	SF-268	NCI-H460	MCF-7
1	0.1	0.1	0.06	0.1	0.08
2	0.09	0.1	0.08	0.1	0.1
cisplatin	11.6	20.6	15.6	25.1	19.1

4678

Supramolecular squares of porphyrazines

Kai Fan Cheng, Ngee Ai Thai, Lucile C. Teague, Klaus Grohmann and Charles Michael Drain*

The formation of porphyrazine arrays requires new supramolecular methods. Porphyrazine squares, for example, have different optical properties than the widely studied porphyrinsquares. The porphyrazine building blocks have complementary topologies to a variety of metal ions.



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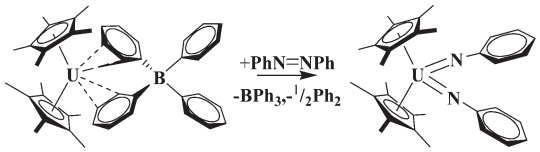
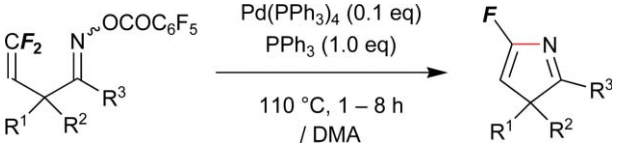


$[(C_5Me_5)_2U][(\mu\text{-}Ph)_2BPh_2]$ as a four electron reductant

William J. Evans,* Stosh A. Kozimor and Joseph W. Ziller

Comparison of the reactivity of $[(C_5Me_5)_2U][(\mu\text{-}Ph)_2BPh_2]$ with the four- and eight-electron reductive chemistry of $(C_5Me_5)_3U$ and $[(C_5Me_5)_2U]_2(C_6H_6)$ revealed that the tetraphenylborate complex surprisingly functions as a four-electron reductant.

4684

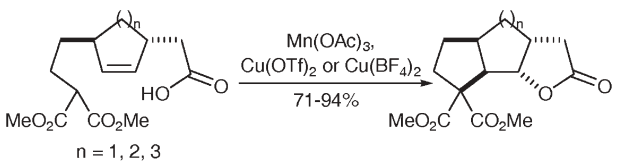


Heck-type 5-*endo-trig* cyclization promoted by vinylic fluorines: synthesis of 5-fluoro-3*H*-pyrroles

Kotaro Sakoda, Jun Mihara and Junji Ichikawa*

A 5-*endo-trig* alkene insertion proceeds under palladium catalysis *via* aminopalladium species starting from 3,3-difluoroallyl ketone *O*-pentafluorobenzoyloximes, providing a facile access to 5-fluoro-3*H*-pyrroles.

4687

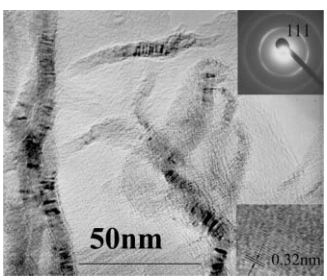


Synthesis of fused tricyclic γ-lactones mediated by manganese(III) acetate

David G. Hulcoop and Jonathan W. Burton*

Exposure of cyclic alkenes bearing a carboxylic acid and a malonate group to manganese(III) acetate and an appropriate copper(II) salt provides the corresponding tricyclic γ-lactones in good yield.

4690



Synthesis of silicon nanowires and nanoparticles by arc-discharge in water

Shu-Man Liu, Mikihiro Kobayashi, Seiichi Sato and Keisaku Kimura*

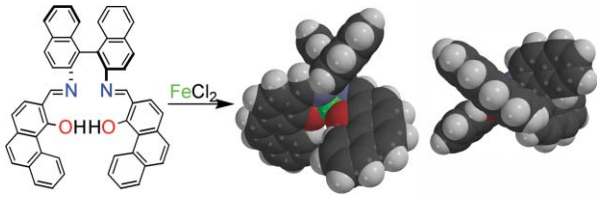
Si nanowires were synthesized by a simple method, using only arc-discharge between two Si electrodes submerged in water, in which no metal catalysts were used.

4693

Iron(II) and zinc(II) monohelical binaphthyl salen complexes

Alexander V. Wiznycia, John Desper and Christopher J. Levy*

A new chiral salen ligand with an (*R*)-binaphthyl backbone and rigid phenanthryl sidearms produces monohelical Fe(II) and Zn(II) complexes with exclusively *M* handedness.

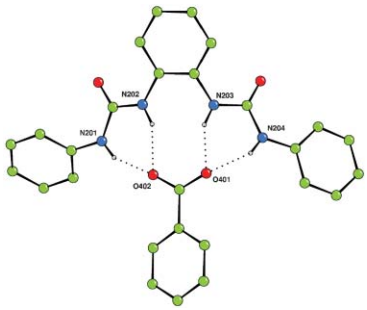


4696

Carboxylate complexation by 1,1′-(1,2-phenylene)bis(3-phenylurea) in solution and the solid state

Simon J. Brooks, Philip A. Gale* and Mark E. Light

A simple *ortho*-phenylenediamine bis-urea compound shows high affinity for carboxylate anions in DMSO-d_6–0.5% water solution.

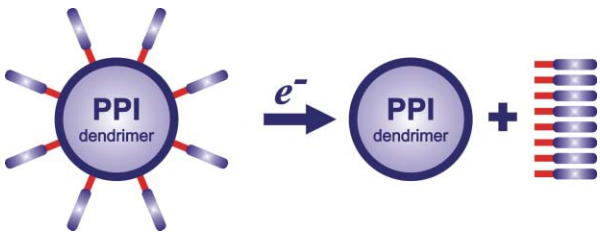


4699

Redox-driven shaving of dendrimers

Winston Ong and Robin L. McCarley*

Despite the complexity of the poly(propylene imine) dendrimer structures, a new redox-based methodology that triggers the simple, zero-order shaving of their end groups has been developed.

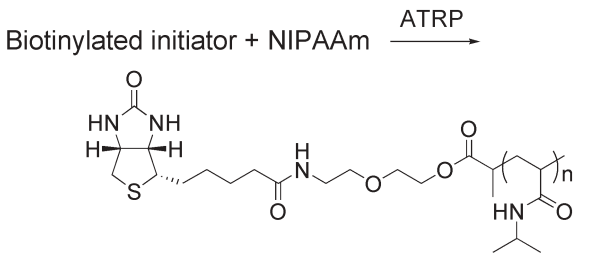


4702

One-step synthesis of low polydispersity, biotinylated poly(*N*-isopropylacrylamide) by ATRP

Debora Bontempo, Ronald C. Li, Tiffany Ly, Carrie E. Brubaker and Heather D. Maynard*

Low polydispersity poly(*N*-isopropylacrylamide) with a biotin end-group was obtained in one step from a biotinylated initiator for atom transfer radical polymerization and interacted with streptavidin to generate the thermosensitive polymer–protein conjugate.



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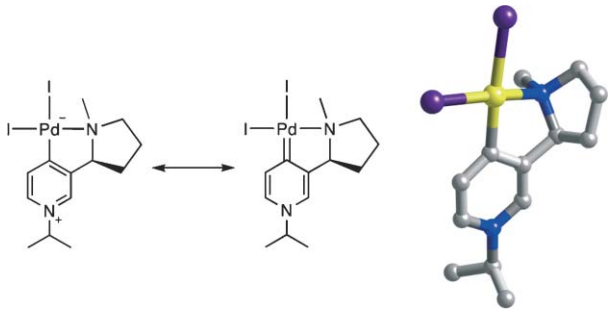
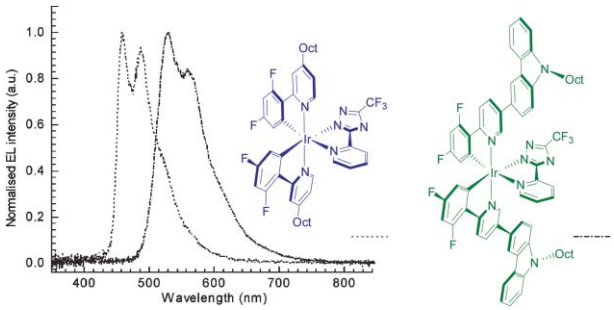


Catalytically active palladium pyridylidene complexes: pyridinium ionic liquids as *N*-heterocyclic carbene precursors

Martin Albrecht* and Helen Stoeckli-Evans

Palladation of pyridinium ions similar to pyridinium-based ionic liquids gives unusual pyridylidene-type *N*-heterocyclic carbene complexes which homogeneously catalyze the Suzuki–Miyaura cross-coupling of arenes.

4708

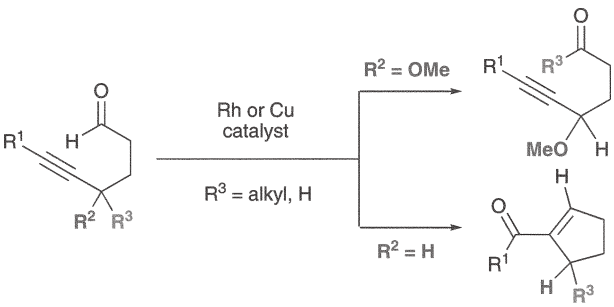


Blue-to-green electrophosphorescence of iridium-based cyclometallated materials

Chris S. K. Mak, Anna Hayer, Sofia I. Pascu, Scott E. Watkins, Andrew B. Holmes,* Anna Köhler and Richard H. Friend

The photo- and electro-luminescence properties of a series of novel, heteroleptic, *mer*-cyclometallated iridium complexes have been fine-tuned from green to blue by changing the substituents on the pyridyl ring of the phenylpyridine ligand.

4711

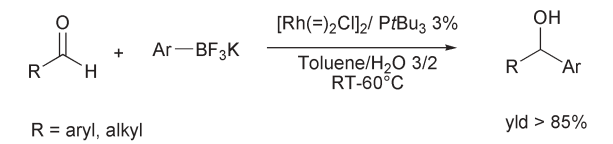


Transition-metal-catalyzed rearrangement of 5-alkynals to γ-alkynylketones and 1-cyclopentenylketones

Ken Tanaka,* Kaori Sasaki, Kenzo Takeishi and Koudai Sugishima

The transition-metal-catalyzed rearrangement of 5-alkynals to γ-alkynylketones and 1-cyclopentenylketones was developed using $[Rh(P(OPh)_3)_2]BF_4$ or $Cu(OTf)_2$ as a catalyst.

4714



Carbinol derivatives *via* rhodium-catalyzed addition of potassium trifluoro(organo)borates to aldehydes

Mathieu Pucheault, Sylvain Darses* and Jean-Pierre Genet*

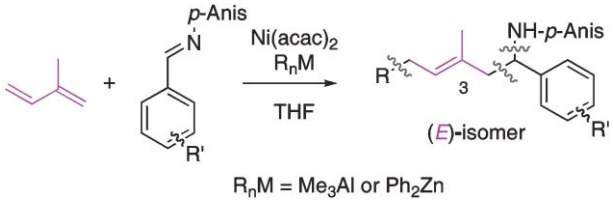
Reaction of potassium aryltrifluoroborates with aldehydes, in the presence of a rhodium catalyst, afforded carbinol derivatives in high yields under mild aqueous conditions.

4717

Nickel-catalyzed four-component connection of oraganoaluminium (organozinc), isoprene, aldehydes and amines: stereo- and regioselective synthesis of trisubstituted (*E*)-homoallylamines

Keisuke Kojima, Masanari Kimura and Yoshinao Tamaru*

$Ni(acac)_2$ catalyzes the four-component connection reaction of trimethylaluminium, isoprene, aromatic aldehydes and *p*-anisidine and provides (*E*)-1-aryl-1-(*p*-methoxyphenyl)amino-3-methyl-3-hexenes selectively in good yield. Diphenylzinc works similarly well.

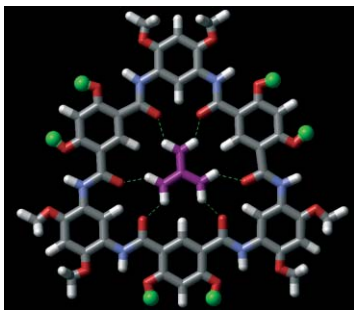


4720

Cyclic aromatic oligoamides as highly selective receptors for the guanidinium ion

Adam R. Sanford, Lihua Yuan, Wen Feng, Kazuhiro Yamato, Robert A. Flowers and Bing Gong*

A class of six-residue, shape-persistent aromatic oligoamide macrocycles bind the guanidinium ion with very high selectivity.

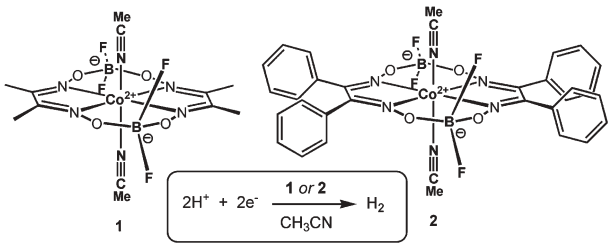


4723

Electrocatalytic hydrogen evolution by cobalt difluoroboryl-diglyoximate complexes

Xile Hu, Brandi M. Cossairt, Bruce S. Brunschwig, Nathan S. Lewis and Jonas C. Peters*

In the presence of moderately strong acids in CH_3CN, cobalt complexes with BF_2-bridged diglyoxime ligands are active catalysts for the reduction of protons to H_2 at potentials as positive as −0.28 V *vs.* SCE.

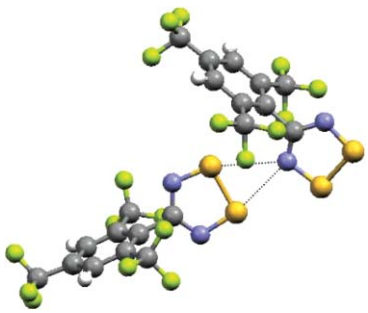


4726

Crystal structures and magnetic properties of a sterically encumbered dithiadiazolyl radical, 2,4,6-$(F_3C)_3C_6H_2CNSSN^{\bullet}$

Antonio Alberola, Caroline S. Clarke, Delia A. Haynes, Sofia I. Pascu and Jeremy M. Rawson*

The title radical is polymorphic with radicals in both phases linked *via* heterocyclic S···N contacts. Both show antiferromagnetic exchange interactions between radicals.



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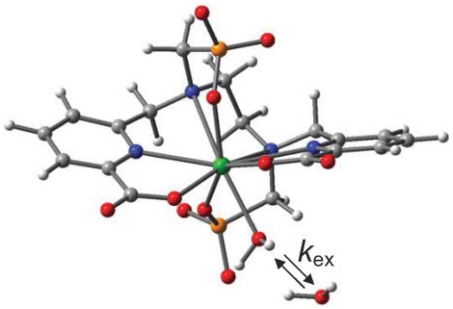
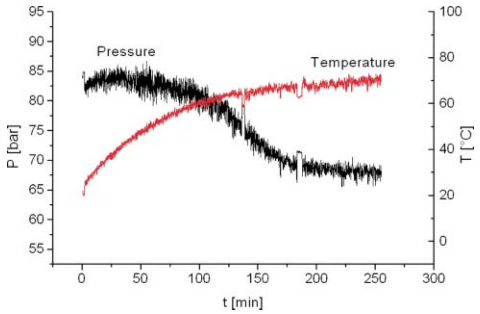


The highest water exchange rate ever measured for a Gd(III) chelate

Marta Mato-Iglesias, Carlos Platas-Iglesias,* Kristina Djanashvili, Joop A. Peters, Éva Tóth, Edina Balogh, Robert N. Muller, Luce Vander Elst, Andrés de Blas* and Teresa Rodríguez-Blas*

This contribution details how a flexible coordination environment for Gd(III) can engender fast water exchange rates, which are vital to the optimisation of contrast agents for use in magnetic resonance imaging.

4732

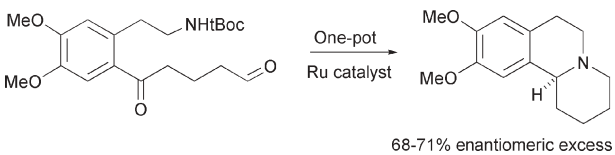


One-step direct synthesis of a Ti-doped sodium alanate hydrogen storage material

José M. Bellosta von Colbe, Michael Felderhoff,* Borislav Bogdanović, Ferdi Schüth and Claudia Weidenthaler

Ti-doped $NaAlH_4$ which has among the best reported hydrogen adsorption–desorption rates, has been synthesized in a special ball mill, allowing parameters such as temperature and pressure to be recorded *in situ*.

4735

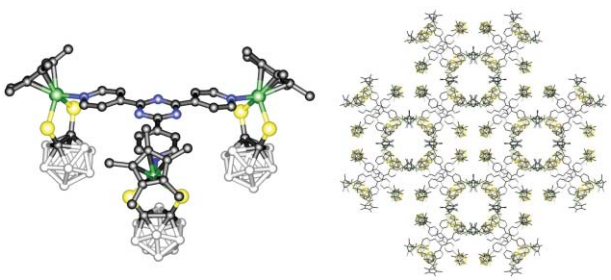


One-pot formation of nitrogen-containing heterocyclic ring systems using a deprotection–cyclisation–asymmetric reduction sequence

Glynn D. Williams, Charles E. Wade and Martin Wills*

A one-pot process for the asymmetric synthesis of N-heterocycles using a Ru(II) asymmetric transfer hydrogenation catalyst is described.

4738



Route to multicluster containing ancillary *ortho*-carborane-1,2-dithiolato ligands†

Jian-Qiang Wang, Chun-Xia Ren and Guo-Xin Jin*

Multicluster molecules $[Cp^*IrS_2C_2(B_{10}H_{10})]_n(L)$ [n = 3 (tpt), 2 (bpy)], connected with pyridyl-based ligands, were prepared and characterized by X-ray crystallography.

4741

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

Goverdhan Mehta and Subhrangsu Roy

AUTHOR INDEX

Alberola, Antonio, 4726
Albrecht, Martin, 4705
Argent, Stephen P., 4647
Ayesh, Samar, 4658
Bae, Ah-Hyun, 4655
Balogh, Edina, 4729
Bellosta von Colbe, José M., 4732
Biron, Eric, 4652
Bogdanović, Borislav, 4732
Bontempo, Debora, 4702
Brooks, Simon J., 4696
Brubaker, Carrie E., 4702
Brunschwig, Bruce S., 4723
Burton, Jonathan W., 4687
Bustos, Erika, 4672
Che, Chi-Ming, 4675
Cheng, Kai Fan, 4678
Clarke, Caroline S., 4726
Cossairt, Brandi M., 4723
Darses, Sylvain, 4714
de Blas, Andrés, 4729
Desper, John, 4693
Djanashvili, Kristina, 4729
Doedens, Robert J., 4658
Drain, Charles Michael, 4678
Ema, Tadashi, 4650
Evans, William J., 4681
Felderhoff, Michael, 4732
Feng, Wen, 4720
Flowers, Robert A., 4720
Fraile, José M., 4669
Friend, Richard H., 4708
Fujii, Toshiyuki, 4650
Gale, Philip A., 4696
García, José I., 4669
Genet, Jean-Pierre, 4714
Godínez, Luis A., 4672
Gong, Bing, 4720
Grohmann, Klaus, 4678
Hamada, Natsuki, 4666
Harding, Lindsay P., 4647
Harvey, John D., 4663
Hayer, Anna, 4708
Haynes, Delia A., 4726
Herrerías, Clara I., 4669
Herrick, Richard S., 4663
Holmes, Andrew B., 4708
Hu, Xile, 4723
Hughes, David L., 4661
Hulcoop, David G., 4687
Hwang, Seok-Ho, 4672
Ichikawa, Junji, 4684
Ishaque Khan, M., 4658
Jeffery, John C., 4647
Jin, Guo-Xin, 4738
Kabuto, Chizuko, 4666
Kaneko, Kenji, 4655
Kimura, Keisaku, 4690
Kimura, Masanari, 4717
Kira, Mitsuo, 4666
Kobayashi, Mikihiro, 4690
Köhler, Anna, 4708
Kojima, Keisuke, 4717
Korenaga, Toshinobu, 4650
Kozimor, Stosh A., 4681
Levy, Christopher J., 4693
Lewis, Nathan S., 4723
Li, Chun, 4655
Li, Ronald C., 4702
Licht, Stuart, 4635
Light, Mark E., 4696
Liu, Shu-Man, 4690
Ly, Tiffany, 4702
Ma, Dik-Lung, 4675
Mak, Chris S. K., 4708
Manríquez, Juan, 4672
Mato-Iglesias, Marta, 4729
Maynard, Heather D., 4702
Mayoral, José A., 4669
McCarley, Robin L., 4699
Mihara, Jun, 4684
Moorefield, Charles N., 4672
Muller, Robert N., 4729
Newkome, George R., 4672
Numata, Munenori, 4655
O'Connor, Charles J., 4658
Ong, Winston, 4699
Ozaki, Misa, 4650
Pascu, Sofia I., 4708, 4726
Peters, Jonas C., 4723
Peters, Joop A., 4729
Platas-Iglesias, Carlos, 4729
Pucheault, Mathieu, 4714
Rawson, Jeremy M., 4726
Rejzek, Martin, 4661
Ren, Chun-Xia, 4738
Riis-Johannessen, Thomas, 4647
Rodríguez-Blas, Teresa, 4729
Sakai, Takashi, 4650
Sakoda, Kotaro, 4684
Sakurai, Kazuo, 4655
Sanford, Adam R., 4720
Sasaki, Kaori, 4711
Sato, Seiichi, 4690
Schüth, Ferdi, 4732
Setaka, Wataru, 4666
Shaw, Janet L., 4663
Shinkai, Seiji, 4655
Shum, Tina Yuen-Ting, 4675
Stockman, Robert A., 4661
Stoeckli-Evans, Helen, 4705
Sugishima, Koudai, 4711
Takeishi, Kenzo, 4711
Tamaru, Yoshinao, 4717
Tanaka, Ken, 4711
Teague, Lucile C., 4678
Thai, Ngee Ai, 4678
Tóth, Éva, 4729
Vander Elst, Luce, 4729
van Maarseveen, Jan H., 4661
Voyer, Normand, 4652
Wade, Charles E., 4735
Wang, Jian-Qiang, 4738
Wang, Pingshan, 4672
Ward, Michael D., 4647
Watkins, Scott E., 4708
Weidenthaler, Claudia, 4732
Williams, Glynn D., 4735
Wills, Martin, 4735
Wiznycia, Alexander V., 4693
Yamato, Kazuhiro, 4720
Yang, Mengsu, 4675
Yu, Minghui, 4658
Yuan, Lihua, 4720
Zhang, Fuyi, 4675
Ziegler, Christopher J., 4663
Ziller, Joseph W., 4681

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