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IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (17) 1665-1756 (2007)



See A. Marx et al., p. 1692. The image shows the on-chip approach in genotyping singlenucleotide variations (SNPs). Enhanced discrimination in multiplexed allele-specific primer extensions is obtained through 4'-Cmethoxymethylene modified thymine or cytidine derivatives at the SNP-interrogating 3'-end of immobilized primer probes. Image reproduced by permission of Jens Gaster, Gopinath Rangam and Andreas Marx from Chem. Commun., 2007, 1692.



Inside cover

See T. Zhang et al., page 1695. Ir-substituted hexaaluminates can act as promising catalysts for high concentration of N₂O decomposition which is potentially applicable in spacecraft propulsion systems. Image reproduced by permission of Shaomin Zhu, Xiaodong Wang, Aigin Wang, Yu Cong and Tao Zhang from Chem. Commun., 2007, 1695.

CHEMICAL BIOLOGY

B33

Drawing together research highlights and news from all RSC publications, *Chemical Biology* provides a 'snapshot' of the latest developments in chemical biology, showcasing newsworthy articles and significant scientific advances.



May 2007/Volume 2/Issue 5

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FEATURE ARTICLE

1683

Creation of quaternary stereocenters in carbonyl allylation reactions

Ilan Marek* and Genia Sklute

In this feature article, the most relevant examples for the preparation of quaternary stereocenters via the reaction of 3,3'-disubstituted allylmetal derivatives (allylboronates, bisphosphoramide-catalyzed allyltrichlorosilanes and allylzinc) with aldehydes are presented.

Preparation? Chiral induction? OH
$$R^{1} \longrightarrow ML_{n} + R$$

$$R^{1} \ne R^{2} \ne H$$

$$ML_{n} = B(OR)_{2}, SiCl_{3}, ZnR$$

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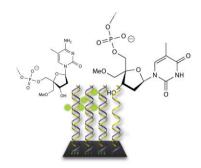
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1692

Increased single nucleotide discrimination in arrayed primer elongation by 4'C-modified primer probes

Jens Gaster, Gopinath Rangam and Andreas Marx*

4'C-modification of immobilized primer probes increases the selectivity for detection of single nucleotide variations in arrayed primer extension by a DNA polymerase.

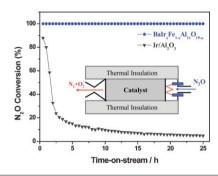


1695

A novel Ir-hexaaluminate catalyst for N₂O as a propellant

Shaomin Zhu, Xiaodong Wang, Aiqin Wang, Yu Cong and Tao Zhang*

Ir-substituted hexaaluminates show promising catalytic properties for N₂O decomposition which is potentially applicable in spacecraft propulsion systems.

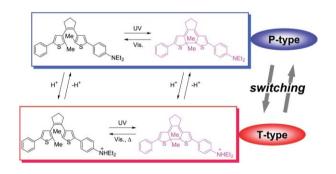


1698

Acid-induced photochromic system switching of diarylethene derivatives between P- and T-types

Seiya Kobatake* and Yuko Terakawa

Diethylamino-substituted diarylethenes can switch on photochromic systems between thermally stable type (P-type) and thermally unstable type (T-type) of the photogenerated isomers by protonation and deprotonation.

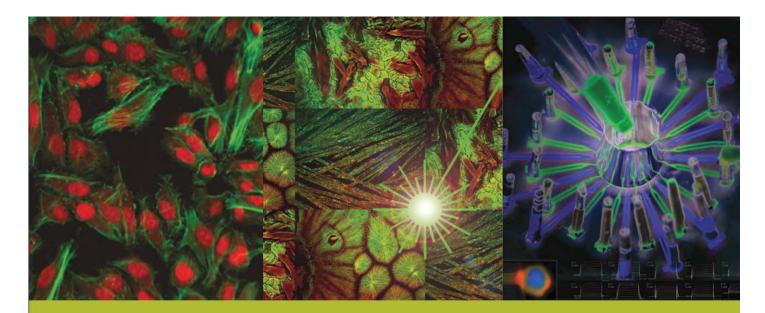


1701

Active site mutagenesis of the putative Diels-Alderase macrophomate synthase

Jörg M. Serafimov, Hans Christian Lehmann. Hideaki Oikawa and Donald Hilvert*

Macrophomate synthase catalyzes the multi-step conversion of a 2-pyrone and oxaloacetate to macrophomate. Mutagenesis shows that only three active site residues – Asp70, His73 and Arg101 – are absolutely required for oxaloacetate decarboxylation and trapping of the resulting pyruvate enolate by the pyrone; the other residues that line the binding pocket are remarkably tolerant to substitution.



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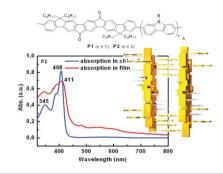
COMMUNICATIONS

1704

Conjugated alternating copolymers containing both donor and acceptor moieties in the main chain

Ming Zhang, Changduk Yang, Ashok K. Mishra, Wojciech Pisula, Gang Zhou, Bruno Schmaltz, Martin Baumgarten and Klaus Müllen*

Two novel conjugated alternating copolymers consisting of 2,7-linked carbazole donor and ladderized pentaphenylene with diketone bridge acceptor are reported. Studies on their energy and charge transfer properties, and supramolecular organization indicate a promising potential for photovoltaic devices.

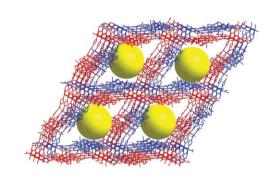


1707

An unprecedented twofold interpenetrating (3,4)-connected 3-D metal-organic framework

Seunghee Hong, Yang Zou, Dohyun Moon and Myoung Soo Lah*

A Cu_3L_4 -type metal—organic framework with large 1-D solvent channels was prepared using N,N',N''-tris(4-pyridinyl)-1,3,5-benzenetricarboxamide (L) as a trigonal three-connection node and the copper(II) ion as a square planar four-connection node.

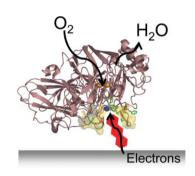


1710

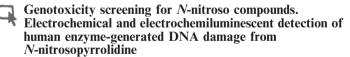
A stable electrode for high-potential, electrocatalytic O₂ reduction based on rational attachment of a blue copper oxidase to a graphite surface

Christopher F. Blanford, Rachel S. Heath and Fraser A. Armstrong*

A stable electrode for rapid, efficient four-electron electroreduction of O_2 is produced by linking a 'blue' Cu enzyme known as laccase to a graphite surface modified by attachment of anthracene units.

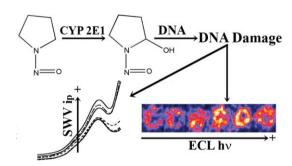


1713



Sadagopan Krishnan, Eli G. Hvastkovs, Besnik Bajrami, Ingela Jansson, John B. Schenkman and James F. Rusling*

The first application of voltammetric and electrochemiluminescent sensors to predict genotoxicity from human cytochrome P450 2E1 metabolized *N*-nitroso compounds is reported.





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1716

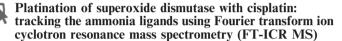
Luminescent lanthanide bimetallic triple-stranded helicates as potential cellular imaging probes

Caroline D. B. Vandevyver,* Anne-Sophie Chauvin,* Steve Comby and Jean-Claude G. Bünzli

New water-soluble bimetallic lanthanide helicates are synthesized which display intense luminescence and the europium compound is shown to be a potential luminescent stain for cell imaging, demonstrated here on the HeLa cell line.

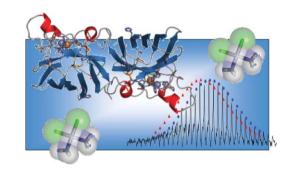


1719



Stefan K. Weidt, C. Logan Mackay, Pat R. R. Langridge-Smith and Peter J. Sadler*

The products from the reaction of erythrocyte superoxide dismutase with the anticancer drug cisplatin in solution retain their ammine ligands, in contrast to a recent X-ray crystallographic study.

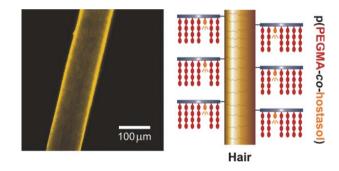


1722

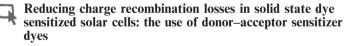
Bioconjugation onto biological surfaces with fluorescently labeled polymers

Julien Nicolas, Ezat Khoshdel and David M. Haddleton*

Direct bioconjugation onto hair fibers, monitored by confocal laser scanning microscopy and differential scanning calorimetry, has been performed using NHS α -functional fluorescently tagged polymers synthesised by living radical polymerisation.

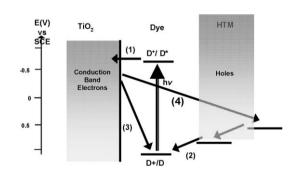


1725



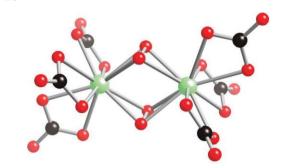
Samantha Handa, Helga Wietasch, Mukundan Thelakkat,* James R. Durrant and Saif A. Haque*

The application of supramolecular dyes to control charge recombination between photo-injected electrons and oxidized hole-transporting material.



COMMUNICATIONS

1728

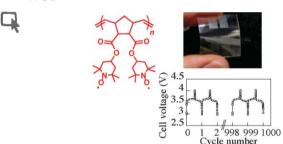


Synthesis and structural characterization of a molecular plutonium(IV) compound constructed from dimeric building blocks

Wolfgang Runde,* Lia F. Brodnax, George S. Goff, Shane M. Peper, Felicia L. Taw and Brian L. Scott

Single crystals of the first plutonium(IV) peroxide compound, $Na_8Pu_2(O_2)_2(CO_3)_6\cdot 12H_2O$, were synthesized and structurally characterized. The molecular compound consists of unprecedented dimeric $Pu_2(O_2)_2(CO_3)_6^{8-}$ anions exhibiting bridging μ^2, η^2-O_2 ligands around ten-coordinate Pu atoms.

1730



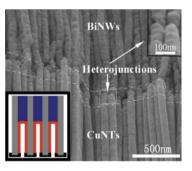
Photocrosslinked nitroxide polymer cathode-active materials for application in an organic-based paper battery

Takeo Suga, Hiroaki Konishi and Hiroyuki Nishide*

A nitroxide radical functional polymer was photocrosslinked for the first time without significant side reactions, producing a cathode-active thin film, leading to an organic-based paper battery.

1733





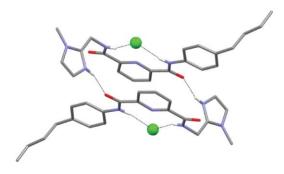
Electrochemical synthesis of metal and semimetal nanotube—nanowire heterojunctions and their electronic transport properties

Dachi Yang, Guowen Meng,* Shuyuan Zhang, Yufeng Hao, Xiaohong An, Qing Wei, Min Ye and Lide Zhang

Metal and semimetal nanotube—nanowire (NT–NW) nanoheterojunction arrays have been achieved by sequential electrochemicaldeposition. The electronic transport of metal NTs and semimetal NWs shows metal—metal junction behavior, while that of semimetal NTs and metal NWs shows metal—semiconductor behavior.

1736





Conformational control of HCl co-transporter: imidazole functionalised isophthalamide *vs.* 2,6-dicarboxamidopyridine

Philip A. Gale,* Joachim Garric, Mark E. Light, Beth A. McNally and Bradley D. Smith*

Replacement of the central isophthalamide core in a synthetic HCl co-transport carrier, with a 2,6-dicarboxamidopyridine, leads to a more preorganised molecular structure that exhibits higher chloride affinity and membrane transport flux.

1739

Catalytic asymmetric hydrogenation of aldehydes

Xiaoguang Li and Benjamin List*

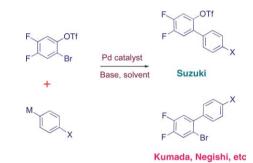
Racemic α-arylaldehydes provide the corresponding primary alcohols via dynamic kinetic resolution in excellent enantioselectivities and yields upon hydrogenation using a Noyori ruthenium catalyst. For example, (S)-ibuprofen was synthesized via catalytic enantioselective hydrogenation of aldehyde 1f followed by oxidation with potassium permanganate in 76% isolated yield and 96: 4 er.

1742

Aryl bromide/triflate selectivities reveal mechanistic divergence in palladium-catalysed couplings; the Suzuki-Miyaura anomaly

Gustavo Espino, Almira Kurbangalieva and John M. Brown*

In palladium-catalysed cross-coupling reactions, the outcome of competition between aryl bromides and aryl triflates depends on the nucleophilic partner. Suzuki couplings with R-B generally follow a different pattern from other R-M species.

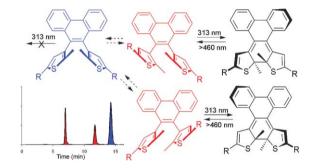


1745

The isolation and photochemistry of individual atropisomers of photochromic diarylethenes

Martin Walko and Ben L. Feringa*

All three atropisomers of photochromic diarylethenes were isolated for the first time and the stereospecific photochemical switching process studied by UV-vis and CD spectroscopy.



1748

Trimorphism in solid resorcinarenes

Charles J. M. Stirling,* L. Johan Fundin and Nicholas H. Williams³

Reduced solubility at high temperature reveals the trimorphic phase behaviour of resorcinarenes.





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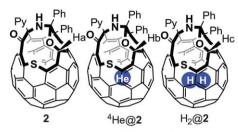
1751



The outside knows the difference inside: trapping helium by immediate reduction of the orifice size of an open-cage fullerene and the effect of encapsulated helium and hydrogen upon the NMR of a proton directly attached to the outside

Shih-Ching Chuang, Yasujiro Murata,* Michihisa Murata and Koichi Komatsu*

A methodology to entrap ⁴He inside an open-cage fullerene by immediate reduction of the size of an orifice was developed, and the effects of encapsulated He and H_2 on the chemical shift of a proton directly attached to the outer fullerene sphere were revealed.



 $\Delta (\delta Hb - \delta Ha) = 0.36 Hz$ $\Delta (\delta Hc - \delta Ha) = 1.9 Hz$



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