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ISSN 1359-7345 CODEN CHCOFS (24) 2701-2816 (2008)



Cover

See Peter Fristrup *et al.*, pp. 2750–2752. A mechanistic study of gold-nanoparticle catalyzed oxidations sheds more light on the fundamental aspects of this important green chemical reaction. Image reproduced by permission of Peter Fristrup, Louise Bahn Johansen and Claus Hviid Christensen from *Chem. Commun.*, 2008, 2750.



Inside cover

See Jieshan Qiu et al., pp. 2747–2749. Well-defined carbon polyhedrons with hexagonal, heptagonal, octagonal cross-sections and hollow central cavities have been fabricated via in situ self-assembly of carbon nanotubes inside microchannels. Image reproduced by permission of Jiangying Qu, Zongbin Zhao, Jieshan Qiu and Yury Gogotsi from Chem. Commun., 2008, 2747.

FEATURE ARTICLES



2717

Molecules and crystals with both icosahedral and cubic symmetry

Jorge Echeverría, David Casanova, Miquel Llunell, Pere Alemany and Santiago Alvarez*

Shape and symmetry measures of nested polyhedral molecules show that cubic symmetry is latent in icosahedral polyhedra and may be the origin of cubic crystal structures found for such molecules as fullerene, dodecahedrane or the $(H_2O)_{100}$ nanodroplets characterized by Müller and co-workers, shown in an fcc packing.

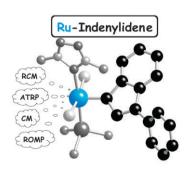


2726

Ruthenium-indenylidene complexes: powerful tools for metathesis transformations

Fabien Boeda, Hervé Clavier and Steven P. Nolan*

Ruthenium-indenylidene complexes represent a class of robust and efficient pre-catalysts for olefin metathesis reactions. The authors provide an overview of the various complexes belonging to this family and summarise their use in various applications.



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Gold(1)-catalyzed intramolecular hydroamination of unactivated C=C bonds with alkyl ammonium salts

Christopher F. Bender and Ross A. Widenhoefer*

Primary and secondary 4-alkenyl ammonium salts and primary 5-hexenyl ammonium salts underwent intramolecular hydroamination in the presence of a catalytic 1:1 mixture of (5)AuCl $\{5 = PCy_2[2-(2,6-C_6H_3(OMe)_2)C_6H_4]\}$ and AgOTf in toluene at 80 °C.

2744

Gold-catalysed intramolecular *trans*-allylsilylation of alkynes forming 3-allyl-1-silaindenes

Takanori Matsuda, Sho Kadowaki, Yoshiyuki Yamaguchi and Masahiro Murakami*

3-Allyl-1-silaindenes are synthesised from alkynes having an allylsilane moiety by a gold-catalysed intramolecular *trans*-allylsilylation reaction.

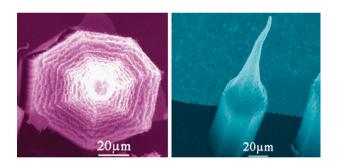
$$\begin{array}{c} \text{R} \\ \text{CH}_2\text{CI}_2, \text{ rt} \\ \text{Me}_2 \end{array}$$

2747

Self-assembly of carbon nanotube polyhedrons inside microchannels

Jiangying Qu, Zongbin Zhao, Jieshan Qiu* and Yury Gogotsi

Carbon polyhedrons with faceted morphologies and hollow internal structures made of self-organized carbon nanotubes have been fabricated by CVD inside microchannels. The confined space of the microchannels is critical for the formation of polyhedra, and these structures show superhydrophobic properties, with the contact angle up to 162° .

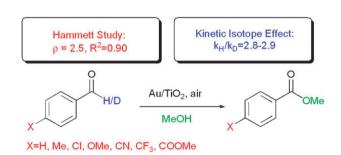


2750

Mechanistic investigation of the gold-catalyzed aerobic oxidation of aldehydes: added insight from Hammett studies and isotopic labelling experiments

Peter Fristrup*, Louise Bahn Johansen and Claus Hviid Christensen*

The title reaction proceeds through development of a partial negative charge and has a significant kinetic isotope effect ($k_{\rm H}/k_{\rm D}=2.8$ –2.9), which illustrates that activation of the C–H bond takes place in the rate-determining step.





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Controlled thermoreversible transfer of poly(oxazoline) micelles between an ionic liquid and water

Carlos Guerrero-Sanchez, Jean-François Gohy, Cecile D'Haese, Hanneke Thijs, Richard Hoogenboom and Ulrich S. Schubert*

The thermoreversible and controlled transfer of poly(2-nonyl-2oxazoline-block-2-ethyl-2-oxazoline) micelles between a hydrophobic ionic liquid and water is demonstrated. The approach may allow the development of advanced heterogeneous micellar catalytic systems with novel separation processes.

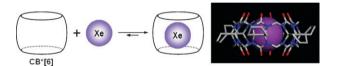


2756

Water soluble cucurbit[6]uril derivative as a potential Xe carrier for 129 Xe NMR-based biosensors

Byoung Soo Kim, Young Ho Ko, Youngkook Kim, Hyeong Ju Lee, N. Selvapalam, Hee Cheon Lee* and Kimoon Kim*

The water soluble cucurbit[6]uril derivative CB*[6] forms a thermodynamically and kinetically stable host-guest complex with xenon in water, which suggests that it may serve as an effective molecular "carrier" for ¹²⁹Xe NMR-based biosensors.

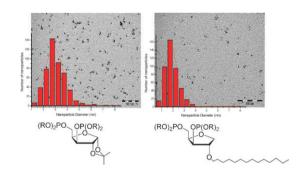


2759

Diphosphite ligands derived from carbohydrates as stabilizers for ruthenium nanoparticles: promising catalytic systems in arene hydrogenation

Aitor Gual, M. Rosa Axet, Karine Philippot,* Bruno Chaudret, Audrey Denicourt-Nowicki, Alain Roucoux,* Sergio Castillon and Carmen Claver*

Diphosphite ligands, derived from carbohydrates and containing a lipidic chain, stabilize nanoparticles of small size and good dispersity, which provides high activity and selectivity in arene hydrogenation.

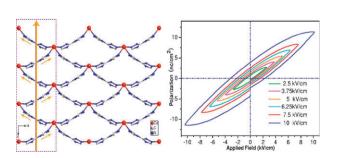


2762

Nonlinear optical and ferroelectric properties of a 3-D $Cd(\Pi)$ triazolate complex with a novel $(6^3)_2(6^{10}\cdot 8^5)$ topology

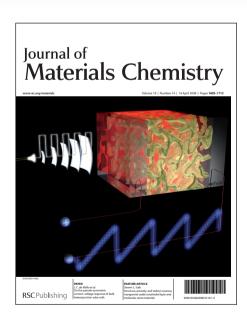
Wei-Wei Zhou, Jiu-Tong Chen,* Gang Xu, Ming-Sheng Wang, Jian-Ping Zou, Xi-Fa Long, Guo-Jian Wang, Guo-Cong Guo* and Jin-Shun Huang

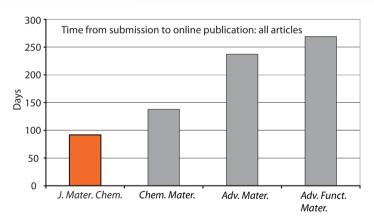
A solvothermally synthesized 3-D Cd(II) complex with an unprecedented $(6^3)_2(6^{10} \cdot 8^5)$ topology was found to adopt a non-centrosymmetric polar packing arrangement, resulting in strong SHG response and ferroelectric property.





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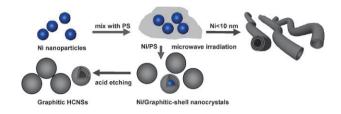
*Data taken from published issues from September to December (inclusive) 2007.



Graphitic carbon nanostructures *via* a facile microwave-induced solid-state process

Kai Chen, Chunlei Wang, Ding Ma,* Weixin Huang and Xinhe Bao*

A novel, mild and facile approach to synthesize highly graphitic nanostructured carbons by microwave irradiation is demonstrated. Narrowly distributed metal/graphitic-shell nanocrystals, graphitic hollow carbon nanospheres with well-controlled sizes and CNTs can be obtained within one minute.

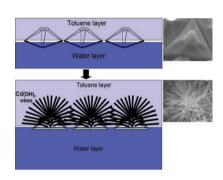


2768

Deposition of hierarchical Cd(OH)₂ anisotropic nanostructures at the water-toluene interface and their use as sacrificial templates for CdO or CdS nanostructures

Sibusiso N. Mlondo, Ellen M. Andrews, P. John Thomas and Paul O'Brien*

Hierarchical anisotropic structures ranging from triangular 'platelets' to nanofibres of Cd(OH)₂ are grown at a water—toluene interface, and are further used to produce CdO wires and CdS nanostructures.



2771

In situ synthesis of gold-cross-linked poly(ethylene glycol) nanocomposites by photoinduced electron transfer and free radical polymerization processes

Yusuf Yagci,* Marco Sangermano* and Giancarlo Rizza

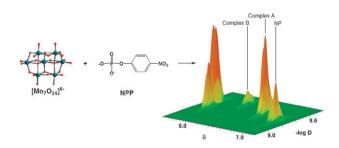
Gold-cross-linked poly(ethylene glycol) nanocomposites were prepared by simultaneous photoinduced electron transfer and free radical polymerization processes.

2774

Phosphoesterase activity of polyoxomolybdates: diffusion ordered NMR spectroscopy as a tool for obtaining insights into the reactivity of polyoxometalate clusters

Luk Van Lokeren, Els Cartuyvels, Gregory Absillis, Rudolph Willem and Tatjana N. Parac-Vogt*

Diffusion ordered NMR spectroscopy (DOSY NMR) is shown to be an excellent tool for observing reactive transients in the hydrolysis of the phosphatase model substrate (p-nitrophenyl)phosphate (NPP) promoted by $\left[\mathrm{Mo_7O_{24}}\right]^{6-}$ cluster.



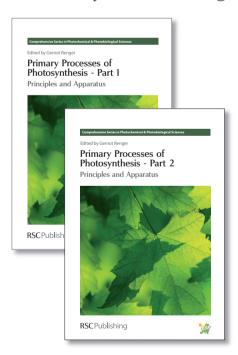
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Facile intramolecular C(sp³)-H bond activation with Pd^{II}

Martin Bröring* and Christian Kleeberg

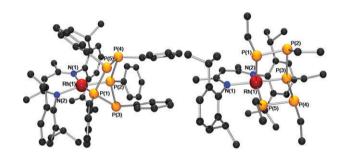
Non-activated C(sp³)–H bonds are cleanly broken by acetatopalladium(II) species at ambient temperature. This is the result of a coordination study of a sterically hindered bis(4-aminothiazolyl)isoindoline ligand to divalent palladium. The product contains a hemilabile S-bonded thiazole cis to the Pd-C bond and thus shows potential for mechanistic studies.

2779

Activation of P_5R_5 (R = Ph, Et) by a Rh- β -diketiminate complex

Stephen J. Geier and Douglas W. Stephan*

(NacNac)Rh(C₈H₁₄)(N₂) reacts with P₅R₅ to give complexes of formula $(NacNac)Rh(P_5R_5)$ (R = Ph, Et); in the former species inversion of a P atom of P₅Ph₅ allows coordination to a Rh(I) centre, whereas in the later species a P-P bond undergoes oxidative addition to give a formally Rh(III) species.

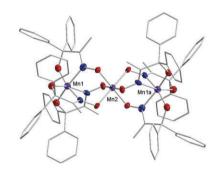


2782

A rare ligand bridged ferromagnetically coupled Mn^{IV}₃ complex with a ground spin state of S = 9/2

Thushan Pathmalingam, Serge I. Gorelsky, Tara J. Burchell, Anne-Catherine Bédard, André M. Beauchemin,* Rodolphe Clérac and Muralee Murugesu*

An exclusively chelating ligand bridged high-valent [Mn^{IV}₃] complex has been synthesized, in which all Mn^{IV} ions are ferromagnetically-coupled to exhibit an $S_T = 9/2$ spin ground state.

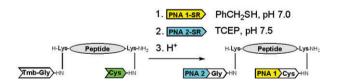


2785

Orthogonal ligation: a three piece assembly of a PNA-peptide-PNA conjugate

Fabienne Burlina,* David D. Dixson, Robert P. Doyle, Gérard Chassaing, Christopher N. Boddy, Philip Dawson and John Offer*

The authors describe the development of an orthogonal ligation strategy, enabling regiospecific amide bond ligation in aqueous buffer with three components and no requirement for protecting groups.



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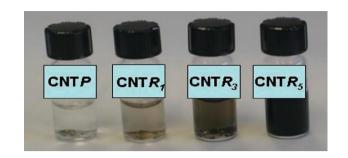
COMMUNICATIONS

2788

Ultra-fast and scalable sidewall functionalisation of single-walled carbon nanotubes with carboxylic acid

Brenda Long, Tan Man Wu and Francesco Stellacci*

A simple and fast method for the functionalisation of singlewalled carbon nanotubes with carboxylic acid terminated molecules, at varying molar fractions, is presented.

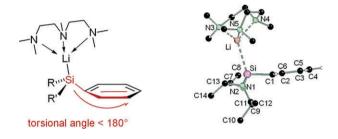


2791

Bent phenyl groups in lithiosilanes—crystal structures and interpretation of this unanticipated feature

Carsten Strohmann* and Christian Däschlein

The bend of aromatic substituents in anionic group fourteen compounds (third row and higher) in their crystal structures is explained by means of quantum chemical calculations.



2794

Highly fluorescent supramolecular gels with chirality transcription through hydrogen bonding

Jangwon Seo, Jong Won Chung, Eun-Hye Jo and Soo Young Park*

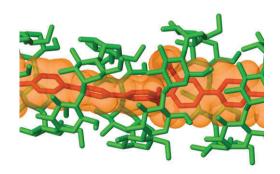
A highly fluorescent chiral organogel with transparency was prepared *via* the H-bonding mediated supramolecular assembly between non-fluorescent and achiral CN-TFMBPPE and chiral sergeant L-tartaric acid.

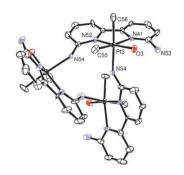
2797

Amylose-wrapped luminescent conjugated polymers

Michael J. Frampton, Timothy D. W. Claridge, Gianluca Latini, Sergio Brovelli, Franco Cacialli* and Harry L. Anderson*

Highly luminescent inclusion complexes consisting of poly(*para*-phenylene) (**PPP**) or poly(4,4'-diphenylene-vinylene) (**PDV**) in the helical cavity of amylose have been synthesised, structurally characterised by nuclear Overhauser spectroscopy and used to fabricate electroluminescent light-emitting diodes.

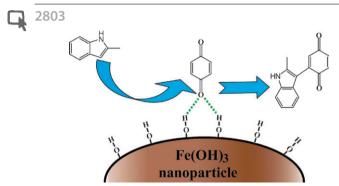




Hydrogen bonding directs the H₂O₂ oxidation of platinum(II) to a *cis*-dihydroxo platinum(IV) complex

Russell A. Taylor, David J. Law, Glenn J. Sunley, Andrew J. P. White and George J. P. Britovsek*

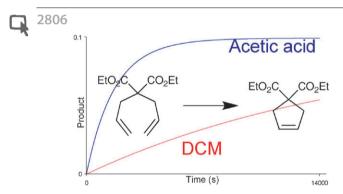
The use of ligands with proximate hydrogen bonding substituents in the oxidation of platinum(II) dimethyl complexes with H_2O_2 leads to the exclusive formation of an unusual *cis*-dihydroxo platinum(IV) complex, which can dehydrate to form a trinuclear metalla-azacrown complex.



Promotion of organic reactions by interfacial hydrogen bonds on hydroxyl group rich nano-solids

Fang Niu, Chang-Chang Liu, Zhi-Min Cui, Jin Zhai, Lei Jiang and Wei-Guo Song*

Surface hydroxyl group rich nano-solids dramatically increase the rate of several organic reactions. Such effect is attributed to the formation of interfacial hydrogen bonds between the surface hydroxyl groups and reactant molecules. This promotion effect is versatile and applicable for a broad range of reaction conditions.

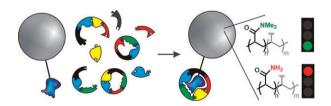


Solvents for ring-closing metathesis reactions

Claire S. Adjiman,* Adam J. Clarke, Gregory Cooper and Paul C. Taylor*

A study of the effects of eight diverse solvents on a Grubbs II-catalysed ring-closing metathesis (RCM) reaction reveals a complex dependence of the different reaction steps on the solvent and suggests acetic acid as a useful solvent for RCM reactions.

2809



Polymer-supported cationic templates for molecular recognition of anionic hosts in water

Pol Besenius, Peter A. G. Cormack,* R. Frederick Ludlow, Sijbren Otto* and David C. Sherrington*

Translocation of molecular recognition from aqueous to solid phase is reported using a poly(dimethylacrylamide)-immobilised cationic guest and a DCL of anionic hosts, enabling selective amplification and facile isolation of favoured hosts.



Azacalix[4]arene cation radicals: spin-delocalised doublet- and triplet-ground states observed in the macrocyclic *m*-phenylene system connected with nitrogen atoms

Koichi Ishibashi, Hirohito Tsue,* Naoko Sakai, Satoshi Tokita, Kazuhiro Matsui, Jun Yamauchi and Rui Tamura

Electron paramagnetic resonance spectroscopy has unmasked for the first time the spin-delocalised doublet- and triplet-ground states of azacalix[4]arene cation radicals.





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