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C49

Cover (far left)



Inside cover (left) Flexible mesoporous nanocrystalline titania (pp. 1460–1461).

The cover illustrates the processes occurring in natural photosynthesis and the efforts aimed at mimicking mother Nature using zeolite encapsulated photocatalysts (pp. 1443–1459).

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July 2004/Volume 1/Issue 7 www.rsc.org/chemicalscience 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, as well as the most significant scientific advances.



EATURE ARTICL

Zeolite-based photocatalysts

Avelino Corma* and Hermenegildo Garcia*

Encapsulation of a photoactive compound inside the rigid framework of microporous zeolites renders photocatalysts in which the adsorption ability of the zeolite host co-operates increasing the efficiency of the photocatalytic reaction; in addition the zeolite provides a compartmentalised space to assemble multi-component systems in a way reminiscent of enzymes of photosynthetic centers; areas of application of these zeolite-based photocatalysts are discussed.



OMMUNICATIONS

Towards flexible inorganic "mesomaterials": one-pot low temperature synthesis of mesostructured nanocrystalline titania

Sönke Haseloh, Sung Yeun Choi, Marc Mamak, Neil Coombs, Srebri Petrov, Naveen Chopra and Geoffrey A. Ozin*

We hereby report a simple route for the low temperature synthesis of mesoporous nanocrystalline titania involving brief hydrothermal treatment of butanolic precursors and non-ionic tri-block-copolymer surfactant at 100 °C, followed by evaporation induced self assembly to make a crack-free flexible film. At no time in the film-forming process is a temperature of more than 120 °C reached, thereby permitting the use of substrates that are not stable to higher temperatures.

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Chemical Communications (print: ISSN 1359-7345; electronic: ISSN 1364-548X) is published 24 times a year by the Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge, UK CB4 0WF. All orders accompanied by payment should be sent directly to Turpin Distribution Services Ltd, Blackhorse Road, Letchworth, Herts, UK SG6 1HN, 2004 Annual (print + electronic) subscription price: £1045: US\$1725, 2004 Annual (electronic) subscription price: £940; US\$1552. Customers in Canada will be subject to a surcharge to cover GST. Customers in the EU subscribing to the electronic version only will be charged VAT. If you take an institutional subscription to any RSC journal you are entitled to free, site-wide web access to that journal. You can arrange access via Internet Protocol (IP) address at www.rsc.org/ip. Customers should make payments by cheque in sterling payable on a UK clearing bank or in US dollars payable on a US clearing bank. Periodicals postage paid at Rahway, NJ, USA and at additional mailing offices. Airfreight and mailing in the USA by Mercury Airfreight International Ltd., 365 Blair Road, Avenel, NJ 07001, USA. US Postmaster: send address changes to Chemical Communications, c/o Mercury Airfreight International Ltd., 365 Blair Road, Avenel, NJ 07001. All despatches outside the UK by Consolidated Airfreight. PRINTED IN THE UK.

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Soft nanotubes from amphiphilic ABA triblock macromonomers

Julie Grumelard, Andreas Taubert and Wolfgang Meier*

Soft, water-filled polymer nanotubes of several tens of μ m in length have been prepared *via* self-assembly of amphiphilic ABA-triblock macromonomers in aqueous media; the tubes are mechanically and chemically stable and can be loaded with water-soluble substances.

Self-assembly of aluminium-salen coupled nanostructures from encoded modules with cleavable disulfide DNA-linkers

Raymond S. Brown, Morten Nielsen and Kurt V. Gothelf*



Linear organic modules containing cleavable disulfide linkers are covalently coupled in DNA-directed reactions by formation of aluminium–salen bridges. Disulfide linkers enable subsequent reduction with TCEP and release of DNA.



Washing-free electrochemical DNA detection using double-stranded probes and competitive hybridization reaction

Kyuwon Kim,* Haesik Yang,* Se Ho Park, Dae-Sik Lee, Sung-Jin Kim, Yong Taik Lim and Youn Tae Kim

We have demonstrated a new electrochemical DNA detection method using double-stranded probes and competitive hybridization reaction and it offers highly selective discrimination of single base mismatch without posthybridization washing.

Encapsulation of gases in the solid state

Alexander V. Leontiev and Dmitry M. Rudkevich*



Cavity-containing solids reversibly encapsulate, store and exchange gases.

LA December 22 Dec



pH Indicating resins

Jin Ku Cho, Lu Shin Wong, Tony W. Dean, Osamu Ichihara, Christophe Muller and Mark Bradley*

pH Indicating resins were prepared by covalently attaching dyes onto resin beads and analysed visually and with a micro UV/Vis spectrometer.



$+ H_2O$

Synthesis and X-ray crystal structures of the first antimony and bismuth calixarene complexes

Lihua Liu, Lev N. Zakharov, Arnold L. Rheingold* and Tracy A. Hanna*

The reaction of the monosodium salt of *p*-tert-butylcalix[4]arene ($\mathbf{Bu}^{t}\mathbf{C4}$) with 2 equiv. of SbCl₃ provided **Bu^tC4**(SbCl)₂. The first Bi(III) calixarene complex was prepared by treatment of *p*-tert-butylcalix[8]arene (**Bu^tC8**) with Bi[N(SiMe₃)₂]₃.

A novel crownophane trapping CO₂ as carbonic acid at room temperature

Kazuhisa Hiratani,* Nobuko Sakamoto, Naohiro Kameta, Michinori Karikomi and Yoshinobu Nagawa

A 25 membered crownophane with two hydroxy and two amide groups has been reported for the first time to make a stable 1 : 1 complex with carbonic acid formed from CO₂ and water at room temperature.

Density functional calculations of a tetradecametallic iron(III) cluster with a very large spin ground state.

Gopalan Rajaraman, Joan Cano, Euan K. Brechin* and Eric J. L. McInnes*

DFT calculations and Monte Carlo simulations are used to calculate the exchange interactions in the Fe(III) cluster [Fe₁₄(bta)₆O₆(OMe)₁₈Cl₆], impossible to determine by conventional methods - the results support a very high ground state spin arising from competing antiferromagnetic interactions.



Interstrand communication between 2'-N-(pyren-1-yl)methyl-2'-amino-LNA monomers in nucleic acid duplexes: directional control and signalling of full complementarity

Patrick J. Hrdlicka, B. Ravindra Babu, Mads D. Sørensen and Jesper Wengel*

Molecular communication systems, based on interstrand pyrene excimer formation, have been obtained as the first demonstration of chemical engineering at the Ångström scale using functionalized 2'-amino-LNA building blocks.

Helix stabilization through pyridinium- π interactions

Jennifer M. Heemstra and Jeffrey S. Moore*

oligomer too short to form pyridinium-13 15 17

Intramolecular cation $-\pi$ interactions between a methyl pyridinium ion and a phenyl ring stabilize the folded structure of a phenyleneethynylene oligomer.





v



Metric engineering of perfluorocarbon–hydrocarbon layered solids driven by the halogen bonding

Pierangelo Metrangolo,* Tullio Pilati, Giuseppe Resnati* and Andrea Stevenazzi

Halogen bonding has been used for the metric engineering of layered PFC–HC co-crystals. The 1D chain pitch length (d) correlates linearly with the number of methylene (2m) and difluoromethylene (2n) groups in starting modules.

Ionic liquid-immobilized catalytic system for biomimetic dihydroxylation of olefins

Adam Closson, Mikael Johansson and Jan-E. Bäckvall*

An immobilized biomimetic catalytic system in an ionic liquid $([bmim]PF_6)$ is highly efficient for dihydroxylation of olefins and can be recovered and reused.

Controllable AuPt bimetallic hollow nanostructures

Han-Pu Liang, Yu-Guo Guo, Hui-Min Zhang, Jin-Song Hu, Li-Jun Wan* and Chun-Li Bai*

One step, large-scale synthesis of AuPt bimetallic hollow 1-D nanostructures and nanospheres is described using Co nanoparticles as sacrificial templates.

Room temperature olefins oligomerization over sulfated titania

Angeles Mantilla,* Francisco Tzompantzi, Gerardo Ferrat, Alfonso López-Ortega, Eduardo Romero, Emma Ortiz-Islas, Ricardo Gómez and Miguel Torres

Catalytic behaviour of the isobutene oligomerization over sulfated titania was evaluated using mild conditions. Total isobutene conversion, long time stability and high selectivity to C_8-C_{12} olefins fractions (87%) were obtained.

New aerobic oxidation of benzylic compounds: efficient catalysis by *N*-hydroxy-3,4,5,6-tetraphenylphthalimide (NHTPPI)/CuCl under mild conditions and low catalyst loading

Malek Nechab, Cathy Einhorn and Jacques Einhorn*

NHTPPI, in combination with CuCl, has been found to catalyse efficiently the aerobic oxidation of various benzylic compounds at mild temperature and only 1% catalyst loading.



TiO₂

1504

1506

1508

1510

A novel one-pot four-component access to tetrahydro-βcarbolines by a coupling-amination-aza-annulation-Pictet–Spengler sequence (CAAPS)

Alexei S. Karpov, Thomas Oeser and Thomas J. J. Müller*

The four-component coupling-amination-aza-annulation-Pictet–Spengler (CAAPS) sequence of acid chlorides **1**, terminal alkynes **2**, tryptamine derivatives **6**, and acryloyl chloride derivatives **4** represents a rapid one-pot access to tetrahydro-β-carbolines **7**.



In formamide and urea photocatalytic degradation the final fate of nitrogen is linked to the carbon (and not nitrogen) oxidation state.

$V_2Al_5Ge_5{:}$ first ternary intermetallic in the V–Al–Ge system accessible in liquid aluminium

Xiuni Wu, Daniel Bilc, Subhendra D. Mahanti and Mercouri G. Kanatzidis*

 $V_2Al_5Ge_5$ is stabilized in liquid aluminium and is the first reported example of a compound in this ternary system. It features an anisotropic structure with extensive one-dimensional V–V bonding.

Ir-catalyzed C–H activation in the synthesis of borylated ferrocenes and half sandwich compounds

Anupama Datta, Axel Köllhofer and Herbert Plenio*



The 12[Ir(OMe)(cod)]₂/dtby catalyzed CH-activation is an efficient tool for the functionalization of ferrocenes and related half sandwich compounds which is highly tolerant towards various functional groups.

Solvent tuned excited state configuration mixing in a π -conjugated metal–organic oligomer

Shengxia Liu and Kirk S. Schanze*



The photophysical properties of a π -conjugated metal–organic oligomer vary smoothly with solvent composition. The variation is believed to arise from solvent-tuned configuration mixing of ${}^{3}\pi,\pi^{*}$ and ${}^{3}MLCT$ levels.



CdS

polymer



silicate

polymer-silica hybrid mesoporous material

1526

1528

Polymer/nanoparticle

adsorption

aggregation

polymer-silicate

surfactant

Preparation and characterization of polyaniline microwires containing **CdS** nanoparticles

Xiaofeng Lu, Youhai Yu, Liang Chen, Huaping Mao, Wanjin Zhang* and Yen Wei*

We describe the synthesis and characterization of PANI microwires containing CdS nanoparticles. We succeed in homogeneous dispersion of CdS nanoparticles for the first time, using hydrogen bonding and/or electrostatic interaction between the carbonyl groups capped CdS nanoparticles and the polyaniline molecules.

Direct synthesis of ordered mesoporous materials constructed with polymer-silica hybrid frameworks

Yoon-Sok Kang, Hyung Ik Lee, Ye Zhang, Yong Jin Han, Jae Eui Yie, Galen D. Stucky* and Ji Man Kim*

Highly ordered mesoporous materials constructed with polymer-silica frameworks can be obtained via a one-step synthetic strategy using a mixture of polymer and silicate as the framework source.

A stereodivergent asymmetric approach to difluorinated aldonic acids

Christophe Audouard, Igor Barsukov, John Fawcett, Gerry A. Griffith, Jonathan M. Percy,* Stéphane Pintat and Clive A. Smith



A difluorinated alkyne building block and glycolaldehyde are used to assemble a substrate for asymmetric dihydroxylation and phenyl group oxidation, delivering a novel enantiomerically-enriched difluorinated aldonic acid.

Enzyme encapsulation in nanoporous silica spheres

Yajun Wang and Frank Caruso*

Encapsulating enzymes in mesoporous silica spheres via immobilization, followed by deposition of polymer/nanoparticle shells, yields particles that have high enzyme loadings, enzymatic activity and stability.

1530 H₂L^F

Enzyme

Mesoporous silica

sphere

Control of molecular architecture by use of the appropriate ligand isomer: a mononuclear "corner-type" versus a tetranuclear $[2 \times 2]$ grid-type cobalt(III) complex

Julia Hausmann and Sally Brooker*

Employing two isomeric pyrazine-based ligands a $[2 \times 2]$ grid-type tetranuclear cobalt(III) complex, incorporating doubly deprotonated $(\mathbf{L}^{\mathbf{a}})^{2-}$ ligands, and a "corner-type" mononuclear cobalt(III) complex, incorporating neutral H₂L^p ligands in a zwitterionic form, have been synthesised and structurally characterised.

Enzyme encapsulated in

mesoporous silica sphere

iх



Fullerene-linked Pt nanoparticle assemblies

C. Roth,* I. Hussain, M. Bayati, R. J. Nichols and D. J. Schiffrin

Fullerene–Pt nanoparticle assemblies were prepared by attachment and immobilisation of Pt nanoparticles on a gold electrode using molecular layers of C_{60} . These assemblies were active for the methanol oxidation following treatment with CO.

BuOHF127=3,...4 provide the second s



Michael Schmittel,* Venkateshwharlu Kalsani and Lorenz Kienle*

Simple and supramolecular copper complexes as precursors in the HRTEM induced formation of crystalline copper nanoparticles

Radiation damage is the reason why in HRTEM investigations of copper(I) bisphenanthroline nanoscaffolds and of simple complexes 3–5 nm sized crystalline copper particles are found that can easily be confused with the original aggregates.

Transformation of highly ordered large pore silica mesophases (Fm3m, Im3m and p6mm) in a ternary triblock copolymer–butanol–water system

Freddy Kleitz, Leonid A. Solovyov, Gopinathan M. Anilkumar, Shin Hei Choi and Ryong Ryoo*

Exceptional control of the phase behavior of highly ordered large pore mesostructured silica (with the choice of Fm3m, Im3m or p6mm symmetry) is achieved using a triblock copolymer (EO₁₀₆PO₇₀EO₁₀₆) and butanol at low acid concentrations.

[2 + 2]Photocyclization in a single-crystal-to-single-crystal transformation of a TTF-amido-pyridine

Thomas Devic, Patrick Batail* and Narcis Avarvari*

The irradiation of a single crystalline sample of the redox active ligand EDT-TTF-CONH-3-Py afforded the corresponding cyclobutane derivative through a [2 + 2] photodimerization process, as demonstrated by single crystal X-ray analysis.

Zinc-proline catalyzed pathway for the formation of sugars

 Jacob Kofoed, Miguel Machuqueiro, Jean-Louis Reymond* and Tamis Darbre*

Zn-proline complex catalyzes the aldolisation of glycolaldehyde in water to give tetroses and hexoses; threose (33% of the product mixture) was formed with 10% enantiomeric excess of the D-isomer. The new reaction adds to possible prebiotic synthesis of sugars.

х



emission is sensitised by the Re^I MLCT excited states.

хi

0

H

1556



New, highly acidic ionic liquid systems and their application in the carbonylation of toluene

Nicole Brausch, Andreas Metlen and Peter Wasserscheid*

A new class of highly acidic ionic systems of the type $[cation][(CF_3SO_2)_2N]$ -AlCl₃ has been developed and successfully applied in the carbonylation of toluene.



Olefin copolymerization *via* **reversible addition–fragmentation chain transfer** Rajan Venkatesh, Bastiaan B P Staal and Bert Klumperman*

 α -Olefins and (meth)acrylates are copolymerized *via* reversible addition–fragmentation chain transfer mediated radical polymerization. The incorporation of the α -olefin in the polymer chain is proven by various techniques including MALDI-TOF MS.

A simple poly(3,4-ethylene dioxythiophene)/poly(styrene sulfonic acid) transistor for glucose sensing at neutral pH

Zheng-Tao Zhu, Jeffrey T. Mabeck, Changcheng Zhu, Nathaniel C. Cady, Carl A. Batt and George G. Malliaras*

A simple transistor, which is based on the conducting polymer PEDOT : PSS, and is capable of sensing glucose in a neutral pH buffer solution, is demonstrated.



ADDITIONS AND CORRECTIONS

Omowunmi A. Sadik and Fei Yan

Jin Ku Cho, Lu Shin Wong,

Christophe Muller and

Mark Bradley

Tony W. Dean, Osamu Ichihara,

Novel fluorescent biosensor for pathogenic toxins using cyclic polypeptide conjugates

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pH Indicating resins

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Rheingold, Arnold L., 1472 Romero, Eduardo, 1498 Roth, C., 1532 Rudkevich, Dmitry M., 1468 Ryoo, Ryong, 1536 Sadik, Omowunmi A., 1558 Sakamoto, Nobuko, 1474 Sauthier, Mathieu, 1520 Schanze, Kirk S., 1510 Schiffrin, D. J., 1532 Schmittel, Michael, 1534 Smith, Clive A., 1526 Solovyov, Leonid A., 1536 Song, Myung-Geun, 1514 Sørensen, Mads D., 1478 Staal, Bastiaan B P. 1554 Stenzel, Martina H., 1546 Stevenazzi, Andrea, 1492 Stucky, Galen D., 1524 Tang, Yong, 1516 Taniguchi, Isao, 1518 Taubert, Andreas, 1462 Tominaga, Masato, 1518 Torres, Miguel, 1498 Tzompantzi, Francisco, 1498 Valerga, Pedro, 1490 Venkatesh, Rajan, 1554 Wan, Li-Jun, 1496 Wang, Yajun, 1528 Wang, Yue, 1484 Wasserscheid, Peter, 1552 Wei, Yen, 1522 Weng, Lin-Hong, 1542 Wengel, Jesper, 1478 Wong, Lu Shin, 1470, 1558 Wu, Xiuni, 1506 Xiang, Hai-Feng, 1484 Yan, Fei, 1558 Yanagida, Shozo, 1486 Yang, Haesik, 1466 Yao, Shao O., 1512 Yie, Jae Eui, 1524 Yu, Xiao-Yan, 1542 Yu, Youhai, 1522 Zakharov, Lev N., 1472 Zhang, Hui-Min, 1496 Zhang, Wanjin, 1522 Zhang, Ye, 1524 Zhu, Changcheng, 1556 Zhu, Qing, 1512 Zhu, Zheng-Tao, 1556

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