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ISSN 1359-7345 CODEN CHCOFS (10) 989-1096 (2007)



See Francesco Naso et al., page 1003. The image shows the structures of durable fluorinated materials superimposed on the everlasting "Castel del Monte", a castle built by the Swabian Emperor Frederick II near Bari (Italy) in 1245. Image reproduced by permission of Francesco Babudri, Gianluca M. Farinola, Francesco Naso and Roberta Ragni, from Chem. Commun., 2007, 1003.



Inside cover

See Shunsaku Kimura et al., page 1023. A novel polypseudorotaxane composed of a peptide nanotube and poly(ethylene glycol) having a large dipole. Image reproduced by permission of Tatsuya Hirata, Futoshi Fujimura and Shunsaku Kimura, from Chem. Commun., 2007, 1023.

CHEMICAL TECHNOLOGY

T17

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March 2007/Volume 4/Issue 3

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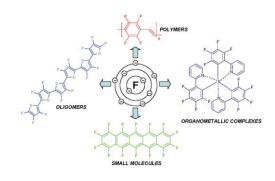
FEATURE ARTICLE

1003

Fluorinated organic materials for electronic and optoelectronic applications: the role of the fluorine atom

Francesco Babudri, Gianluca M. Farinola, Francesco Naso* and Roberta Ragni

In this article we highlight the features of some classes of fluorinated conjugated materials and their use in electronic devices. A variety of fluorinated conjugated systems are dealt with.



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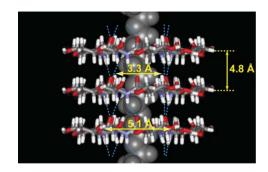
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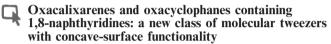
A novel polypseudorotaxane composed of cyclic β-peptide as bead component

Tatsuva Hirata, Futoshi Fujimura and Shunsaku Kimura*

The authors prepared a novel polypseudorotaxane composed of a PEG chain and cyclic hexa-β-peptides having sugar units. A notable feature of this polyrotaxane is the self-assembling of the beads into a peptide nanotube.

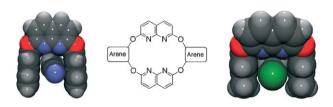


1026



Jeffrey L. Katz,* Bram J. Geller and Peter D. Foster

The first examples of oxacalix[4]arenes and [14]oxacyclophanes bearing 1,8-naphthyridine units are reported, and these systems function as molecular tweezers containing inner-cavity hydrogen bond acceptors.

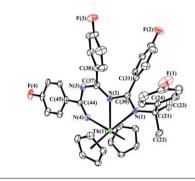


1029

Actinide-mediated coupling of 4-fluorobenzonitrile: synthesis of an eight-membered thorium(IV) tetraazametallacycle

Eric J. Schelter, David E. Morris, Brian L. Scott and Jaqueline L. Kiplinger*

An eight-membered thorium(IV) tetraazamacrocycle is produced by the sequential, metal-mediated coupling of four equivalents of 4-fluorobenzonitrile; its formation is consistent with the involvement of an imido intermediate, generated from a thorium ketimide complex.

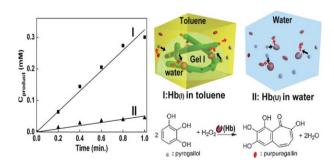


1032

Molecular hydrogel-immobilized enzymes exhibit superactivity and high stability in organic solvents

Qigang Wang, Zhimou Yang, Ling Wang, Manlung Ma and Bing Xu'

The use of a molecular hydrogel to immobilize enzymes attains superactivity and exceptional stability in an organic solvent.







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1035

Pd-mediated synthesis of substituted benzenes fused with carbocycle/heterocycle

Nalivela Kumara Swamy, Lakshmi Kumar Tatini, J. Moses Babu, Pazhanimuthu Annamalai and Manojit Pal*

The Pd-mediated coupling reaction of α-haloenone with terminal alkynes under a Cu-free condition provided a new and one-pot synthetic procedure for the construction of benzene ring fused with carbocyclic and heterocyclic

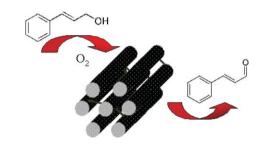
1038



Molecular level dispersed Pd clusters in the carbon walls of ordered mesoporous carbon as a highly selective alcohol oxidation catalyst

An-Hui Lu, Wen-Cui Li, Zhenshan Hou and Ferdi Schüth

Ordered mesoporous carbon containing molecular-level dispersed Pd clusters in the carbon walls was synthesized by the nanocasting pathway, and shows high selectivity for the oxidation of alcohols to aldehydes.



Pd-OMC

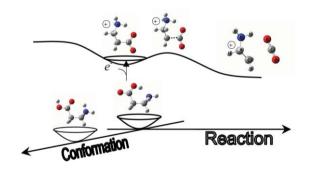
1041



A highly conformationally specific α- and β-Ala⁺ decarboxylation pathway

Kyo-Won Choi, Doo-Sik Ahn, Joo-Hee Lee and Sang Kyu Kim*

A new dissociative ionization channel is found for alanine and β-alanine. This channel giving rise to CO₂ proceeds via highly conformer specific intramolecular hydrogen transfer.

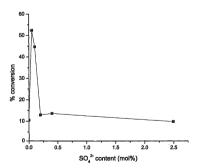


1044

Dramatic promotion of gold/titania for CO oxidation by sulfate ions

P. Mohapatra, John Moma, K. M. Parida, W. A. Jordaan and Mike S. Scurrell*

The presence of sulfate ions at very low levels dramatically increases the CO oxidation activity of gold/titania catalysts. At least some of the sulfur introduced interacts directly with the gold centres.



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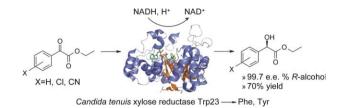
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1047

Identification of Candida tenuis xylose reductase as highly selective biocatalyst for the synthesis of aromatic α-hydroxy esters and improvement of its efficiency by protein engineering

Regina Kratzer and Bernd Nidetzky*

Wild-type Candida tenuis xylose reductase and two Trp-23 mutants thereof catalyze NADH-dependent reduction of a homologous series of aromatic α-keto esters with absolute pseudo re-face stereoselectivity and broad tolerance for the substituent on the aromatic ring.

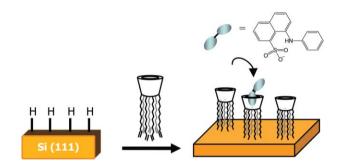


1050

Functionalization of silicon surfaces with Si-C linked **β-cyclodextrin monolayers**

Corinne Lagrost,* Gilles Alcaraz, Jean-François Bergamini, Bruno Fabre and Iuliana Serbanescu

Heptakis {6-deoxy-6-[undec-10-enamido]}-β-cyclodextrins react with monocrystalline Si-H surfaces to generate robust molecular recognition devices.

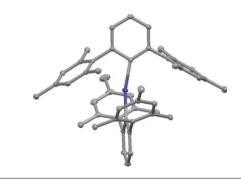


1053

Monomeric, two-coordinate Mn, Fe and Co(II) complexes featuring 2,6-(2,4,6-trimethylphenyl)phenyl ligands

Deborah L. Kays (née Coombs)* and Andrew R. Cowley

The reaction of [2,6-Mes₂C₆H₃Li]₂ with first-row transition-metal halides yields the monomeric complexes $(2,6-\text{Mes}_2\text{C}_6\text{H}_3)_2\text{M}$ (Mes = mesityl, M = Mn, Fe, Co), of which the cobalt analogue is the first structurally authenticated two-coordinate, homoleptic cobalt(II) aryl complex.



1056

Superoxide dismutase mimetic properties exhibited by vacancy engineered ceria nanoparticles

Cassandra Korsvik, Swanand Patil, Sudipta Seal and William T. Self*

SOD mimetics are currently being tested in clinical trials as novel drugs to reduce superoxide levels in tissues. Vacancy Engineered nanoceria exhibits potent SOD mimetic activity and thus may represent a novel class of nanomaterials that can be further developed into clinical applications in the near future.



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In its February 2007 special issue *Chem Soc Rev* celebrates two landmark anniversaries in the field of Supramolecular Chemistry:

1967: Charles Pedersen's first paper on the synthesis and metal binding properties of crown ethers is published in the *Journal of the American Chemical Society*.

1987: the Nobel prize in chemistry is awarded to Charles Pedersen, Jean-Marie Lehn and Donald Cram in recognition of their pioneering work in Supramolecular Chemistry.

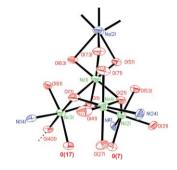
010764

1059

A one-pot synthesis of a paramagnetic high-nuclearity nickel(II) cluster: an octadecanuclear $Ni^{II}_{16}Na^{I}_{2}$ metal

Biplab Biswas, Sumit Khanra, Thomas Weyhermüller and Phalguni Chaudhuri*

An unusual Ni^{II}₁₆Na^I₂ cluster which features formate as a bridging clamp between two octanuclear nickel cages is reported; preliminary magnetic studies exhibit paramagnetic low-lying states resulting from dominating antiferromagnetic interactions between the nickel(II) centers.

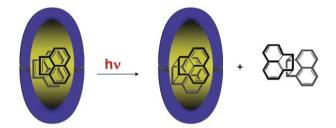


1062

Photodimerization of acenaphthylene within a nanocapsule: excited state lifetime dependent dimer selectivity

Lakshmi S. Kaanumalle and V. Ramamurthy*

The dimer selectivity from acenaphthylene@octa acid is dependent on the lifetime of the reactive state.



1065

A new type of soluble pentacene precursor for organic thin-film transistors

Kew-Yu Chen, Hsing-Hung Hsieh, Chung-Chih Wu,* Jiunn-Jye Hwang and Tahsin J. Chow*

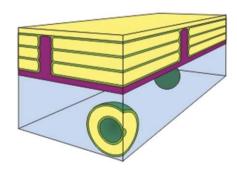
A stable and soluble pentacene precursor is prepared, which extrudes a unit of CO upon heating at 150 °C, to produce pure pentacene suitable for OTFT applications.

1068

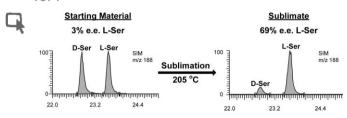
Formation of robust, free-standing nanostructured membranes from catanionic surfactant mixtures and hydrophilic polymers

Benjamin M. D. O'Driscoll, E. Anne Nickels and Karen J. Edler

Highly ordered and robust nanostructured membranes self-assemble over arbitrarily large areas from solutions of water-soluble polymers and catanionic surfactant mixtures. The films retain their structure when dried.



1071



Serine sublimes with spontaneous chiral amplification

Richard H. Perry, Chunping Wu, Marcela Nefliu and R. Graham Cooks*

Sublimation of near-racemic samples of serine (Ser) yields a sublimate which is highly enriched in the major enantiomer. This simple one-step process occurs under relatively mild conditions, and represents a possible mechanism for the chiral amplification step in homochirogenesis.

1074

O O PhoP=O TfoO O O R'-NHo, NMP

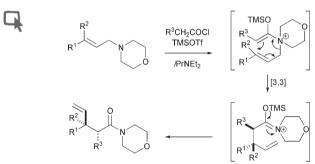
MW, 140 °C

Trichlorophenol (TCP) sulfonate esters: A selective alternative to pentafluorophenol (PFP) esters and sulfonyl chlorides for the preparation of sulfonamides

Jonathan D. Wilden,* Lynsey Geldeard, Chieh C. Lee, Duncan B. Judd and Stephen Caddick*

2,4,6-Trichlorophenol (TCP) sulfonate esters are an effective replacement for PFP-sulfonates and sulfonyl chlorides. They undergo microwave enhanced aminolysis, but are less reactive than PFP-sulfonate esters, allowing chemoselective aminolysis of the PFP-sulfonates in the presence of TCP-sulfonates.

1077

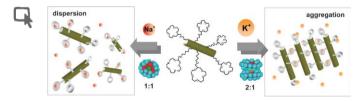


Silyl-modified Belluš-Claisen rearrangement

Donald Craig,* N. Paul King and David M. Mountford

A silyl-modified, metal-free Lewis acid-assisted Belluš-Claisen reaction is described; the generality of the rearrangement is demonstrated with a range of allylic amines and ketenes.

1080



Anisotropic assembly of gold nanorods assisted by selective ion recognition of surface-anchored crown ether derivatives

Hiroshi Nakashima,* Kazuaki Furukawa, Yoshiaki Kashimura and Keiichi Torimitsu

A complex of gold nanorods with crown ethers recognised ions selectively in response to dispersion and aggregation; the preferential end-to-end or side-to-side assembly of nanorods was observed in the aggregates.

1083

Mito-DEPMPO synthesized from a novel NH₂-reactive DEPMPO spin trap: a new and improved trap for the detection of superoxide

Micael Hardy, Florence Chalier, Olivier Ouari, Jean-Pierre Finet, Antal Rockenbauer, Balaraman Kalyanaraman and Paul Tordo*

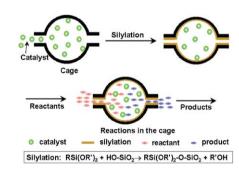
The half-life of the Mito-DEPMPO superoxide adduct was estimated to be ca. 40 min. Using Mito-DEPMPO, reactive oxygen species generated in intact mitochondria were detected and characterized by EPR.

1086

Asymmetric reactions on chiral catalysts entrapped within a mesoporous cage

Hengquan Yang, Jun Li, Jie Yang, Zhimin Liu, Qihua Yang* and Can Li*

The encapsulation of homogeneous chiral catalysts, e.g. Co(Salen) and Ru-TsDPEN, in the mesoporous cage of SBA-16 is demonstrated; the encapsulated catalysts show performance as good as that of the homogeneous catalysts, and can be recycled for more than 10 times without significant loss of catalytic performance.



1089

Preparation and characterization of the first pyrazole-based remote N-heterocyclic carbene complexes of palladium(II)

Yuan Han and Han Vinh Huynh*

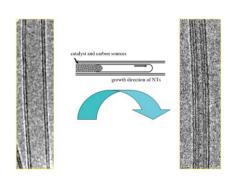
The first pyrazolin-4-ylidene complexes of palladium(II) have been synthesized by oxidative addition of 4-iodopyrazolium salts to Pd₂(dba)₃/PPh₃ and were fully characterized by multinuclear NMR spectroscopies, ESI mass spectrometry and X-ray diffraction studies.

1092

Controllable preparation of triple-walled carbon nanotubes and their growth mechanism

Hanxun Qiu, Zujin Shi,* Zhennan Gu and Jieshan Qiu*

Triple-walled carbon nanotubes (TWNTs) have been selectively synthesized for the first time from decomposition of ferrocene encapsulated in double-walled carbon nanotubes (DWNTs), demonstrating a base-growth mechanism for carbon nanotubes.



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