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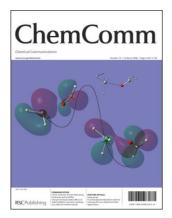
Chemical Communications

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IN THIS ISSUE

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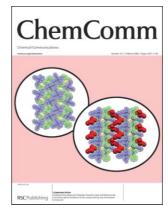


Cover

See Carl H. Schiesser et al., page

Radicals masquerading as electrophiles. Depicting both radical (SOMO-LUMO) and electrophilic (LUMO-HOMO) transition state interactions when a silyl radical reacts with methanimine.

Image reproduced by permission of Carl H. Schiesser, Hiroshi Matsubara, Ina Ritsner and Uta Wille from Chem. Commun., 2006, 1067.



Inside cover

See Reiko Kuroda et al., page

Optical resolutions of 1,1'binaphthyl-2,2'-dicarboxylic acid (ee 98%) and 2-hexanol (ee 62%) achieved by simple successive crystallization using (1R,2R)-diphenylethylenedia-

Image reproduced by permission of Yoshitane Imai, Masatoshi Takeshita, Tomohiro Sato and Reiko Kuroda from Chem. Commun., 2006, 1070.

CHEMICAL TECHNOLOGY

Т9

Chemical Technology highlights the latest applications and technological aspects of research across the chemical sciences.

Chemical Technology

March 2006/Volume 3/Issue 3 www.rsc.org/chemicaltechnology

FEATURE ARTICLE

1049

Functionalized imidazolium salts for task-specific ionic liquids and their applications

Sang-gi Lee

Task-specifically functionalized imidazolium salts, which can be used for catalysis, organic synthesis and extraction as well as for the construction of nanostructures and other novel materials, have been reviewed.



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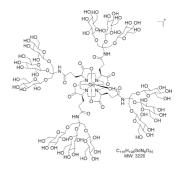
COMMUNICATIONS

1064

Glycoconjugates of gadolinium complexes for MRI applications

David A. Fulton, Elisa M. Elemento, Silvio Aime, Linda Chaabane, Mauro Botta and David Parker*

C-4 symmetric conjugates bearing four dendritic wedges and containing 12 glucose or galactose groups have high relaxivities as a result of effective motional coupling and a large second sphere contribution.

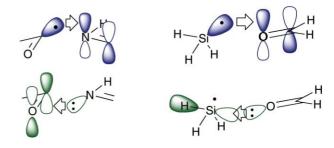


1067

Unexpected dual orbital effects in radical addition reactions involving acyl, silyl and related radicals

Carl H. Schiesser,* Hiroshi Matsubara,* Ina Ritsner and Uta Wille*

Molecular orbital calculations reveal that acyl and silyl radicals add to numerous types of π -systems through simultaneous SOMO-LUMO and LUMO-HOMO interactions.

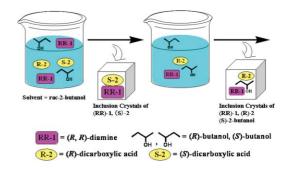


1070

Successive optical resolution of two compounds by one enantiopure compound

Yoshitane Imai, Masatoshi Takeshita, Tomohiro Sato and Reiko Kuroda*

By using (1R,2R)-1,2-diphenylethylenediamine as a single enantiopure compound, we achieved a novel successive optical resolution of two kinds of racemic compounds known to be difficult to optically resolve, through supramolecular crystallization.

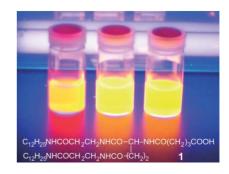


1073

Intense fluorescence-inducing amphiphile in cationic dyes and its applicability

Hiroshi Hachisako* and Ryoichi Murakami

An anionic amphiphile has been found to form extremely hydrophobic sites in water and specifically incorporate stilbazolium-based compact hemicyanine dyes as monomeric species, resulting in induction of intense fluorescence emission.



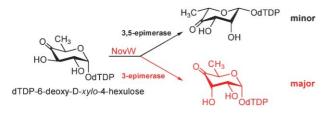


Helical aquatubes of calix[4]arene di-methoxycarboxylic acid

Adina N. Lazar, Nathalie Dupont, Alda Navaza and Anthony W. Coleman*

Dimeric units of calix[4]arene di-methoxycarboxylic acid generate intermeshed triple helical aquatubes that are characterized by a six-pointed star motif.

1079

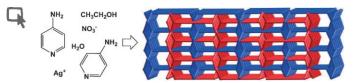


Characterisation of *Streptomyces spheroides* NovW and revision of its functional assignment to a dTDP-6-deoxy-D-*xylo*-4-hexulose 3-epimerase

Mónica Tello, Piotr Jakimowicz, James C. Errey, Caren L. Freel Meyers, Christopher T. Walsh, Mark J. Buttner, David M. Lawson and Robert A. Field*

Contrary to the literature, *Streptomyces spheroides* NovW is not a kinetically competent dual action dTDP-6-deoxy-D-*xylo*-4-hexulose 3,5-epimerase, but possesses only significant 3-epimerase activity *in vitro*.

1082



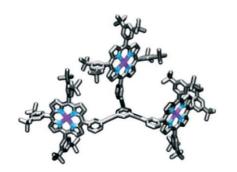
A unique example of a high symmetry three- and four-connected hydrogen bonded 3D-network

Morsy A. M. Abu-Youssef,* Vratislav Langer and Lars Öhrström*

The high symmetry 3D-net presented in this communication has not been observed among the molecular-based nets to date. The usefulness of net-analysis in the understanding of molecular crystal structures is also highlighted.

1085





Large-scale synthesis of alkyne-linked tripodal porphyrins *via* palladium-mediated coupling conditions

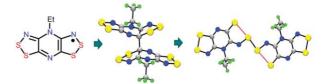
Lok H. Tong, Sofia I. Pascu, Thibaut Jarrosson and Jeremy K. M. Sanders*

Suzuki and Sonogashira couplings have been used in short and efficient sequences to give access to a new family of porphyrin trimers on a practical scale.

Bimodal association of a bis-1,2,3-dithiazolyl radical

Alicea A. Leitch, Courtney E. McKenzie, Richard T. Oakley,* Robert W. Reed, John F. Richardson and Lenora D. Sawyer

The N-ethyl pyrazine-bridged bis-1,2,3-dithiazolyl radical associates at room temperature as a C-C bonded σ-dimer which, on heating, converts to a laterally S–S σ-bonded structure.

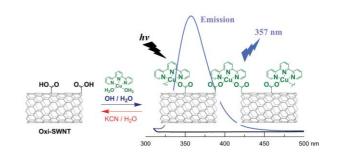


1091

TerpyridineCu^{II}-mediated reversible nanocomposites of single-wall carbon nanotubes: towards metallo-nanoscale architectures

Pingshan Wang, Charles N. Moorefield, Sinan Li, Seok-Ho Hwang, Carol D. Shreiner and George R. Newkome*

Self-assembly of Oxi-SWNTs using terpyridineCu^{II} coordination produced a thermally stable, neutral, and luminescent [(Oxi-SWNT)(tpyCu^{II})_m]_n composite.

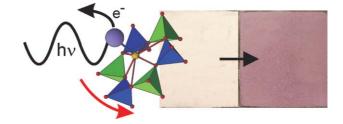


1094

Structural observation of photochromism

Jennifer A. Armstrong and Mark T. Weller

The detailed structural changes that occur in a polycrystalline material following the formation of a coloured, photoexcited state, an F-centre, have been determined using neutron diffraction.

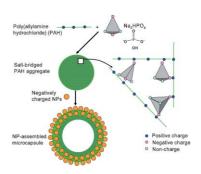


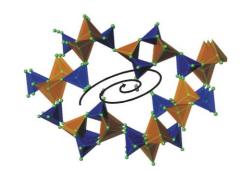
1097

Synthesis of nanoparticle-assembled tin oxide/polymer microcapsules

Jie Yu, Vinit S. Murthy, Rohit K. Rana and Michael S. Wong*

Tin oxide nanoparticles can be assembled into micron-sized hollow capsule structures through a simple mixing procedure based on charge-mediated polymer aggregate templating.



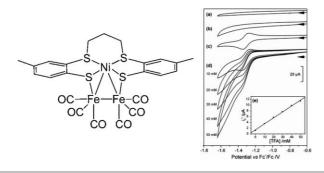


A chiral, 16-ring channel framework and a layered caesium zincoarsenate

Seth B. Wiggin and Mark T. Weller*

Two zincoarsenate frameworks, one with chiral channels delineated by 16 linked tetrahedra and the other having a pocketed layer structure, have been synthesised.

1103

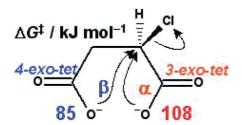


Electrocatalytic production of hydrogen by a synthetic model of [NiFe] hydrogenases

Alessandro Perra, E. Stephen Davies, Jason R. Hyde, Qiang Wang, Jonathan McMaster* and Martin Schröder*

The radical cluster anion [Ni(L)Fe₂(CO)₆] models the activity of the [NiFe] hydrogenases and catalyses the reduction of protons to produce molecular hydrogen at relatively anodic potentials compared to analogues of the [Fe]-only hydrogenases.

1106



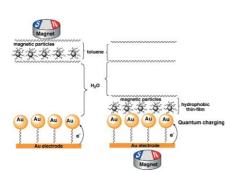
The Walden cycle revisited: a computational study of competitive ring closure to α - and β -lactones

J. Grant Buchanan, Richard A. Diggle, Giuseppe D. Ruggiero and Ian H. Williams*

Ring closure in chlorosuccinate gives β -lactone because O_{nuc} C Cl angle in transition structure is more favourable than for α -lactone formation in PCM(ϵ = 78.4)/B3LYP/6-31+G* calculations.

1109





Magneto-switchable single-electron charging of Au-nanoparticles using hydrophobic magnetic nanoparticles

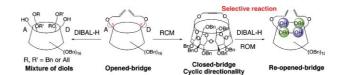
Eugenii Katz, Oleg Lioubashevski and Itamar Willner*

Reversible magneto-switchable quantum charging of a Au nanoparticle array associated with a Au electrode is observed in the presence of hydrophobic magnetic nanoparticles attracted to the functionalized electrode surface.

Sequential ring closing/opening metathesis for the highly selective synthesis of a triply bifunctionalized α-cyclodextrin

Olivia Bistri, Pierre Sinaÿ and Matthieu Sollogoub*

Metathesis versatility has been exploited to reveal the cyclic directionality of cyclodextrins and to selectively synthesise a unique cyclodextrin bearing three pairs of orthogonal protecting groups on its primary rim.

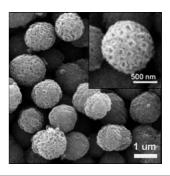


1115

Synthesis of hierarchical nanoporous F-doped TiO₂ spheres with visible light photocatalytic activity

Wingkei Ho, Jimmy C. Yu* and Shuncheng Lee

Hierarchical porous F-doped TiO₂ microspheres exhibiting high visible light photocatalytic activity have been fabricated by a one-step low-temperature hydrothermal approach without using any templates.



1118

The unexpected reactivity of Zeise's anion in strong basic medium discloses new substitution patterns at the platinum centre

Michele Benedetti, Francesco P. Fanizzi,* Luciana Maresca* and Giovanni Natile

Zeise's anion in strongly basic hydroxylated solvents undergoes unprecedented nucleophilic addition of OR (R = H, Me, Et) to the η^2 -ethene giving stable organometallic species the protonolysis of which offers a versatile route to cationic square planar $[PtCl(\eta^2-C_2H_4)(N-N)]^+$ complexes.

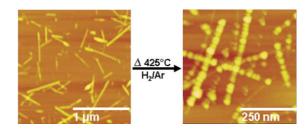
$$\begin{array}{c|c}
Cl & Pt & \\
Cl & Pt & \\
+RO & -Cl & \\
RO & Cl & \\
+RO & \\
-RO & -RO & -RO & -Cl & \\
Cl & Pt & \\
\end{array}$$

1121

From ribbons to nanodot arrays: nanopattern design through reductive annealing

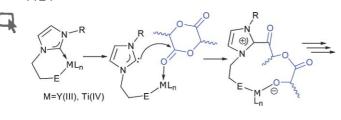
Palaniappan Arumugam, Samuel S. Shinozaki, Ruomiao Wang, Guangzhao Mao and Stephanie L. Brock*

1-D arrays of nickel arsenide nanoparticles can be generated by reduction of nickel arsenate nanoscrolls. This methodology may be suitable for generation of periodic and aperiodic patterns of nanoparticles.



COMMUNICATIONS

1124



Bifunctional yttrium(III) and titanium(IV) NHC catalysts for lactide polymerisation

Dipti Patel, Stephen T. Liddle, Shaheed A. Mungur, Mark Rodden, Alexander J. Blake and Polly L. Arnold*

Lewis acidic Y(III) and Ti(IV) derivatives of anionic, metal-tethered carbenes apparently act as bifunctional catalysts for the polymerisation of D,L-lactide, using both Lewis acid and base functionalities to initiate ring opening; the alcohol- and amino-functionalised carbene ligands provide models for the first insertion step, and display metal-free polymerisation catalysis to generate polylactic acid.

1127

Unusual entry to the novel 8-halo-N1-ribosyl hypoxanthine system by degradation of a cyclic adenosine-5'-diphosphate ribose analogue

Christelle Moreau, Timothy J. Woodman and Barry V. L. Potter*

Cyclic 8-bromo-inosine-5'-diphosphate ribose (8-Br-N1-cIDPR) was cleanly degraded to give 8-bromo-N1-ribosyl hypoxanthine 5'-monophosphate (8-Br-N1-IMP), a novel class of mononucleotide, as the sole product.

1130



$$\left[\begin{array}{c} Rh - \\ Rh - \\$$

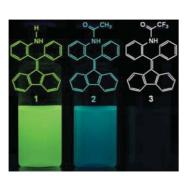
Variation in crystallization conditions allows the isolation of trimeric as well as dimeric and monomeric forms of [(alkyl isocyanide)₄Rh^I]⁺

Ngon T. Tran, Jay R. Stork, David Pham, Marilyn M. Olmstead, James C. Fettinger and Alan L. Balch*

A trimeric form of [(RCN)₄Rh^I]⁺ has been isolated for the first time along with crystals containing dimeric and monomeric versions of the cation.

1133





Tunable aggregation-induced emission of diphenyldibenzofulvenes

Hui Tong, Yongqiang Dong, Matthias Häußler, Jacky W. Y. Lam, Herman H.-Y. Sung, Ian D. Williams, Jingzhi Sun and Ben Zhong Tang*

Aggregation-induced emission of fulvene is tunable by molecular engineering and morphological variation: thus 1 and 2 can be induced to emit by aggregation in aqueous media, but 3 cannot; and crystalline aggregates emit stronger, bluer lights than their amorphous counterparts.

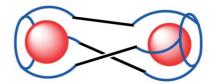
COMMUNICATIONS

1136

Tripodal oxazoline-based homochiral coordination cages with internal binding sites

Jeongryul Kim, Dowook Ryu, Yoshihisa Sei, Kentaro Yamaguchi and Kyo Han Ahn*

Homochiral coordination cages that provide two internal binding sites have been constructed for the first time by Pd(II)mediated self-assembly of chiral tripodal oxazolines containing pyridine pendant groups.

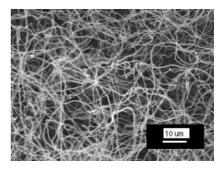


1139

Facile catalytic growth of cyanoacrylate nanofibers

Pratik J. Mankidy, Ramakrishnan Rajagopalan and Henry C. Foley*

Novel, facile and template-less catalytic growth of poly(ethyl 2-cyanoacrylate) nanofibers by vapour phase polymerization.



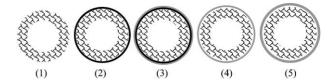
1142



Thin and defect-free Pd-based composite membrane without any interlayer and substrate penetration by a combined organic and inorganic process

Jianhua Tong,* Lingling Su, Kenji Haraya and Hiroyuki Suda

(1) substrate, (2) polymer layer + substrate, (3) Pd layer + polymer layer + substrate, (4) Pd layer + small interstice + substrate, and (5) defect-free Pd layer + small interstice + substrate.



AUTHOR INDEX

Abu-Youssef, Morsy A. M., 1082 Ahn, Kyo Han, 1136 Aime, Silvio, 1064 Armstrong, Jennifer A., 1094 Arnold, Polly L., 1124 Arumugam, Palaniappan, 1121 Balch, Alan L., 1130 Benedetti, Michele, 1118 Bistri, Olivia, 1112 Blake, Alexander J., 1124 Botta, Mauro, 1064 Brock, Stephanie L., 1121 Buchanan, J. Grant, 1106 Buttner, Mark J., 1079 Chaabane, Linda, 1064 Coleman, Anthony W., 1076 Davies, E. Stephen, 1103 Diggle, Richard A., 1106 Dong, Yongqiang, 1133 Dupont, Nathalie, 1076 Elemento, Elisa M., 1064 Errey, James C., 1079 Fanizzi, Francesco P., 1118 Fettinger, James C., 1130 Field, Robert A., 1079 Foley, Henry C., 1139 Freel Meyers, Caren L., 1079 Fulton, David A., 1064 Hachisako, Hiroshi, 1073

Haraya, Kenji, 1142 Häußler, Matthias, 1133 Ho, Wingkei, 1115 Hwang, Seok-Ho, 1091 Hyde, Jason R., 1103 Imai, Yoshitane, 1070 Jakimowicz, Piotr, 1079 Jarrosson, Thibaut, 1085 Katz, Eugenii, 1109 Kim, Jeongryul, 1136 Kuroda, Reiko, 1070 Lam, Jacky W. Y., 1133 Langer, Vratislav, 1082 Lawson, David M., 1079 Lazar, Adina N., 1076 Lee, Sang-gi, 1049 Lee, Shuncheng, 1115 Leitch, Alicea A., 1088 Li, Sinan, 1091 Liddle, Stephen T., 1124 Lioubashevski, Oleg, 1109 Mankidy, Pratik J., 1139 Mao, Guangzhao, 1121 Maresca, Luciana, 1118 Matsubara, Hiroshi, 1067 McKenzie, Courtney E., 1088 McMaster, Jonathan, 1103 Moorefield, Charles N., 1091 Moreau, Christelle, 1127 Mungur, Shaheed A., 1124

Murakami, Ryoichi, 1073 Murthy, Vinit S., 1097 Natile, Giovanni, 1118 Navaza, Alda, 1076 Newkome, George R., 1091 Oakley, Richard T., 1088 Öhrström, Lars, 1082 Olmstead, Marilyn M., 1130 Parker, David, 1064 Pascu, Sofia I., 1085 Patel, Dipti, 1124 Perra, Alessandro, 1103 Pham, David, 1130 Potter, Barry V. L., 1127 Rajagopalan, Ramakrishnan, 1139 Rana, Rohit K., 1097 Reed, Robert W., 1088 Richardson, John F., 1088 Ritsner, Ina, 1067 Rodden, Mark, 1124 Ruggiero, Giuseppe D., 1106 Ryu, Dowook, 1136 Sanders, Jeremy K. M., 1085 Sato, Tomohiro, 1070 Sawyer, Lenora D., 1088 Schiesser, Carl H., 1067 Schröder, Martin, 1103 Sei, Yoshihisa, 1136 Shinozaki, Samuel S., 1121

Shreiner, Carol D., 1091 Sinaÿ, Pierre, 1112 Sollogoub, Matthieu, 1112 Stork, Jay R., 1130 Su, Lingling, 1142 Suda, Hiroyuki, 1142 Sun, Jingzhi, 1133 Sung, Herman H.-Y., 1133 Takeshita, Masatoshi, 1070 Tang, Ben Zhong, 1133 Tello, Mónica, 1079 Tong, Hui, 1133 Tong, Jianhua, 1142 Tong, Lok H., 1085 Tran, Ngon T., 1130 Walsh, Christopher T., 1079 Wang, Pingshan, 1091 Wang, Qiang, 1103 Wang, Ruomiao, 1121 Weller, Mark T., 1094, 1100 Wiggin, Seth B., 1100 Wille, Uta, 1067 Williams, Ian D., 1133 Williams, Ian H., 1106 Willner, Itamar, 1109 Wong, Michael S., 1097 Woodman, Timothy J., 1127 Yamaguchi, Kentaro, 1136 Yu, Jie, 1097 Yu, Jimmy C., 1115

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