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Cover



"What could we do with layered structures with just the right layers? What would the properties of materials be if we could really arrange the atoms the way we want them? They would be very interesting to investigate theoretically. I can't see exactly what would happen, but I can hardly doubt that when we have some *control* of the arrangement of things on a small scale we will get an enormously greater range of possible properties that substances can have, and of different things that we can do." RICHARD FEYNMAN: *There's Plenty of Room at the Bottom* (1959)

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FEATURE ARTICLE

Integral atomic layer architectures of 1D crystals inserted into single walled carbon nanotubes

Jeremy Sloan,* Angus I. Kirkland, John L. Hutchison and Malcolm L. H. Green

Crystal growth within SWNTs is atomically regulated by the size of the encapsulating capillaries and nano-scale crystals with precise integral layer architectures can be formed within.



COMMUNICATIONS

One-step synthesis of hydrophobized gold nanoparticles of controllable size by the reduction of aqueous chloroaurate ions by hexadecylaniline at the liquid–liquid interface



PR. Selvakannan, Saikat Mandal, Renu Pasricha, S. D. Adyanthaya and Murali Sastry*

Vigorous stirring of a biphasic mixture containing hexa-decylaniline in chloroform and aqueous chloroauric acid results in the formation of gold nanoparticles of controllable size in the organic phase.

Friedel–Crafts reactions in water of carbonyl compounds with heteroaromatic compounds

Wei Zhuang and Karl Anker Jørgensen*



The development of addition of heteroaromatic compounds to glyoxylate to give Friedel–Crafts addition adducts in H₂O solutions is presented.

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COMMUNICATIONS

Coordinative control of photoinduced electron transfer: bulky carboxylates as molecular curtains



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RC

1350

Irene Bruseghini, Luigi Fabbrizzi,* Maurizio Licchelli and Angelo Taglietti

An intramolecular photoinduced electron transfer which takes place in a Zn^{II} polyamine complex is interrupted through coordination of a bulky carboxylate anion, acting as a curtain.

Intramolecular hydrogen bond assisted planarization and self-assembly of simple disc-shaped molecules in mesophases

Wenmiao Shu and Suresh Valiyaveettil*

Planarization of a disc-shaped molecule using strong intramolecular hydrogen bonds and the self-assembly of the target molecule in the mesophase is described.

$Crystallographic characterization of Kr@C_{60} in (0.09Kr@C_{60}/0.91C_{60}) \cdot \{Ni^{II}(OEP)\} \cdot 2C_6H_6$

Hon Man Lee, Marilyn M. Olmstead, Tomohiro Suetsuna, Hidekazu Shimotani, Nita Dragoe, R. James Cross, Koichi Kitazawa and Alan L. Balch*

A sample of C_{60} containing *ca*. 9% Kr@ C_{60} has been used to form crystalline $(0.09 \text{Kr}@C_{60}/0.91 C_{60}) \cdot \{\text{Ni}^{II}(\text{OEP})\} \cdot 2C_6 H_6$ whose X-ray crystal structure reveals that the Kr atom is centered within the carbon cage and does not produce a detectable change in the size of the fullerene.

A three-dimensional nanoporous flexible network of 'square-planar' copper(II) centres with an unusual topology

Lucia Carlucci, Nicola Cozzi, Gianfranco Ciani,* Massimo Moret, Davide M. Proserpio and Silvia Rizzato

The novel 3D two-fold interpenetrated network $[Cu(4,4'-bipy)_2(CF_3SO_3)_2]$, formed by pseudo-square planar nodes and consisting of fused crossing layers of large rhombic meshes (22 × 22 Å), shows an unusual topology and an interesting nanoporous behaviour.

Facile syntheses of tridentate ligands for room-temperature luminescence in ruthenium complexes

Matthew I. J. Polson, Nicholas J. Taylor and Garry S. Hanan*

A new family of tridentate terpyridine-like ligands are available in multi-gram quantities and their Ru(II) complexes exhibit room-temperature luminescence. The new triazine-based ligands are easily synthesised and functionalised, which makes them ideal candidates for incorporation into larger supramolecular systems.





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E (MPa) 600 500 400 Elastic Modulus, 300 200 100 0 0 40 50 60 10 20 30 Plasticizer Content, wt %

1370

1374



COMMUNICATIONS

Conventional free radical polymerization in room temperature ionic liquids: a green approach to commodity polymers with practical advantages

Kunlun Hong, Hongwei Zhang, Jimmy W. Mays,* Ann E. Visser, Christopher S. Brazel,* John D. Holbrey, W. Matthew Reichert and Robin D. Rogers*

Free radical polymerizations in the ionic liquids 1-butyl-3-methylimidazolium and 1-hexyl-3-methylimidazolium hexafluorophosphate using conventional organic initiators are more rapid, and yield polymers with up to $10 \times$ greater molecular weights than in conventional VOC solvents under comparable conditions.

Application of ionic liquids as plasticizers for poly(methyl methacrylate)

Mark P. Scott, Christopher S. Brazel,* Michael G. Benton, Jimmy W. Mays, John D. Holbrey and Robin D. Rogers*

The ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate is an effective plasticizer for *in situ* polymerized poly(methyl methacrylate), and displays similar characteristics comparable to the commonly used plasticizer dioctyl phthalate, but has significantly better high temperature stability.

3-Component palladium-indium mediated diastereoselective cascade allylation of imines with allenes and aryl iodides

Ian R. Cooper, Ronald Grigg, William S. MacLachlan, Mark Thornton-Pett and Visuvanathar Sridharan

A new palladium–indium diastereoselective cascade allylation of imines using allenes and aryl iodides.

Synthesis of carbamoylphosphonate silanes for the selective sequestration of actinides

Jerome C. Birnbaum, Brad Busche, Yuehe Lin, Wendy J. Shaw and Glen E. Fryxell*

The synthesis of carbamoylphosphonate silanes (CMPO analogs) designed for sequestering actinide cations in self-assembled monolayers on mesoporous supports (SAMMS) is described.

Stable N-functionalised 'pincer' bis carbene ligands and their ruthenium complexes; synthesis and catalytic studies

Andreas A. Danopoulos,* Scott Winston and William B. Motherwell

Deprotonation of 2,6-bis(arylimidazolium)pyridine dibromide with $KN(SiMe_3)_2$ gave thermally stable 2,6-bis(arylimidazol-2-ylidene)pyridine, which was further used to prepare ruthenium 'pincer' complexes; the latter show catalytic activity in transfer hydrogenation of carbonyl compounds.



 $Ar_{N} = C_{C}^{N} C_{C}$

v

1: X = H 2: X = CH₂(CHOH)₂CH₂OH

1380

1382

1384

1386



rG: R = OH dG: R = H OF

Novel oxidation products from guanine nucleosides reacted with dimethyldioxirane

R. Jeremy H. Davies,* Clarke Stevenson, Shiv Kumar, Jason Lyle, Lisa Cosby, John F. Malone, Derek R. Boyd, Narain D. Sharma, Ann P. Hunter and Bridget K. Stein

Treatment of guanosine with dimethyldioxirane leads to the formation of 4-amidinocarbamoyl-5-hydroxyimidazole via a new oxidative pathway. Remarkably, the corresponding product from 2'-deoxyguanosine incorporates a trihydroxybutyl substituent in the imidazole ring.

CsPb₃Bi₃Te₈ and CsPb₄Bi₃Te₉: low-dimensional compounds and the homologous series CsPb_mBi₃Te_{5+m}

Kuei-Fang Hsu, Sangeeta Lal, Tim Hogan and Mercouri G. Kanatzidis*

The quaternary compounds CsPb₃Bi₃Te₈ and CsPb₄Bi₃Te₉ are part of a new homologous series of the type $CsPb_mBi_3Te_{5+m}$ with systematically varying structure and composition. The long lattice period and the two-dimensional structure play an important role in suppressing the thermal conductivity in these systems.

Mesoporous hybrid materials containing functional organic groups inside both the framework and the channel pores

Robert J. P. Corriu,* Ahmad Mehdi, Catherine Reyé and Chloé Thieuleux



Mesoporous hybrid materials containing cyclam moieties inside the framework are particularly suitable for grafting functional groups inside the channel pores.



Ustalic acid as a toxin and related compounds from the mushroom Tricholoma ustale

Yosuke Sano, Kazutoshi Sayama, Yasushi Arimoto, Takahiro Inakuma, Kimiko Kobayashi, Hiroyuki Koshino and Hirokazu Kawagishi*

Ustalic acid and related compounds having unique structures were isolated as toxic principles from a poisonous mushroom Tricholoma ustale.

First rhenium complexes based on cyclotriphosphazene scaffolds with exocyclic pyrazolyl substituents

Michael Harmjanz, Brian L. Scott and Carol J. Burns*



The facile synthesis of pyrazole substituted site-differentiated cyclotriphosphazenes is described and the coordination behavior of these ligands and $P_3N_3(3,5-Me_2Pz)_6$ towards the formation of Re(I) carbonyl complexes is detailed.





COMMUNICATIONS

Unprecedented carbon dioxide effect on a Pd-catalysed oxidative carbonylation reaction: a new synthesis of pyrrole-2-acetic esters

Bartolo Gabriele,* Giuseppe Salerno,* Alessia Fazio and Fausto Bruno Campana



1408

It has been found for the first time that carbon dioxide is able to selectively activate a palladium-catalysed oxidative carbonylation reaction.



DDO

Unusual crystalline heterobimetallic trinuclear β -diketiminates [Yb{L(μ -Li(thf)}] and [Yb{L'(μ -Li(thf)] ·thf [L, L' = {N(SiMe_3)C(R)}2CH, R = Ph, C₆H₄Ph-4]

Anthony G. Avent, Alexei V. Khvostov, Peter B. Hitchcock and Michael F. Lappert*

Treatment of YbCl₃ with successively 2KL or 2LiL' and then >2Li in thf is shown to yield crystalline [Yb{L(μ -Li(thf)}₂] or [Yb{L'(μ -Li(thf)}₂]-thf, characterised by single crystal X-ray, multinuclear NMR spectral and VT magnetic susceptibility data; L or L', is believed to be dianionic in the complexes.

Divergent enantioselective synthesis of (P)- and (M)dihydro[5]helicenequinones from a common tetrahydroaromatic precursor

M. Carmen Carreño,* Susana García-Cerrada and Antonio Urbano

Compounds (R)-4 having central chirality lead, in a divergent way, to helically chiral (P) or (M) enantiomers of dihydro[5]helicenequinones simply by selecting the common oxidant reagent which makes the final aromatization.

Stereochemical control of $Zn(\pi)/Cu(\pi)$ selectivity in piperidine tripod ligands

Stereochemistry controls selectivity toward Zn(II) over Cu(II) of some tripodal ligands with a central piperidine scaffold, one of which acts as a

Zhaohua Dai, Xiaodong Xu and James W. Canary*



Zn(II)/Cu(II) 10⁻⁵ selectivity 10-

(R)-4

R = Me, TBDMS

A novel two-dimensional mixed molybdenum–vanadium polyoxometalate with two types of cobalt(II) complex fragments as bridges

Cai-Ming Liu, De-Qing Zhang,* Ming Xiong and Dao-Ben Zhu*

fluorescent zinc sensor with nanomolar sensitivity.

 $[Co(en)_2][Co(bpy)_2]_2[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]\cdot 4.5H_2O$ (en = ethylenediamine, bpy = 2,2'-bipyridine) is the first example of a two-dimensional framework in which polyoxometalate anions are linked by two types of complex fragments.

`OΜ∈

(M)-(90% ee)

10-1

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1416

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 $Me_2SiC_3H_5^+$ isomer.

The trimethylsilylation of acetylene

B. Chiavarino, M. E. Crestoni* and S. Fornarini



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λ_{em,max}: **469** nm





Crystal engineering of metalloporphyrin assemblies. New supramolecular architectures mediated by bipyridyl ligands

Unexpectedly, an adduct ion is formed from the reaction of gaseous Me₃Si⁺ ions with acetylene in the low-pressure regime of FT-ICR mass spectrometry. Collision induced dissociation and bimolecular reactivity of the C5H11Si⁺ adduct were

compared with those of model ions pointing to a skeletal rearrangement to an

Yael Diskin-Posner, Goutam Kumar Patra and Israel Goldberg*

New spectacular porphyrin-based supramolecular architectures in crystals were designed by a concerted mechanism of molecular recognition, using [tetrakis(4hydroxyphenyl)porphyrinato]zinc and bipyridyl ligands as building blocks.

Synthesis and single crystal X-ray structure of the first imido analog of an eight-membered aluminophosphinate heterocycle

Tillmann Bauer, Stephan Schulz,* Martin Nieger and Ingo Krossing*

The equimolar reaction of *t*-BuP(NH₂)₂ and Et₂AlH yields [*t*-Bu(H)P(NH)₂AlEt₂]₂, the first structurally characterized aluminonitridophosphinate containing an eightmembered AINP-heterocycle. Computational calculation gives further information on the most likely reaction mechanism.

Novel zinc fluorescent probe bearing dansyl and aminoquinoline groups

Pengju Jiang, Lizhen Chen, Jun Lin, Qin Liu, Jun Ding, Xiang Gao and Zijian Guo*

The newly designed fluorescent probe is highly sensitive and selective towards Zn(II) ions and demonstrated a combined properties of both PET and PCT fluoroionophore.



 $\lambda_{ex,max}$: 395 nm

.: 547 nm

...:: **357** nm

A new molecular switch: redox-driven translocation mechanism of the copper cation

Daniel Kalny, Mourad Elhabiri, Tamar Moav, Alexander Vaskevich, Israel Rubinstein, Abraham Shanzer* and Anne-Marie Albrecht-Gary*

The synthesis of a novel molecular switch based on a heteroditopic ligand, which operates through the Cu^{II}/Cu^I couple, is reported. Reversible motion of the copper cation between the two binding sites is driven by auxiliary oxidation and reduction reaction. The rate-limiting steps of this translocation process were determined as well as the corresponding kinetic parameters.

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* Indicates the author for correspondence: see article for contact details. Supplementary crystallographic data are available: see article for further information.

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