

IN THIS ISSUE

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Cover

See Fang *et al.*, pp. 4093–4095. Silicon nanowires assembled in micro-sized semispheres were synthesized through simple thermal evaporation without using any templates and metal particle catalysts. Image reproduced by permission of Xiaosheng Fang, Yoshio Bando, Changhui Ye, Guozhen Shen, Ujjal K. Gautam, Chengchun Tang and Dmitri Golberg from *Chem. Commun.*, 2007, 4093.

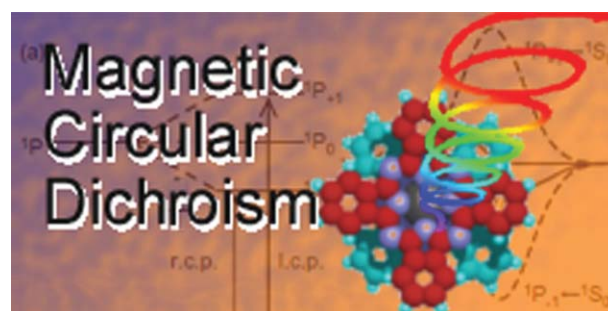
FEATURE ARTICLE

4077

Applications of magnetic circular dichroism spectroscopy to porphyrins and phthalocyanines

Nagao Kobayashi* and Katsunori Nakai

This review deals with recent applications of magnetic circular dichroism (MCD) spectroscopy to porphyrinoid and phthalocyanine systems. Citing examples of analysis, the effectiveness of MCD spectroscopy in the elucidation of electronic structures is reiterated.



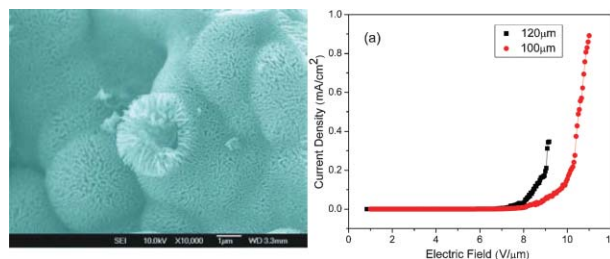
COMMUNICATIONS

4093

Si nanowire semisphere-like ensembles as field emitters

Xiaosheng Fang,* Yoshio Bando, Changhui Ye, Guozhen Shen, Ujjal K. Gautam, Chengchun Tang and Dmitri Golberg

Silicon nanowires assembled in micro-sized semispheres were synthesized through simple thermal evaporation without using any templates and metal particle catalysts. Electron microscopy revealed that the nanowires within semisphere ensembles are well-aligned and evenly distributed. A typical nanowire array density was of $\sim 4 \times 10^9 \text{ cm}^{-2}$. Field-emitting characteristics of the arrays were analyzed.



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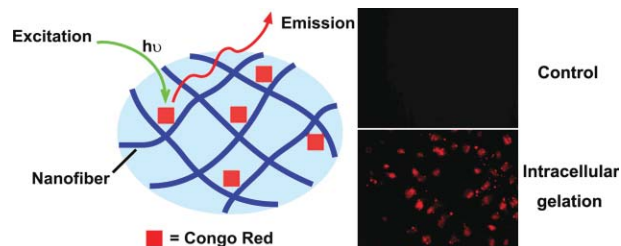
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4096

Using Congo red to report intracellular hydrogelation resulted from self-assembly of small molecules

Gaolin Liang, Keming Xu, Lihua Li, Ling Wang, Yi Kuang, Zhimou Yang and Bing Xu*

Congo red stains the nanofibers of self-assembled small molecules extra- and intracellularly.

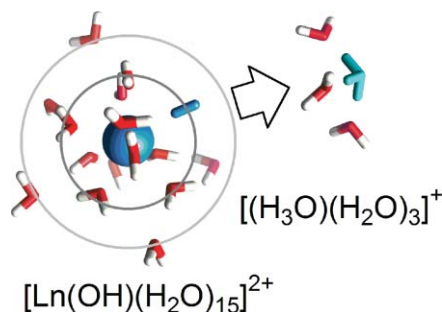


4099

Direct observation of ion evaporation from a triply charged nanodroplet

Keri McQuinn, Fraser Hof* and J. Scott McIndoe*

The evaporation of an Eigen cation, $[(\text{H}_3\text{O})(\text{H}_2\text{O})_3]^+$, from a charged nanodroplet has been directly observed using electrospray ionization mass spectrometry.

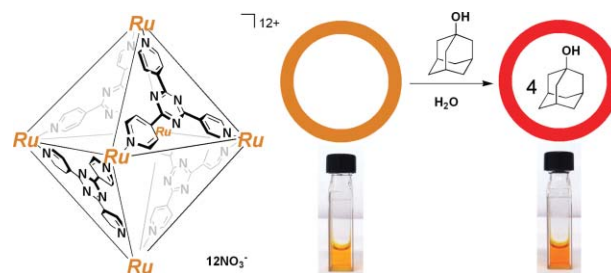


4102

Ru(II)-cornered coordination cage that senses guest inclusion by color change

Ken-ichi Yamashita, Masaki Kawano and Makoto Fujita*

A hexa-ruthenium coordination cage that can encapsulate some organic molecules is self-assembled. This complex can sense guest recognition by chromic shifts that result from the conformational change in the panel ligand.

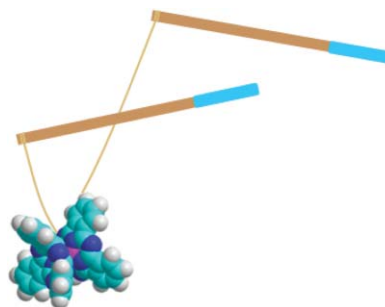


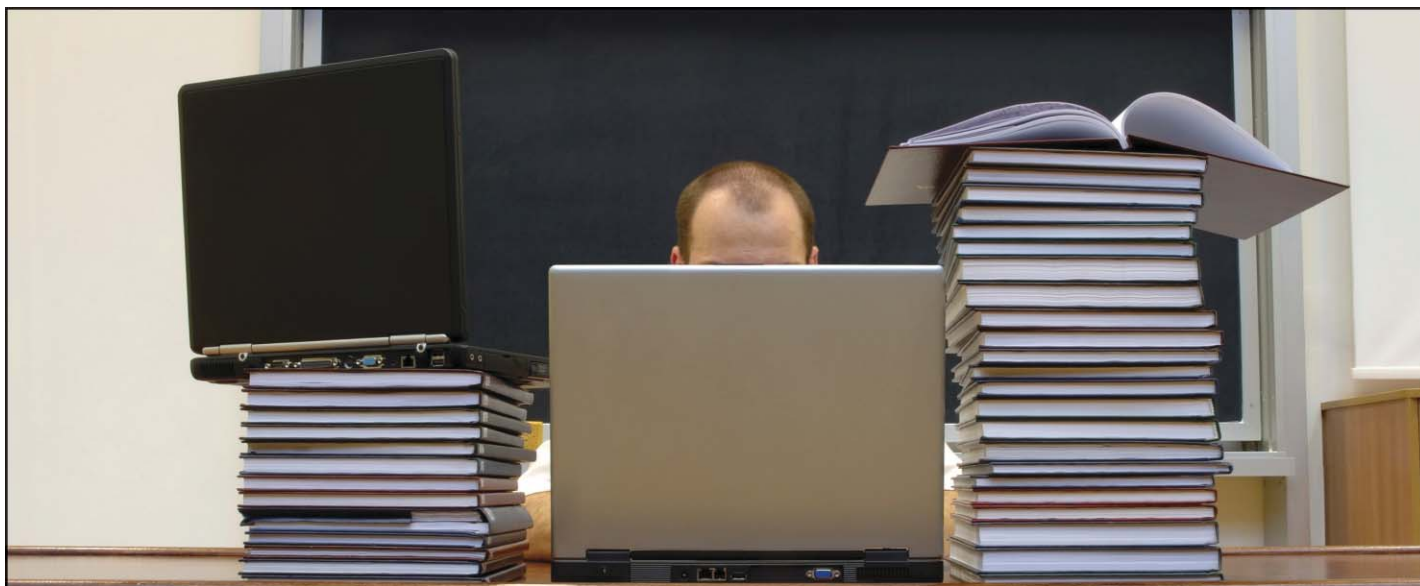
4104

Molecular diabolos: synthesis of subphthalocyanine-based diboranes

Anke K. Eckert, M. Salomé Rodríguez-Morgade and Tomás Torres*

Genuine B–B linked subphthalocyanine dimers are synthesized through Wurtz coupling of readily accessible chlorosubphthalocyanines. The two electronically decoupled macrocyclic halves are arranged in a linear and rigid manner.





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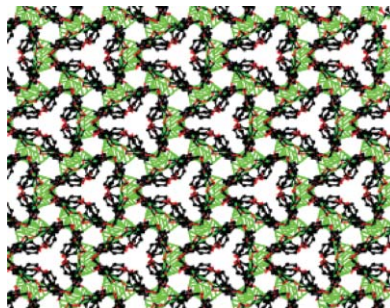
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4107

A 3D chiral Zn(II) coordination polymer with triple Zn–oba–Zn helical chains (oba = 4,4'-oxybis(benzoate))

Yi Ma, Zhengbo Han,* Yongke He and Liguo Yang

The solvothermal reaction of Zn(II) and 4,4'-oxybis(benzoic acid) in the presence of anhydrous ethanol leads to the generation of a novel 3D chiral coordination polymer with triple helical chains; the resulting crystals were not racemic, which was confirmed by the measurement of the optical rotation of bulk samples using solid state vibrational circular dichroism (VCD).

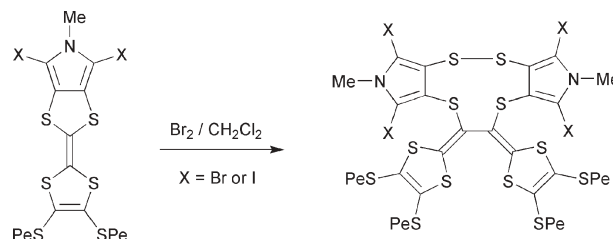


4110

A bromine catalysed dimerisation of α,α' -dihalomonopyrrolo-TTF

Hemant Gopee, Bo M. Petersen, Andrew D. Bond and Jan O. Jeppesen*

Dihalomonopyrrolo-TTF undergoes a bromine catalysed dimerisation reaction to yield a novel type of extended TTF derivative.

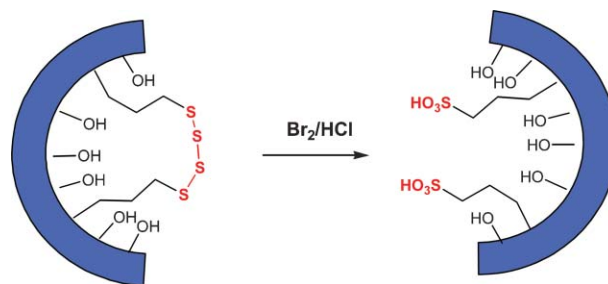


4113

Exceptional performance of sulfonic acid-incorporated-MCM-41 mesoporous materials prepared using a silane containing polysulfide linkages in the acetylation of anisole

OZoon Kwon, SeMin Park and Gon Seo*

Sulfonic acid-incorporated-MCM-41 mesoporous materials prepared using a silane containing tetrasulfide linkages showed exceptional yields of the acetylated product in the acetylation of anisole due to their high content of strong acid sites.

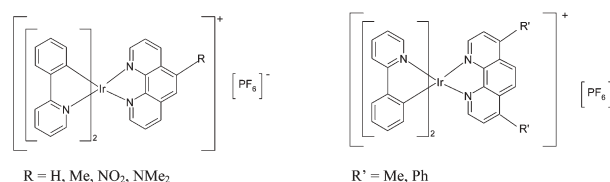


4116

Cyclometallated iridium(III) complexes with substituted 1,10-phenanthrolines: a new class of highly active organometallic second order NLO-phores with excellent transparency with respect to second harmonic emission

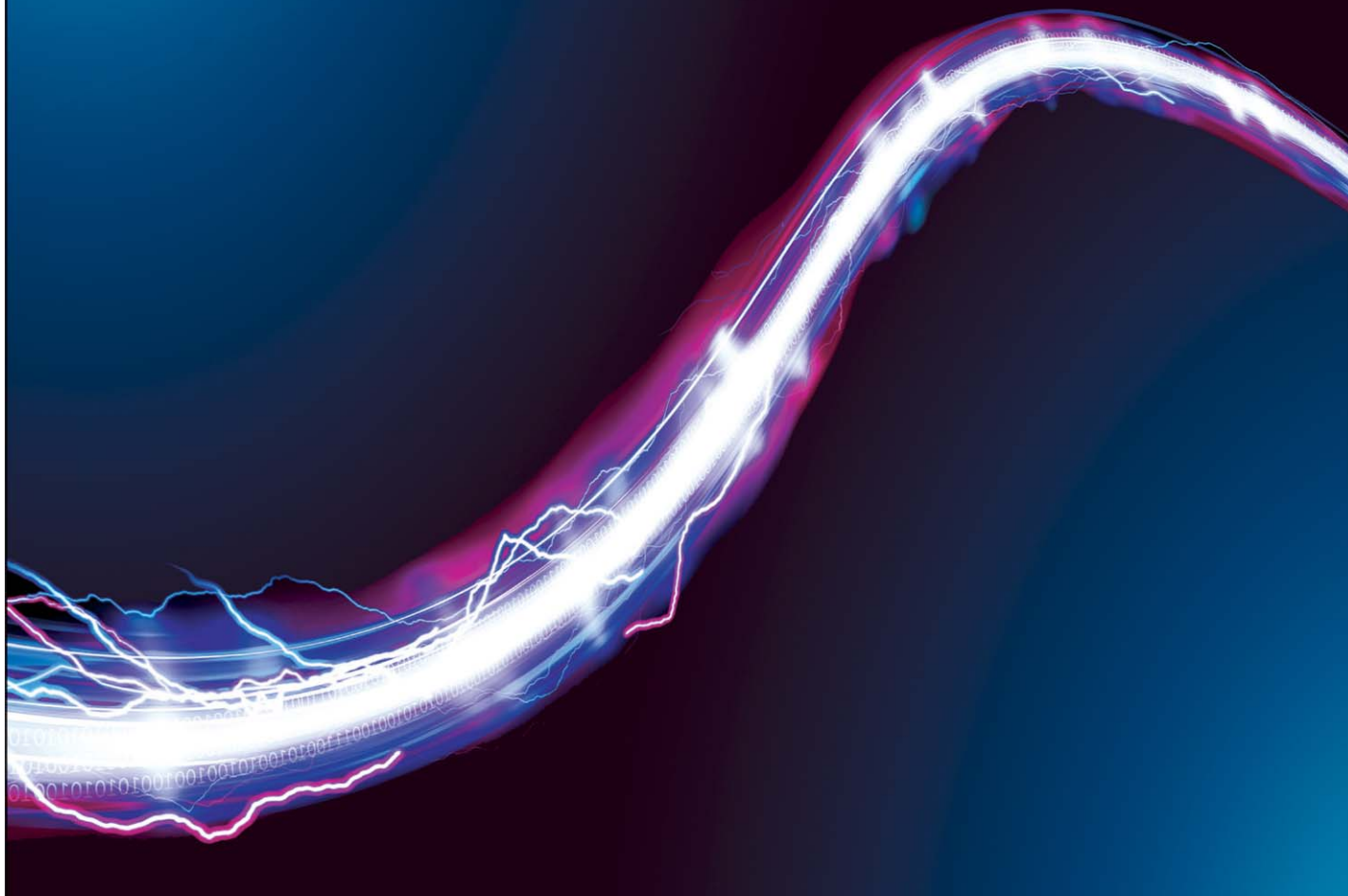
Claudia Dragonetti, Stefania Righetto, Dominique Roberto,* Renato Ugo, Adriana Valore, Simona Fantacci, Antonio Sgamellotti and Filippo De Angelis*

Highly active NLO-phores with excellent transparency: a huge response controlled by MLCT transitions.



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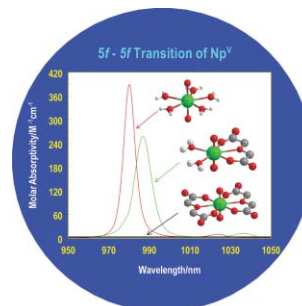
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4119

Symmetry and optical spectra: a “silent” 1 : 2 Np(V)–oxydiacetate complex

Guoxin Tian, Linfeng Rao* and Allen Oliver

The 1 : 2 Np(V)–oxydiacetate complex, $\text{NpO}_2(\text{ODA})_2^{3-}$, identified by single-crystal X-ray diffractometry for the first time, is centrosymmetric around the Np atom so that the f–f transitions of Np(V) are forbidden, resulting in the “silence” of the absorption and diffuse reflectance spectra of this complex in solution and the solid state in the near-IR and visible regions.

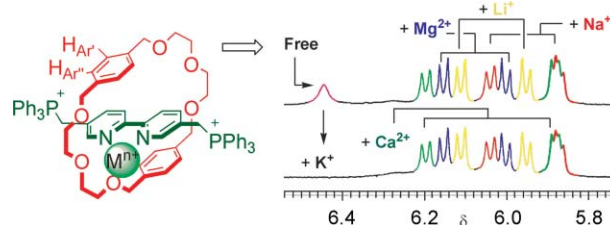


4122

A [2]rotaxane-based ¹H NMR spectroscopic probe for the simultaneous identification of physiologically important metal ions in solution

Nai-Chia Chen, Po-Yi Huang, Chien-Chen Lai, Yi-Hung Liu, Yu Wang, Shie-Ming Peng and Sheng-Hsien Chiu*

¹H NMR spectra of a [2]rotaxane display distinct signals for the complexation of Li^+ , Na^+ , Mg^{2+} and Ca^{2+} ions; thus, the simultaneous identification of these metal ions in solution is possible from the analysis of a single ¹H NMR spectrum.

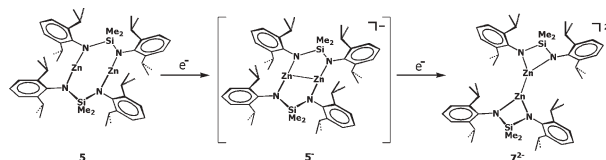


4125

Structural transformations in dinuclear zinc complexes involving Zn–Zn bonds

Yi-Chou Tsai,* Duan-Yen Lu, Yang-Miin Lin, Jenn-Kang Hwang and Jen-Shiang K. Yu

Upon reduction of $\text{Zn}_2(\mu\text{-}\eta^2\text{-Me}_2\text{Si}(\text{NDipp})_2)_2$ in which the diamido ligands span two Zn atoms in a chelating fashion by KC_8 , complex $[(\eta^2\text{-Me}_2\text{Si}(\text{NDipp})_2)\text{ZnZn}(\eta^2\text{-Me}_2\text{Si}(\text{NDipp})_2)]^{2-}$ featuring a Zn–Zn bond was isolated, and the dramatic structural change was *via* a mixed-valence Zn_2^{3+} intermediate, $[\text{Zn}_2(\mu\text{-}\eta^2\text{-Me}_2\text{Si}(\text{NDipp})_2)]^-$, in which a Zn–Zn bond is substantiated by elaborated calculations.

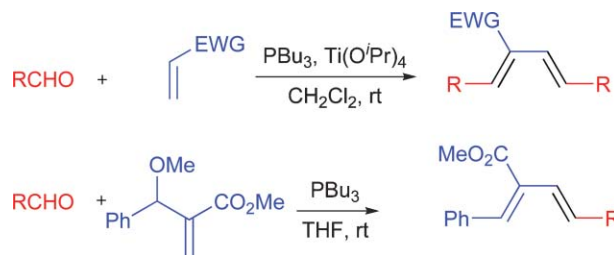


4128

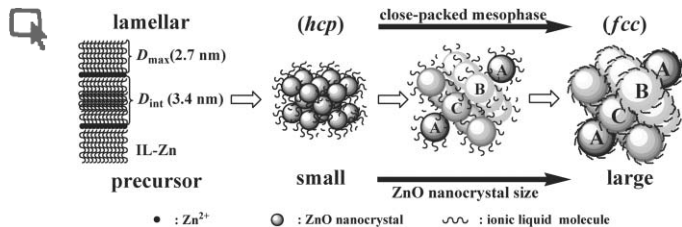
A new manifold for the Morita reaction: diene synthesis from simple aldehydes and acrylates/acrylonitrile mediated by phosphines

Anders Palmelund, Eddie L. Myers, Lik Ren Tai, Steve Tisserand, Craig P. Butts and Varinder K. Aggarwal*

Dienes have been formed with good stereoselectivity and in good yields from simple aldehydes and acrylates/acrylonitrile in the presence of a phosphine and a Lewis acid through a modification of the Morita reaction.



4131

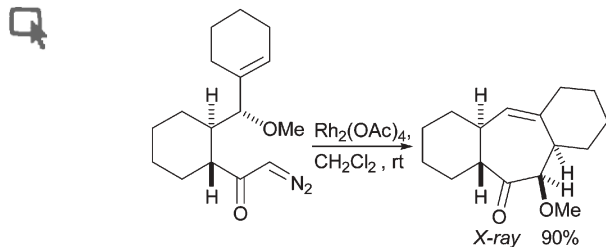


Spontaneous superlattice formation of ZnO nanocrystals capped with ionic liquid molecules

Da-Peng Liu, Guo-Dong Li, Ji-Xue Li, Xin-Hao Li and Jie-Sheng Chen*

The authors report the spontaneous self-assembly of ZnO nanocrystals with different particle sizes to form 3D superlattices, in which the nanocrystals are arranged in either a hexagonal or a cubic close-packing mode.

4134

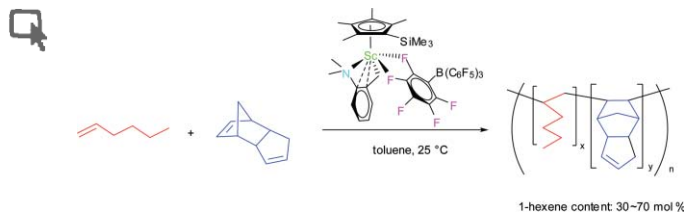


Rapid synthesis of medium-ring fused polycarbocyclic systems by rearrangement of carbenoid-derived oxonium ylides

J. Stephen Clark,* Carine Guérot, Claire Wilson and Alexander J. Blake

Fused tricyclic systems containing a medium-sized carbocycle can be constructed from precursors in which two single rings are tethered together, by rearrangement of a free or metal-bound oxonium ylide produced by reaction of an allylic ether with a metal carbenoid.

4137

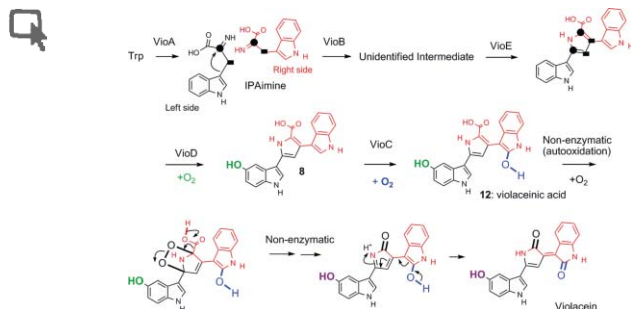


Cationic scandium aminobenzyl complexes. Synthesis, structure and unprecedented catalysis of copolymerization of 1-hexene and dicyclopentadiene

Xiaofang Li, Masayoshi Nishiura, Kyouichi Mori, Tomohiro Mashiko and Zhaomin Hou*

A well-defined THF-free cationic half-sandwich scandium aminobenzyl complex serves as the first catalyst for the copolymerization of 1-hexene with dicyclopentadiene to give the random copolymers with a wide range of 1-hexene contents unavailable previously.

4140



Biosynthesis of violacein: a genuine intermediate, protioviolaceinic acid, produced by VioABDE, and insight into VioC function

Kouhei Shinoda, Takuji Hasegawa, Hiroaki Sato, Masaaki Shinozaki, Hirotomo Kuramoto, Yosuke Takamiya, Tsutomu Sato, Naoki Nikaidou, Takeshi Watanabe and Tsutomu Hoshino*

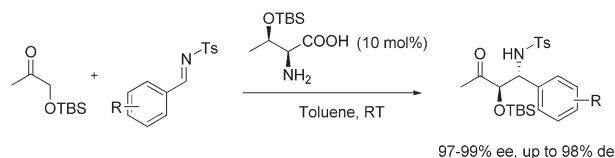
A biosynthetic intermediate of violacein was elucidated.

4143

Highly diastereoselective and enantioselective direct organocatalytic *anti*-selective Mannich reactions employing *N*-tosylimines

Lili Cheng, Xiao Han, Huiming Huang, Ming Wah Wong and Yixin Lu*

Organocatalytic direct Mannich reactions of *O*-TBS-hydroxyacetone with various *N*-tosylimines in the presence of L-threonine-derived catalyst afforded *anti*-1,2-amino alcohols in good yields and with enantioselectivities of 99% in almost all cases.

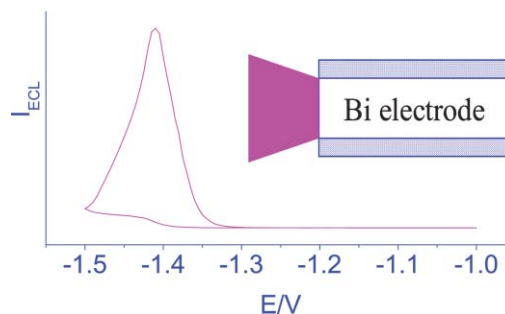


4146

Cathodic electrochemiluminescence in aqueous solutions at bismuth electrodes

Lianzhe Hu, Haijuan Li, Shuyun Zhu, Lishuang Fan, Lihong Shi, Xiaoqing Liu and Guobao Xu*

Because of its high hydrogen evolution overpotential, a bismuth electrode is a powerful electrode for achieving cathodic electrochemiluminescence in aqueous solutions.

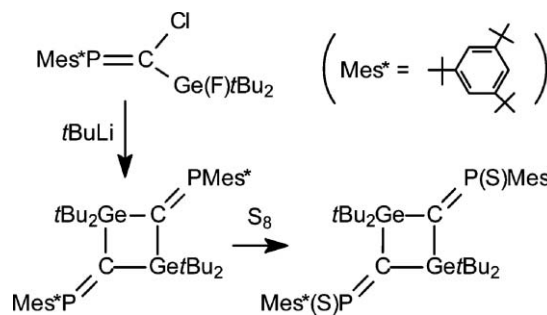


4149

1,3-Digermacyclobutanes with exocyclic C=P and C=P=S double bonds

Petronela Maria Petrar, Gabriela Nemes, Ioan Silaghi-Dumitrescu,* Henri Ranaivonjatovo, Heinz Gornitzka and Jean Escudié*

New 1,3-digermacyclobutanes, with two exocyclic C=PMes* bonds, and the corresponding first bis(methylenethio)phosphoranes with C=P(S)Mes* moieties have been synthesized.

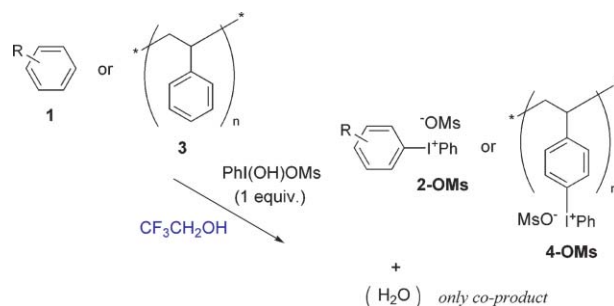


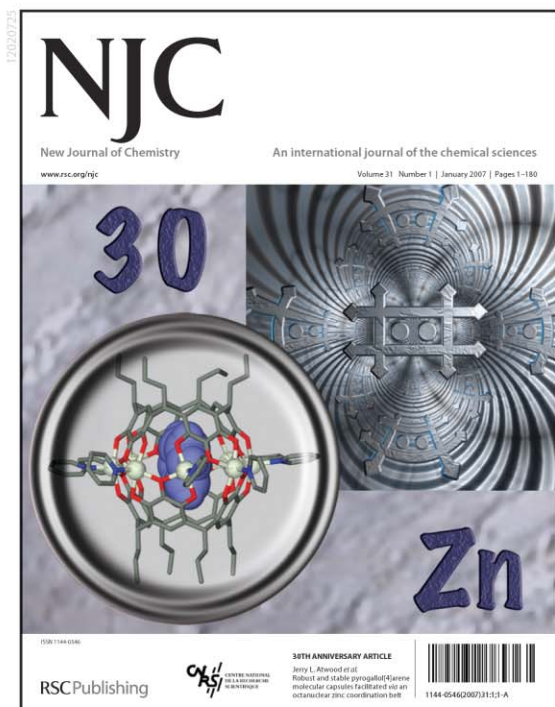
4152

Versatile direct dehydrative approach for diaryliodonium(III) salts in fluoroalcohol media

Toshifumi Dohi, Motoki Ito, Koji Morimoto, Yutaka Minamitsuji, Naoko Takenaga and Yasuyuki Kita*

We have found that the use of fluoroalcohol media greatly enhanced efficiency of the dehydrative condensation of arenes **1** and hypervalent iodine(III) compounds, leading to diaryliodonium salts **2**.





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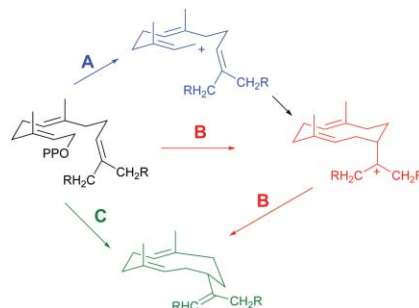


4155

Probing the reaction mechanism of aristolochene synthase with 12,13-difluorofarnesyl diphosphate

Fanglei Yu, David J. Miller and Rudolf K. Allemann*

Probing the reaction mechanism of aristolochene synthase catalysis with 12,13-difluorofarnesyl diphosphate revealed that the initial cyclisation to germacryl cation occurs in a concerted fashion.

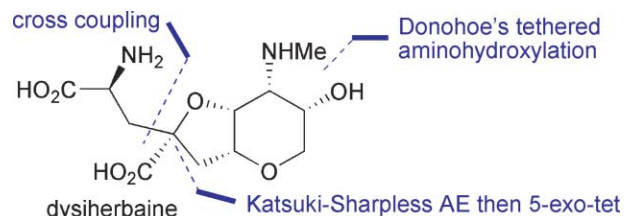


4158

A highly stereocontrolled total synthesis of dysiherbaine

Keisuke Takahashi, Takashi Matsumura, Jun Ishihara and Susumi Hatakeyama*

A total synthesis of dysiherbaine, a potent agonist of AMPA-KA type glutamate receptors, has been accomplished in completely stereocontrolled manner *via* Donohoe's tethered aminohydroxylation, Pd(0)-catalysed cross-coupling and Katsuki-Sharpless epoxidation followed by 5-*exo-tet* cyclisation.

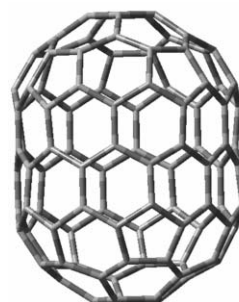


4161

Large fullerenes stabilized by encapsulation of metallic clusters

Ramón Valencia, Antonio Rodríguez-Fortea* and Josep M. Poblet*

Similarly to C₆₈, C₇₈ and C₈₀, large carbon cages such as C₁₀₀ can be stabilized by a charge transfer mechanism when encapsulating metallic clusters in their interior.

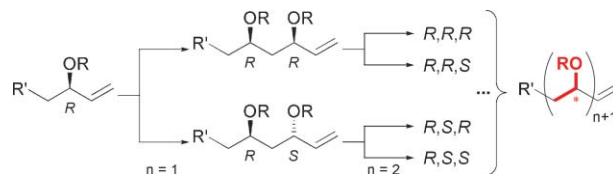
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4164

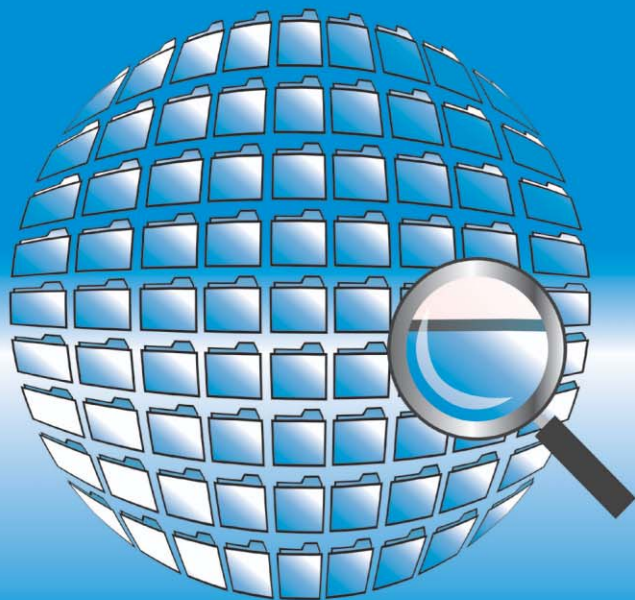
Iterative approach to polyketide-type structures: stereoselective synthesis of 1,3-polyols utilizing the catalytic asymmetric Overman esterification

Jörg T. Binder and Stefan F. Kirsch*

The stereoselective construction of all possible stereoisomers of 1,3-polyols was accomplished by an iterative multistep sequence that provides a chain extension by a C₂-unit through each cycle. For the creation of all stereogenic centres, the asymmetric Overman esterification was utilized.



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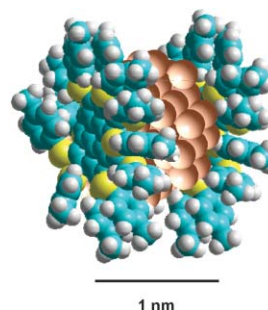
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4167

Synthesis of small gold nanoparticles: Au(I) disproportionation catalyzed by a persulfurated coronene dendrimer

Giacomo Bergamini, Paola Ceroni,* Vincenzo Balzani, Marc Gingras,* Jean-Manuel Raimundo, Vittorio Morandi and Pier Giorgio Merli

A new route to obtain gold nanoparticles with average diameter of 1.0 nm and narrow size distribution is reported, based on the disproportionation of Au⁺ in the presence of a persulfurated coronene dendrimer.

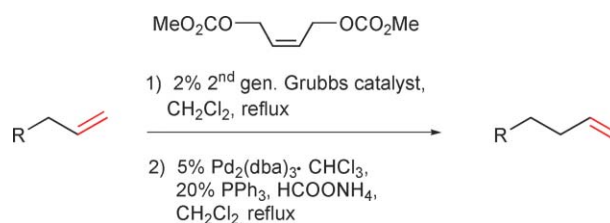


4170

One-pot terminal alkene homologation using a tandem olefin cross-metathesis/allylic carbonate reduction sequence

Daniel L. Comins,* Jason M. Dinsmore and Lucas R. Marks

A simple, one-pot procedure for the homologation of terminal alkenes is reported. This method broadens the scope of the popular allylation chemistry using allylmetal reagents.

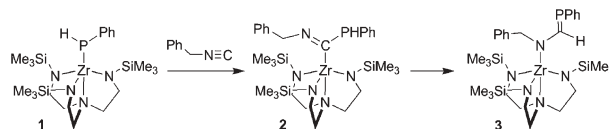


4172

Insertion of benzyl isocyanide into a Zr–P bond and rearrangement. Atom-economical synthesis of a phosphalkene

Samantha N. MacMillan, Joseph M. Tanski and Rory Waterman*

Reaction of (N₃N)ZrPPh (1) with PhCH₂N=C gave the 1,1-insertion product (N₃N)Zr[C(PPh)=NCH₂Ph] (2), which thermally rearranges to the structurally characterized phosphalkene-containing complex, (N₃N)Zr[N(CH₂Ph)C(H)=PPh] (3), with perfect atom economy.




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