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IN THIS ISSUE

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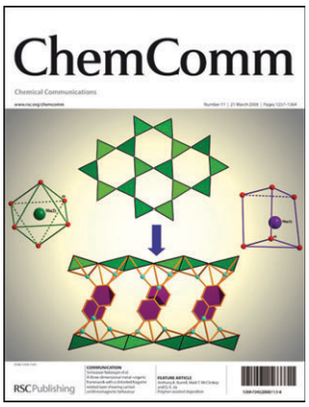


Cover
See Srinivasan Natarajan *et al.*, pp. 1278–1280.
Canted antiferromagnetic behaviour observed in a three-dimensional MOF possessing distorted Kagome lattice formed by two geometrically different Mn^{2+} ions.
Image reproduced by permission of Partha Mahata, Diptiman Sen and Srinivasan Natarajan from *Chem. Commun.*, 2008, 1278.

CHEMICAL SCIENCE

C17

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 and significant scientific advances.

Chemical Science
March 2008/Volume 5/Issue 3
www.rsc.org/chemicalscience

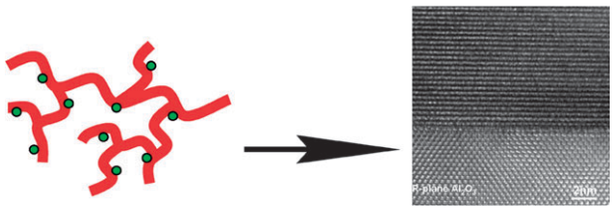
FEATURE ARTICLE

1271

Polymer assisted deposition

Anthony K. Burrell,* T. Mark McCleskey and Q. X. Jia

A chemical route using polymer assisted deposition (PAD) produces epitaxial thin films of metal oxides. This method is a bottom-up technique that enables controlled growth of specific structural phases based on the substrate lattice.



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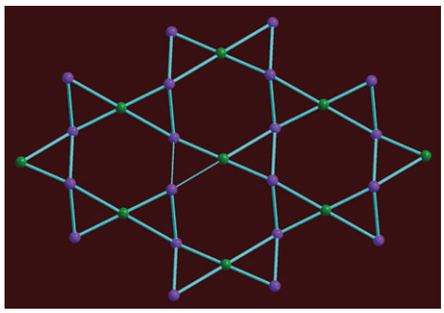
1278

A three-dimensional metal–organic framework with a distorted Kagome related layer showing canted antiferromagnetic behaviour

Partha Mahata, Diptiman Sen* and Srinivasan Natarajan*

Two geometrically different Mn^{2+} species form a Kagome-like topology in a three-dimensional metal–organic framework, which exhibits canted antiferromagnetic behaviour.

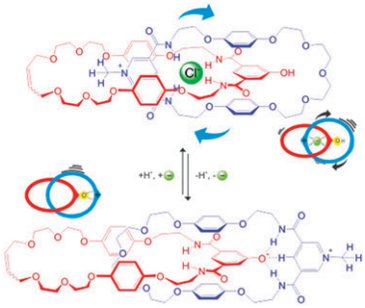


1281

Anion induced and inhibited circumrotation of a [2]catenane

Ka-Yuen Ng, Vitor Felix, Sérgio M. Santos, Nicholas H. Rees and Paul D. Beer*

The first example of a catenane capable of performing circumrotation *via* an anion switching methodology is described; of particular interest is a conformational locking mechanism which results from chloride coordination in the catenane binding cavity.

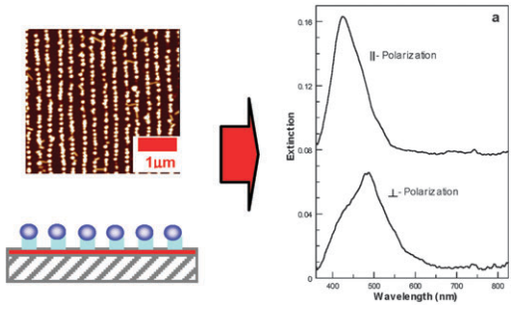


1284

Fabrication of optically active flexible polymer films with embedded chain-like arrays of silver nanoparticles

Bogdan Zdyrko, Mark K. Kinnan, George Chumanov* and Igor Luzinov*

A method for preparation of freestanding transparent polymer film containing 2D silver nanoparticle arrays and possessing polarization-sensitive optical properties is reported. Potentially the method may lead to 'mass production' of the optically active polymeric film.

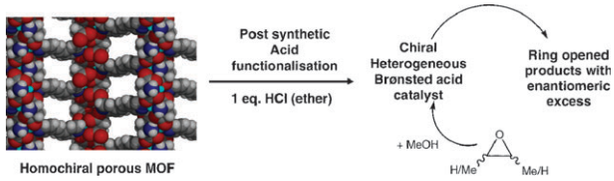


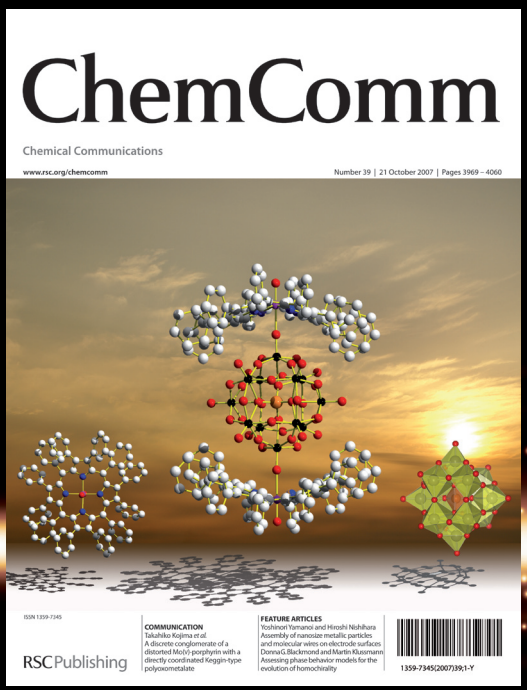
1287

Generation of a solid Brønsted acid site in a chiral framework

Michael J. Ingleson, Jorge Perez Barrio, John Bacsa, Calum Dickinson, Hyunsoo Park and Matthew J. Rosseinsky*

Protonation of chiral porous materials introduces a Brønsted acid centre, the structure of which is unique to the heterogeneous phase requiring pore wall confinement for stable isolation.





Making an impact

Success for First *ChemComm* International Symposium

The first in a series of *ChemComm* International Symposia was held, with great success, in China in December 2007. The meeting, on Polymers and Polymer Science, featured a mix of speakers from the UK, The Netherlands, the US and China and was held in three different venues: The Institute of Chemistry of the Chinese Academy of Sciences, Beijing; Fudan University, Shanghai; and Sun Yat-Sen University, Guangzhou.

ChemComm editor Sarah Thomas explained the aim of the symposium: 'The purpose of this event was to bring together scientists in a stimulating and friendly environment that will foster collaborations between the researchers and the universities involved. This was successfully achieved with the first symposium, which was met with an overwhelmingly positive response from all who took part.'

ChemComm, with an impact factor of 4.521, is the flagship journal of the RSC publishing some of the most significant work in the chemical sciences. A long and successful history has seen the journal adapt and evolve to meet the changing publishing environment. Today the journal is the fastest at publishing general chemistry communications and uses the very latest technologies, including a full electronic tracking system.

May we offer our thanks to all who contributed to making the First *ChemComm* International Symposium a great success. Two more *ChemComm* international symposia are planned over the next eighteen months and both are likely to be held in Asia. Watch the website for details of these events and other exciting *ChemComm* developments.

Speakers and RSC staff at the Beijing symposium, 12th December 2007

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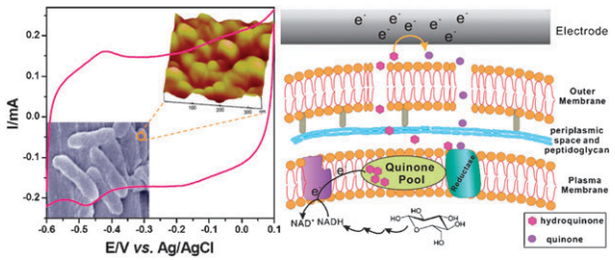
1290

Direct electrochemistry and electrocatalytic mechanism of evolved *Escherichia coli* cells in microbial fuel cells

Yan Qiao, Chang Ming Li,* Shu-Juan Bao, Zhisong Lu and Yunhan Hong

E. coli cells evolved under electrochemical tension in a microbial fuel cell possess direct electrochemical behavior due to the excretion of hydroquinone derivatives through a highly permeable outer membrane, and their catalyzed fuel cell demonstrates excellent performance.

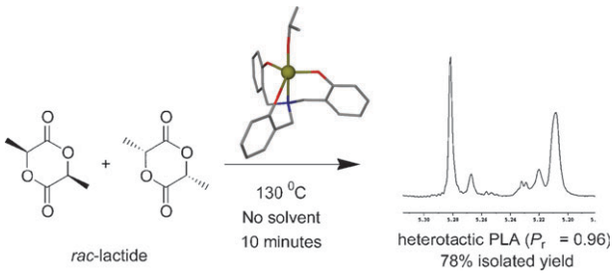


1293

Highly active and stereoselective zirconium and hafnium alkoxide initiators for solvent-free ring-opening polymerization of *rac*-lactide

Amanda J. Chmura, Matthew G. Davidson,* Catherine J. Frankis, Matthew D. Jones and Matthew D. Lunn

Zirconium and hafnium alkoxide complexes of a bulky amine tris(phenolate) ligand exhibit an unprecedented combination of high activity and stereoselectivity for the ring-opening polymerization of *rac*-lactide.

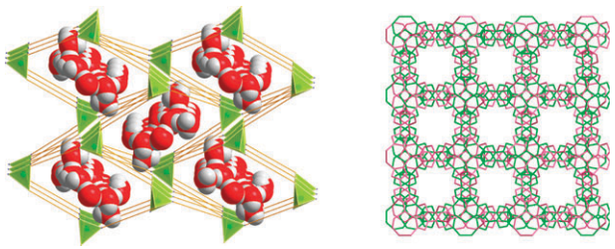


1296

Controllable preparation of Zn^{II} coordination polymers: unusual solvothermal formation of a LiGe-type framework directed by *in situ* S–S coupling of 5-(4-pyridyl)-1*H*-1,2,4-triazole-3-thiol

Xu-Dong Chen, Hui-Fang Wu and Miao Du*

Reaction of Zn^{II} with a multifunctional ligand 5-(4-pyridyl)-1*H*-1,2,4-triazole-3-thiol in conventional or solvothermal condition results in a 3-D pseudo-polyrotaxane architecture or a 2-fold interpenetrating **lig** coordination framework in virtue of unusual *in situ* S–S coupling of ligand.

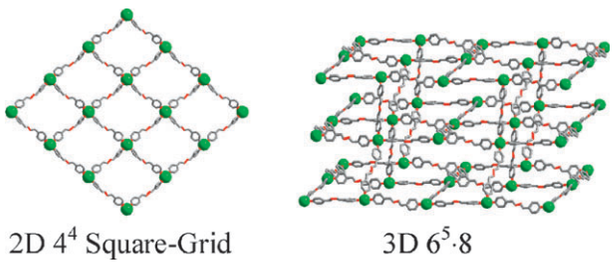


1299

New supramolecular isomers with 2D 4^4 square-grid and 3D $6^5 \cdot 8$ frameworks in a one-pot synthesis; reversible solvent uptake and intriguing luminescence properties

Chih-Chieh Wang,* Wei-Zeng Lin, Wei-Ting Huang, Mei-Ju Ko, Gene-Hsiang Lee, Mei-Lin Ho, Chun-Wei Lin, Chun-Wei Shih and Pi-Tai Chou*

Supramolecular isomers of $[Ni(4\text{-bpd})_2(NCS)_2]$ with 2D 4^4 square-grid (**1**) and 3D $6^5 \cdot 8$ (**2**) frameworks are formed in a one-pot reaction. Their thermal stability and reversible ad/desorption with guest solvents may make them suitable for gas storage.



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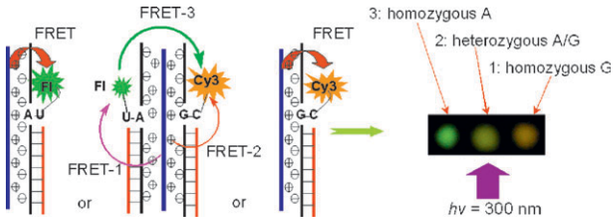
1302

Conjugated polyelectrolyte–DNA complexes for multi-color and one-tube SNP genotyping assays

Xinrui Duan, Shu Wang* and Zhengping Li*

The complexes of a cationic conjugated polymer with DNA are designed as new platforms for homogeneous, sensitive and facile fluorescence assays for SNP genotyping.

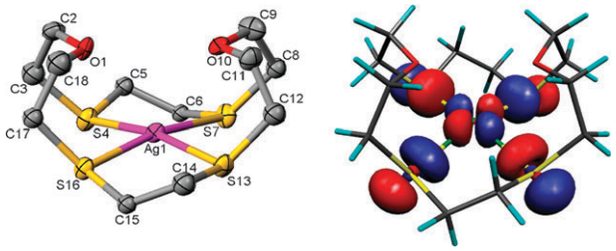


1305

Electronic structure of the mononuclear Ag(II) complex $[Ag([18]aneS_4O_2)]^{2+}$ ([18]aneS$_4$O$_2$ = 1,10-dioxa-4,7,13,16-tetrathiacyclooctadecane)

Deguang Huang, Alexander J. Blake, Eric J. L. McInnes, Jonathan McMaster,* E. Stephen Davies, Claire Wilson, Joanna Wolowska and Martin Schröder*

The mononuclear Ag(II) complex $[Ag([18]aneS_4O_2)]^{2+}$ shows a square-planar S_4 coordination; its SOMO possesses 22.7% Ag $4d_{xy}$ character as determined by multi-frequency EPR spectroscopy supported by DFT calculations.

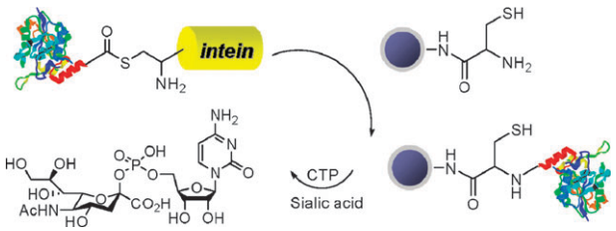


1308

Site-specific immobilization of CMP-sialic acid synthetase on magnetic nanoparticles and its use in the synthesis of CMP-sialic acid

Ching-Ching Yu, Po-Chiao Lin and Chun-Cheng Lin*

CMP-sialic acid synthetase (CSS) was specifically and covalently immobilized on magnetic nanoparticles (MNPs) by combining the intein expression system and native chemical ligation. Compared with conventional immobilization by random amide bond formation, our method of site-specific immobilization of CSS presented excellent enzymatic performance.

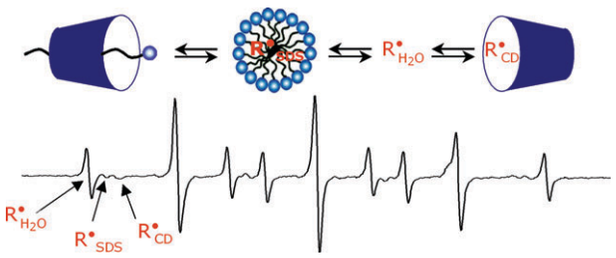


1311

An EPR method for measuring the rate of distribution of organic substrates between cyclodextrin, micelles and water

Elisabetta Mileo, Paola Franchi, Roberto Gotti, Claudia Bendazzoli, Elisabetta Mezzina and Marco Lucarini*

EPR spectroscopy has been succesfully employed for the direct and simultaneous measurement of the concentration of an organic spin probe partitioned in micelles, cyclodextrins and water by performing only a single experiment.



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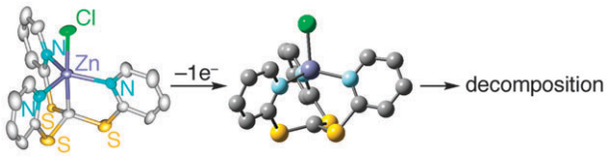
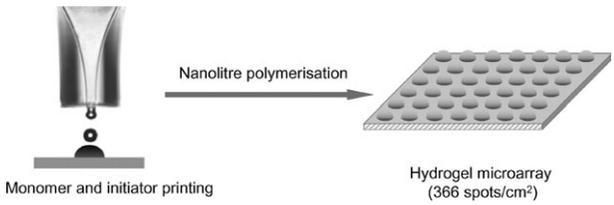


Synthesis and characterization of tris(2-pyridylthio)-methanido Zn complex with a Zn–C bond and DFT calculation of its one-electron oxidized species

Ken'ichi Kitano, Naoto Kuwamura, Rika Tanaka, Ryoko Santo, Takanori Nishioka,* Akio Ichimura and Isamu Kinoshita*

Tris(2-pyridylthio)methane (tptmH) reacts with $ZnCl_2$ producing the Zn–C containing complex of [ZnCl(tptm)], whose cyclic voltammogram shows an irreversible oxidation peak at 0.2 V *vs.* $E^{0'}(Fc^{+/0})$.

1317

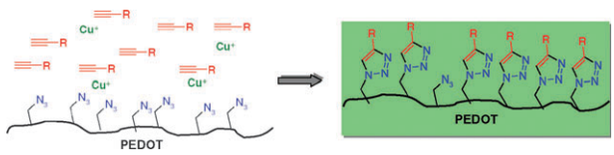


Inkjet fabrication of hydrogel microarrays using *in situ* nanolitre-scale polymerisation

Rong Zhang, Albert Liberski, Ferdous Khan, Juan Jose Diaz-Mochon and Mark Bradley*

Polymer hydrogel microarrays were fabricated through *in situ* pico–nano litre polymerisation using an inkjet printer to deliver monomers and initiators in defined and addressable positions on the glass slide.

1320

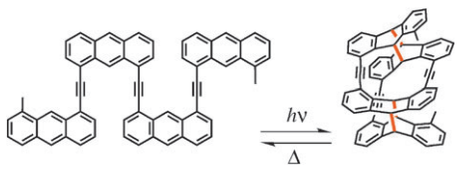


"Click"-functionalization of conducting poly(3,4-ethylenedioxythiophene) (PEDOT)

Hang-Beom Bu, Günther Götz, Egon Reinold, Astrid Vogt, Sylvia Schmid, Raúl Blanco, Jose L. Segura and Peter Bäuerle*

Efficient post-functionalization of conductive polymer films was achieved by Cu^{+}-catalyzed "click"-cycloaddition of novel poly(azidomethyl-EDOT) **P2** and various functionalized terminal alkynes under mild heterogeneous conditions with high conversion efficiencies.

1323



Molecular folding screen: folding and unfolding of 1,8-anthrylene–ethynylene oligomers by photochemical cycloaddition and thermal cycloreversion

Shinji Toyota,* Makoto Kuga, Akiko Takatsu, Michio Goichi and Tetsuo Iwanaga

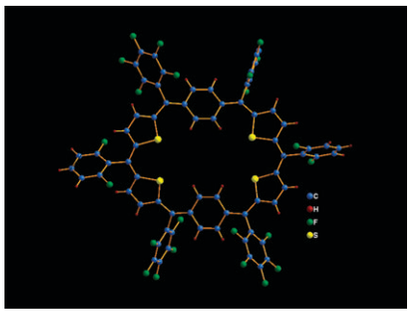
Molecular folding screens consisting of anthracene plates and acetylene linkers stereoselectively fold into a zigzag form by [4 + 4]photocycloaddition, and unfold by thermal cycloreversion.

1326

π-Conjugated macrocycles from thiophenes and benzenes

J. Sreedhar Reddy and Venkataramanarao G. Anand*

A facile synthetic method to construct benzene incorporated π-conjugated macrocycles has been developed in which benzene can exist in both quinoid and Kekule forms.

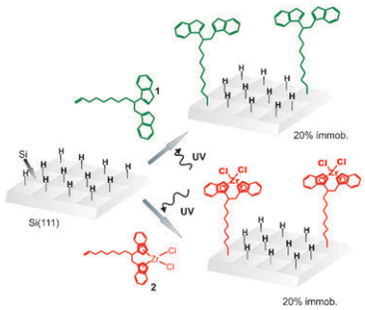


1329

UV-induced immobilization of tethered zirconocenes on H-terminated silicon surfaces

Heidrun Gruber-Woelfler, Sandrine Rivillon Amy, Yves J. Chabal, Georg Schitter, Eleonora Polo, Markus Ringwald and Johannes G. Khinast*

A tethered ethylenebis(indenyl) zirconocene was covalently immobilized on H-terminated Si(111) surfaces using UV-mediated alkene hydrosilylation, thus making possible the development of structured catalytic surfaces with highly controlled properties.

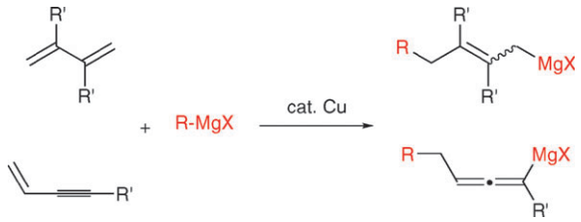


1332

Cu-catalyzed regioselective carbomagnesiation of dienes and enynes with *sec*- and *tert*-alkyl Grignard reagents

Hirohisa Todo, Jun Terao,* Hideyuki Watanabe, Hitoshi Kuniyasu and Nobuaki Kambe*

The carbomagnesiation of dienes and enynes with *sec*- and *tert*-alkyl Grignard reagents has been achieved by using copper salts as catalysts. Thus formed allyl, allenyl or propargyl Grignard reagents generated by the present method could be trapped with a variety of electrophiles.

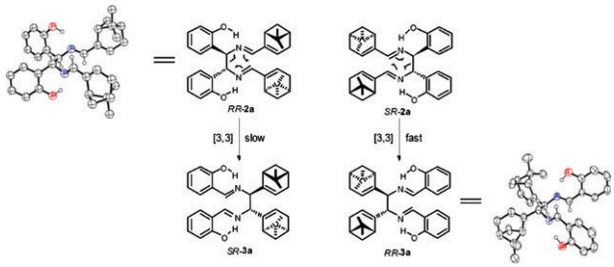


1335

Diastereoselective diaza-Cope rearrangement reaction

Hyunwoo Kim, Doo Seoung Choi, Cindy Pai-Hui Yen, Alan J. Lough, Choong Eui Song* and Jik Chin*

Steric effect is used to obtain a highly diastereoselective rearrangement reaction. *SR*-**2a** undergoes diaza-Cope rearrangement to give *RR*-**3a** whereas *RR*-**2a** does not rearrange under the same condition.



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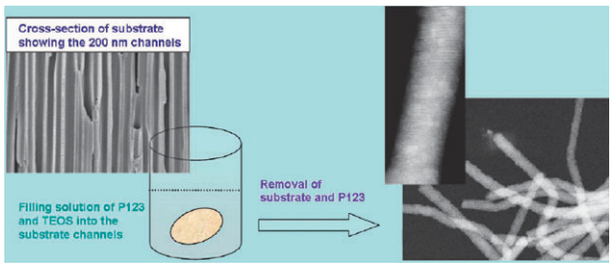
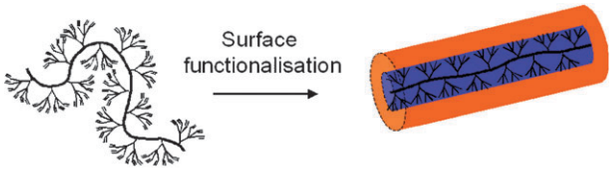


STEM characterization on silica nanowires with new mesopore structures by space-confined self-assembly within nano-scale channels

Peng Lai, Michael Z. Hu,* Donglu Shi and Douglas Blom

"Critical" channel diameters were found in the study of space-confined coassemblies and a new mesopore structure was observed in silica nanowires formed in AAO channels with diameters from 30 to 80 nm.

1341

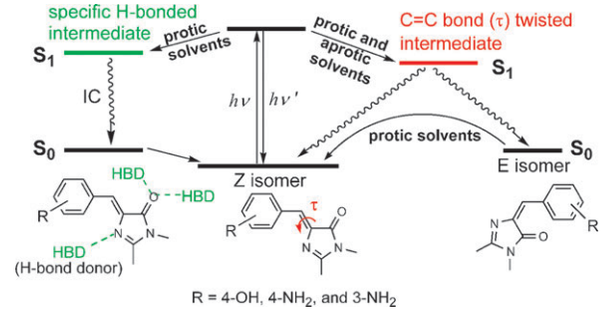


Versatile and efficient functionalisation of multiallylic dendronised polymers: can dense packing be reached?

Firmin Moingeon, Jérôme Roeser, Patrick Masson, Françoise Arnaud and Stéphane Méry*

Surface modification of a dendronised polymer was performed *via* the grafting of functional moieties onto the allyl end-branches; surface congestion is expected to occur when bulky groups are grafted.

1344

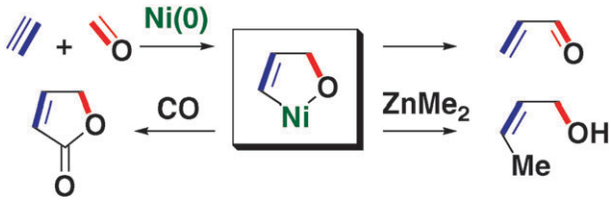


Photoisomerization of the green fluorescence protein chromophore and the *meta*- and *para*-amino analogues

Jye-Shane Yang,* Guan-Jhih Huang, Yi-Hung Liu and Shie-Ming Peng

The $Z \rightarrow E$ photoisomerization dominates the nonradiative decay of the green fluorescence protein chromophore and its amino analogues in aprotic solvents, but specific solute–solvent hydrogen-bonding-induced deactivation plays the major role in protic solvents.

1347



Nickeladihydrofuran. Key intermediate for nickel-catalyzed reaction of alkyne and aldehyde

Sensuke Ogoshi,* Tomoya Arai, Masato Ohashi and Hideo Kurosawa

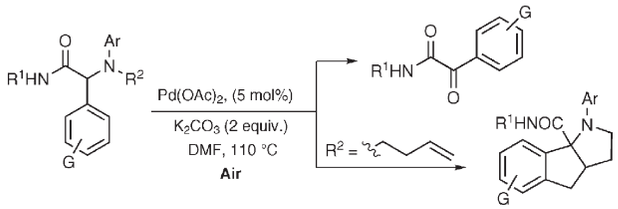
The formation of a nickeladihydrofuran by oxidative cyclization of an alkyne and an aldehyde with nickel(0) has been demonstrated; the transformation of the nickeladihydrofuran into an enone, a lactone and an allylic alcohol suggests that nickeladihydrofuran is an important key intermediate in a variety of catalytic reactions.

1350

New palladium-catalyzed aerobic oxidative cleavage and cyclization of *N*-aryl peptide derivatives

Laurent El Kaïm,* Rocio Gamez-Montaño,* Laurence Grimaud* and Tannya Ibarra-Rivera

Oxidative cleavage and cyclization cascades of *N*-arylamino amides have been achieved under palladium catalysis with air as the sole stoichiometric oxidant.

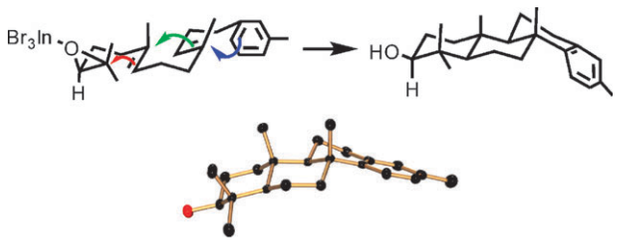


1353

Indium tribromide-promoted arene-terminated epoxy olefin cyclization

Jun-Feng Zhao, Yu-Jun Zhao and Teck-Peng Loh*

An arene-terminated epoxy olefin cyclization was promoted by a water-tolerant Lewis acid to give tri- and tetracyclic 3β-hydroxy terpenoids and steroid derivatives in 57 and 37% yields, respectively, per new formed ring up to 75%.

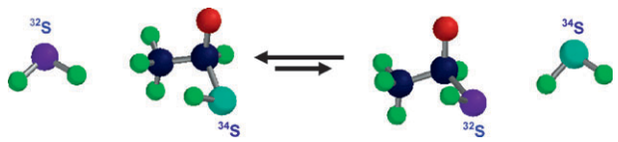


1356

Sulfur isotope fractionation during incorporation of sulfur nucleophiles into organic compounds

Alon Amrani,* Qisheng Ma, Ward Said Ahmad, Zeev Aizenshtat and Yongchun Tang

^{34}S enrichment is shown to occur during sulfurization reactions and for the first time conclusively attributed to an isotope equilibrium effect rather than selective addition of ^{34}S enriched nucleophiles.

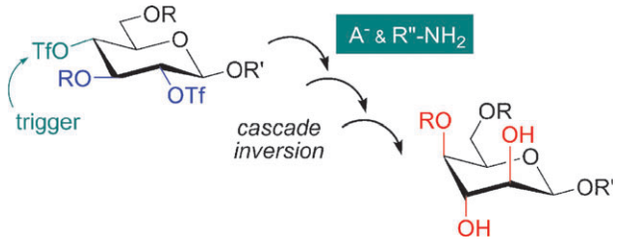


1359

Supramolecular activation in triggered cascade inversion

Hai Dong, Zhichao Pei and Olof Ramström*

Multiple carbohydrate epimerization through quantitative triggered cascade reactions is presented. A dramatic activation effect from combinations of anions and amines is also demonstrated, suggesting a supramolecular process of enhanced deprotonation.



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