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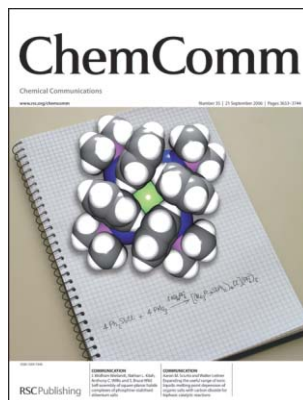
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ISSN 1359-7345 CODEN CHCOFS (35) 3653–3744 (2006)



Cover

See Paul D. Beer *et al.*, page 3676.
An unprecedented anion templated interweaving orthogonal assembling strategy is used to synthesize a chloride selective [2]catenane in very high yield.
Image reproduced by permission of Ka-Yuen Ng, Andrew R. Cowley and Paul D. Beer from *Chem. Commun.*, 2006, 3676.



Inside cover

See S. Bruce Wild *et al.*, page 3679.
Self-assembly of highly symmetrical square-planar halide complexes of phosphine-stabilised stibonium salts.
Image reproduced by permission of J. Wolfram Wielandt, Nathan L. Kilah, Anthony C. Willis and S. Bruce Wild from *Chem. Commun.*, 2006, 3679.

CHEMICAL SCIENCE

C65

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.

Chemical Science

September 2006/Volume 3/Issue 9

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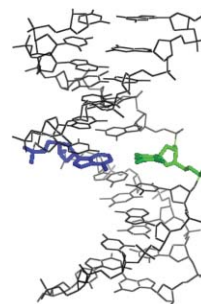
FEATURE ARTICLE

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The difluorotoluene debate—a decade later

Eric T. Kool* and Herman O. Sintim

Difluorotoluene, a nonpolar isostere for the DNA base thymine, is processed efficiently by polymerase enzymes. The observation led to the development of a steric-based hypothesis for replication. The evolution of the debate on this molecule is discussed.



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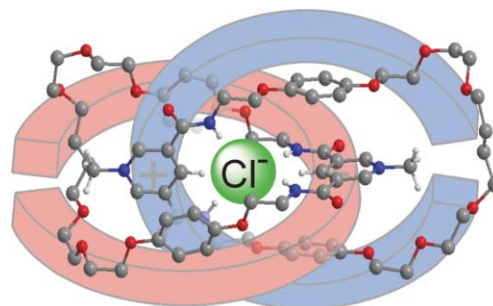
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Anion templated double cyclization assembly of a chloride selective [2]catenane

Ka-Yuen Ng, Andrew R. Cowley and Paul D. Beer*

The interweaving of two identical acyclic positively charged anion recognizing units around a chloride anion template leads to the formation of an orthogonal supramolecular ensemble which upon subsequent double ring cyclization gives a chloride selective [2]catenane in astonishingly high yield.

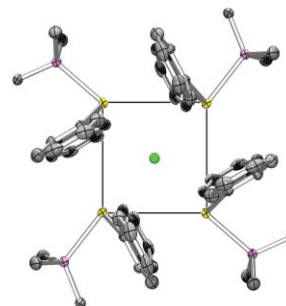


3679

Self-assembly of square-planar halide complexes of phosphine-stabilised stibonium salts

J. Wolfram Wielandt, Nathan L. Kilah, Anthony C. Willis and S. Bruce Wild*

Chloride and bromide ions direct the self-assembly of supramolecular square-planar halide complexes in which four trimethylphosphine-stabilised diphenylstibonium ions surround the central halide ion in discrete centrosymmetrical structures of C_{4h} symmetry.

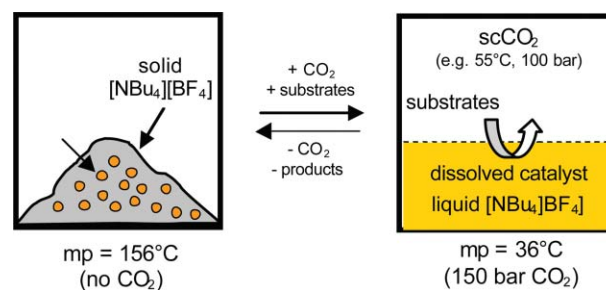


3681

Expanding the useful range of ionic liquids: melting point depression of organic salts with carbon dioxide for biphasic catalytic reactions

Aaron M. Scurto and Walter Leitner*

Large and previously unreported melting point depressions were observed for simple ammonium and phosphonium salts in the presence of compressed CO_2 , bringing them well within the range of typical ionic liquids.

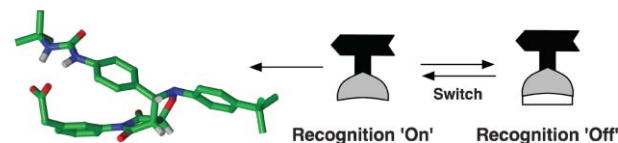


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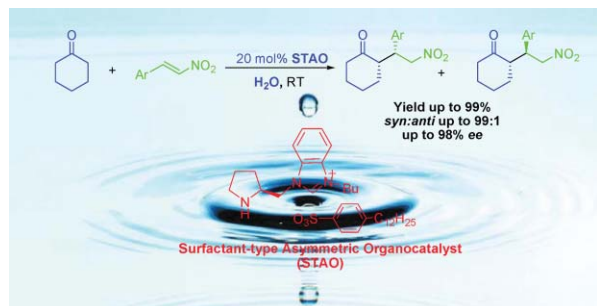
Controlling a recognition-mediated reaction using a pH switch

Simon M. Turega and Douglas Philp*

A pH change can be used to turn molecular recognition 'on' or 'off', facilitating controlled diastereoselective synthesis of a target cycloadduct.



3687

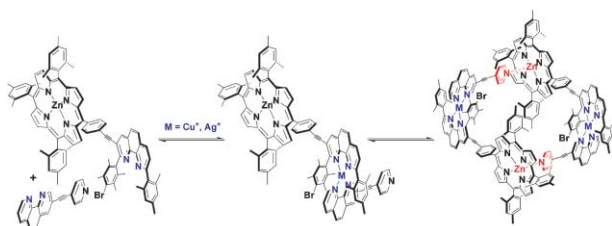


Surfactant-type asymmetric organocatalyst: organocatalytic asymmetric Michael addition to nitrostyrenes in water

Sanzhong Luo,* Xueling Mi, Song Liu, Hui Xu and Jin-Pei Cheng*

Highly efficient asymmetric organocatalysts in water have been realized by appending the anionic surfactant with a chiral catalytic counterion.

3690

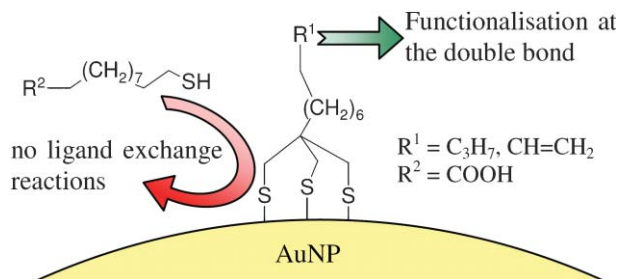


Self-assembly of a bis-porphyrinic supramolecular rectangle using two orthogonal binding strategies

Ravuri S. K. Kishore, Venkateswarlu Kalsani and Michael Schmittel*

A bis-porphyrinic rectangle is created *via* a double self-assembly algorithm using two orthogonal coordination themes: (i) a heteroleptic Cu(I) or Ag(I) bisphenanthroline aggregation followed by (ii) a coordinative dimerization using the pyridine–zinc porphyrin motif.

3693

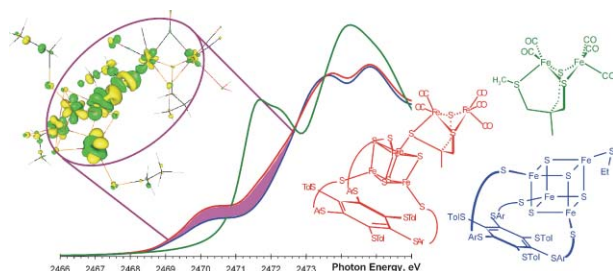


Reliable stabilization and functionalization of nanoparticles through tridentate thiolate ligands

Klaus Wojczykowski, Daniel Meißner, Peter Jutzi,* Inga Ennen, Andreas Hütten, Marc Fricke and Dirk Volkmer

Novel amphiphilic trithiolates are introduced as excellent ligands for gold nanoparticles. They require a comparatively small area per tripod-ligand, are stable towards ligand exchange reactions and easily functionalized at the terminal double bond.

3696



On the electronic structure of the hydrogenase H-cluster

David E. Schwab, Cedric Tard, Eric Brecht, John W. Peters, Christopher J. Pickett and Robert K. Szilagyi*

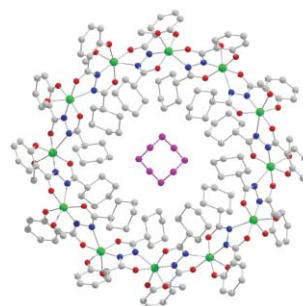
From XAS and DFT, the hydrogenase H-cluster is best described as an electronically inseparable 6Fe-cluster due to extensive delocalization of orbitals of iron centres, sulfide and the non-innocent dithiolate ligands.

3699

Encapsulation of a guest molecule in a strained form: an extended 36-membered dodecanuclear manganese metallamacrocycle that accommodates a cyclooctane in the S_4 symmetry conformation

Rohith P. John, Jaejoon Park, Dohyun Moon, Kyungjin Lee and Myoung Soo Lah*

A manganese-based metallamacrocycle with a hydrophobic cavity was prepared and its ability to accommodate strained molecules was studied by incorporating small hydrocarbons that could match the cavity symmetry.

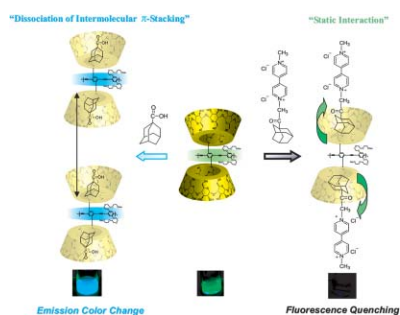


3702

Cyclodextrin-grafted poly(phenylene ethynylene) with chemically-responsive properties

Tomoki Ogoshi, Yoshinori Takashima, Hiroyasu Yamaguchi and Akira Harada*

Water-soluble poly(phenylene ethynylene) carrying β -cyclodextrin showed fluorescence color change or quenching depending on the kinds of guest.

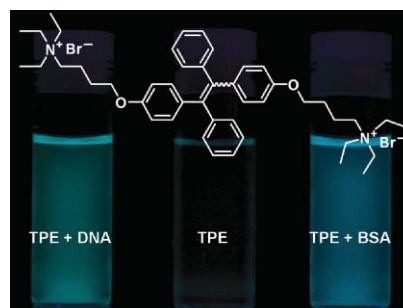


3705

Fluorescent “light-up” bioprobes based on tetraphenylethylene derivatives with aggregation-induced emission characteristics

Hui Tong, Yuning Hong, Yongqiang Dong, Matthias Häußler, Jacky W. Y. Lam, Zhen Li, Zufeng Guo, Zhihong Guo and Ben Zhong Tang*

Fluorescence of non-emissive 1,2-bis{4-[4-(*N,N,N*-triethylammonium)butoxy]phenyl}-1,2-diphenylethene dibromide (TPE) is turned “on” by the addition of DNA or BSA into its aqueous phosphate buffer solution.

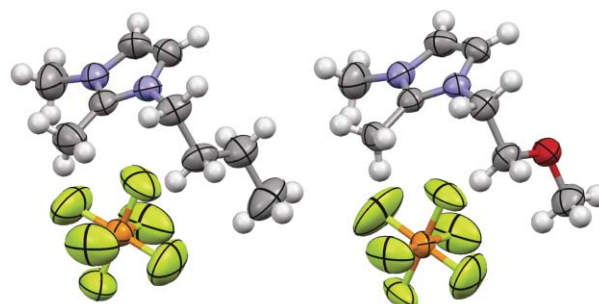


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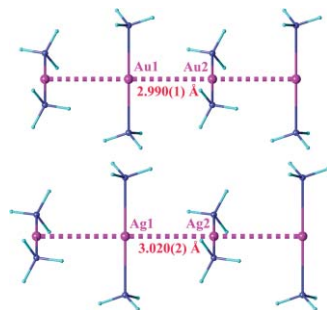
Alkyl vs. alkoxy chains on ionic liquid cations

Wesley A. Henderson, Victor G. Young, Jr., Douglas M. Fox, Hugh C. De Long and Paul C. Trulove*

Replacing a methylene group with an ether oxygen on a typical ionic liquid imidazolium cation leads to significant changes in the salt ion crystal packing and thermal properties.



3711

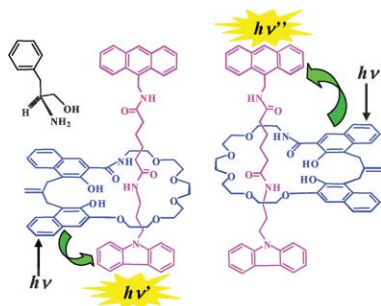


Ligand-unsupported Au(I) chains with short Au(I)⋯Au(I) contacts

Shao-Liang Zheng,* Cara L. Nygren, Marc Messerschmidt and Philip Coppens*

New structures of ligand-unsupported Au(I) chains with short Au⋯Au contacts allow unbiased comparison of Ag⋯Ag and Au⋯Au metallophilic bonding. The latter distances are shorter, in contrast with earlier studies comparing structurally non-identical complexes.

3714

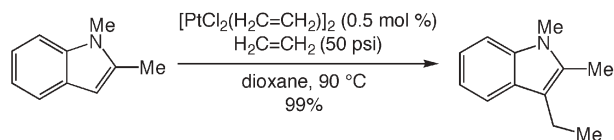


Chiral sensing for amino acid derivative based on a [2]rotaxane composed of an asymmetric rotor and an asymmetric axle

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

A racemic [2]rotaxane was able to recognize the chirality of an amino acid derivative, and showed a fluorescence response based on the variation of energy transfer from the excited naphthyl group of the rotor as donor to the end group of the axle as acceptor when the rotaxane formed a diastereomer with phenylalaninol.

3717

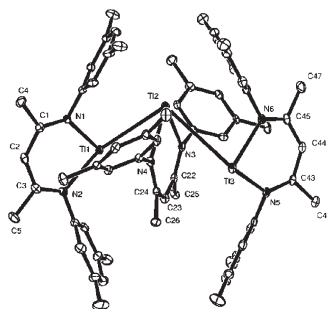


Platinum(II)-catalyzed intermolecular hydroarylation of unactivated alkenes with indoles

Zhibin Zhang, Xiang Wang and Ross A. Widenhoefer*

Ethylene, α -olefins, and vinyl arenes undergo platinum-catalyzed hydroarylation with substituted indoles in moderate to good yield.

3720



Aggregation behaviour of thallium(I) β -diketiminates

Michael S. Hill,* Ruti Pongtavornpinyo and Peter B. Hitchcock

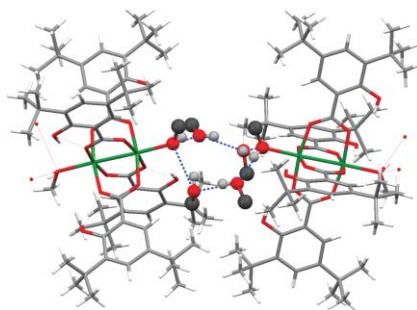
Modulation of the steric requirements of a number of *N*-aryl β -diketimate ligands results in the isolation of a variety of Tl(I) compounds with different stabilities and nuclearities.

3723

The self-assembly between C_2 -symmetric (methanol)₆ or S_6 -symmetric (ethanol)₆ cyclohexamers and paddle-wheel dinuclear copper units leads to unique 1D polymer chains

Laurent Benisvy, Ilpo Mutikainen, Manuel Quesada, Urho Turpeinen, Patrick Gamez and Jan Reedijk*

The first crystallographic evidences of the theoretically suggested C_2 -symmetric cyclohexameric form of liquid methanol and the S_6 -symmetric cyclohexameric form of liquid ethanol are reported, trapped inside a hydrophilic pocket shielded by *tert*-butyl groups.

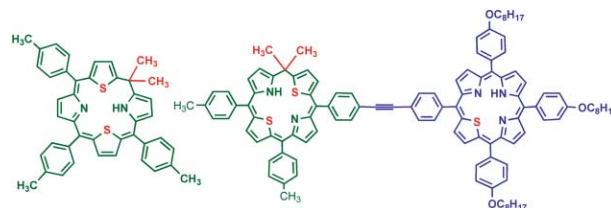


3726

Synthesis of functionalized thia analogues of phlorins and covalently linked phlorin–porphyrin dyads

Iti Gupta, Roland Fröhlich and M. Ravikanth*

The 21,23-dithia and 21-thia analogues of phlorins and mono-functionalized thiaphlorins were synthesized using easily available precursors and the mono-functionalized thiaphlorins were used further to synthesize the first examples of three covalently linked thiaphlorin–porphyrin dyads.

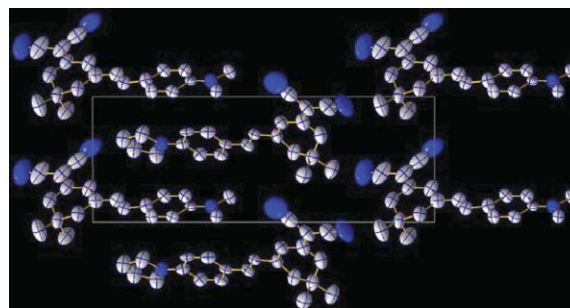


3729

Nonlinear optical co-crystal of analogous polyene chromophores with tailored physical properties

Seong-Ji Kwon, O-Pil Kwon,* Mojca Jazbinsek, Volker Gramlich and Peter Günter

A new organic nonlinear optical co-crystal based on analogous configurationally locked polyene chromophores with noncentrosymmetric packing exhibits a large macroscopic second-order nonlinearity with tailored physical properties.

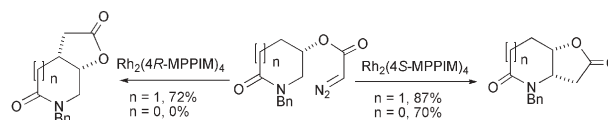


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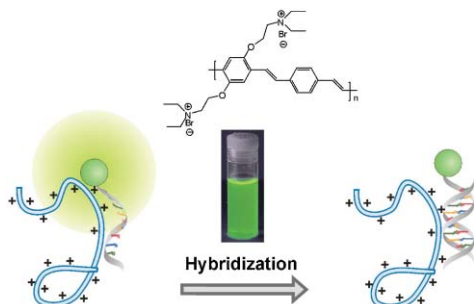
Regio- and diastereocontrolled C–H insertion of chiral γ - and δ -lactam diazoacetates. Application to the asymmetric synthesis of (8*S*,8*aS*)-8-hydroxyindolizidine

Gao-jun Fan, Zhongyi Wang and Andrew G. H. Wee*

Synthetically useful bicyclic lactam lactones are readily accessible *via* the C–H insertion reaction of γ - and δ -lactam diazoacetates catalyzed by $Rh_2(4R\text{- or }4S\text{-MPPIM})_4$.



3735

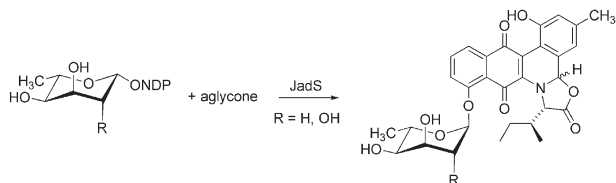


A novel cationic conjugated polymer for homogeneous fluorescence-based DNA detection

Hui Peng, Christian Soeller and Jadranka Travas-Sejdic*

A novel water-soluble cationic and photoluminescent conjugated polymer, poly({2,5-bis[3-(*N,N*-diethylamino)-1-oxapropyl]-*para*-phenylenevinylene}-*alt-pa*-phenylenevinylene) dibromide, was synthesized and used to develop a simple label-free DNA detection assay based on fluorescence energy transfer.

3738



Substrate flexibility of a 2,6-dideoxyglycosyltransferase

David L. Jakeman,* Charles N. Borissow, Cathy L. Graham, Shannon C. Timmons, Taryn R. Reid and Ray T. Syvitski

The first 2,6-dideoxysugar-*O*-glycosyltransferase with substrate flexibility at the 2 position.

ADDITION AND CORRECTION

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Tom Hotchkiss, Holger B. Kramer, Katie J. Doores, David P. Gamblin, Neil J. Oldham and Benjamin G. Davis

Ligand amplification in a dynamic combinatorial glycopeptide library

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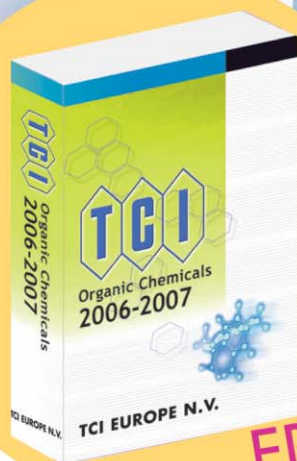
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