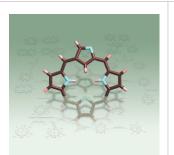
Chem Comm

CHEMICAL COMMUNICATIONS • www.rsc.org/chemcomm



Cover

A confused porphyrin, and in the background, routes to the formation of new porphyrinoids.



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contents

FEATURE ARTICLE



Confusion, inversion, and creation—a new spring from porphyrin chemistry

Hiroyuki Furuta,* Hiromitsu Maeda and Atsuhiro Osuka*



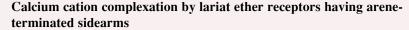




This article mainly deals with the recent serendipity of novel porphyrin analogs such as N-confused porphyrin; the important aspect of dynamic flipping (*inversion*), induced either by *confusion* or *expansion* of the macrocyclic core, that leads to the generation of new porphyrinoids, is emphasized.

COMMUNICATIONS

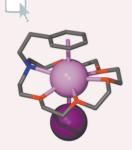




Jiaxin Hu, Leonard J. Barbour, Riccardo Ferdani and George W. Gokel*

The first reported calcium azalariat complex has an arene terminated sidearm that behaves differently from an otherwise identical indole-sidearmed complex; twin phenolic sidearms on a diaza-18-crown-6 lead to an infinite, H-bonded network.



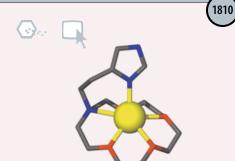


(1808)

$\sigma\text{-}Donor,\,\pi\text{-}donor,$ and anion competition in $\pi\text{-}complexation$ of alkali metal cations

Jiaxin Hu, Leonard J. Barbour and George W. Gokel*

Removal of or replacement of one of two phenylethyl sidearms on azalariats leads to clear evidence for cation– π interactions with the remaining sidearm.



Sodium cation complexation behavior of the heteroaromatic sidechains of histidine and tryptophan

Jiaxin Hu, Leonard J. Barbour, Riccardo Ferdani and George W. Gokel*

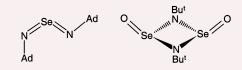
Three of the four essential amino acids that have aromatic sidechains exhibit cation– π interactions with Na⁺ or K⁺; histidine does not and is shown here to be a sigma donor.

(1812)

A monomeric selenium(IV) diimide and a dimeric seleninylamine

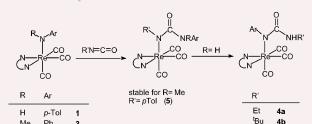
Tiina Maaninen, Risto Laitinen* and Tristram Chivers*

The first X-ray structures of a selenium(IV) diimide and a seleninylamine are described. Di-1-adamantyl selenium diimide is monomeric in the solid state, whereas *tert*-butylseleninylamine is a dimer.



(1814

Different sites of insertion in the reaction of isocyanates with $[Re(N(R)Ar)(CO)_3(bipy)]$ (R = H or Me): N-H vs. Re-N

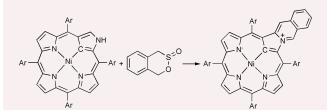


The reactions of isocyanates with $[Re(N(R)Ar)(CO)_3(bipy)]$ complexes lead to R'NCO insertion into the Re–N bond (for R = Me) or the N–H bond (R = H).

Eva Hevia, Julio Pérez,* Víctor Riera and Daniel Miguel

Diels-Alder reactions of nickel(II) N-confused porphyrins as dienophiles

Ziwei Xiao, Brian O. Patrick and David Dolphin*



Diels—Alder reactions of nickel(II) N-confused tetraarylporphyrins as dienophiles with o-benzoquinodimethane yield nickel(II) N-confused isoquinoporphyrins.

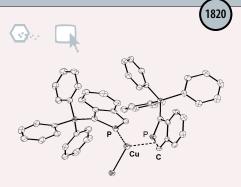
1818

1816

Perfluoroalkylation of simple inorganic molecules: A one step route to novel perfluoroalkylated compounds

Rajendra P. Singh and Jean'ne M. Shreeve*

Perfluoroalkylation of simple inorganic molecules: A one step route to novel perfluoroalkylated compounds.



Unusual properties of the first copper complex containing a $\pi(\eta^2)$ -coordinated phosphorus—carbon double bond moiety

Dietrich Gudat,* Martin Nieger, Katja Schmitz and Laslo Szarvas

The ^{31}P NMR shifts for the $\eta^2(P=C)$ and $\eta^1(P)$ -coordinated benzophospholide ligands in the title complex are surprisingly almost degenerate. Analysis of this effect suggests a novel interpretation of ^{31}P coordination shifts in π -complexes of phosphorus containing multiple bonds.

1822

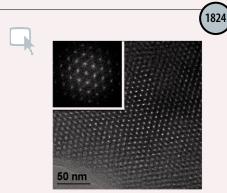
1826

Solution reduction synthesis of surface stabilized silicon nanoparticles

Richard K. Baldwin, Katherine A. Pettigrew, Eva Ratai, Matthew P. Augustine and Susan M. Kauzlarich*



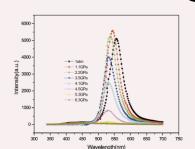
This manuscript presents a surprisingly simple route to chloride terminated silicon nanoparticles that can be further functionalized with passivating alkoxide termination groups.



Fast preparation of highly ordered nonsiliceous mesoporous materials *via* mixed inorganic precursors

Bozhi Tian, Haifeng Yang, Xiaoying Liu, Songhai Xie, Chengzhong Yu, Jie Fan, Bo Tu and Dongyuan Zhao*

Employing metal alkoxide as the main inorganic precursor and anhydrous metal chloride as the pH 'adjuster' and hydrolysis-condensation 'controller', very fast preparation of ordered nonsiliceous mesoporous materials has been demonstrated.



Mechanism of aqueous ultrasonic reaction: controlled synthesis, luminescence properties of amorphous cluster and nanocrystalline CdSe

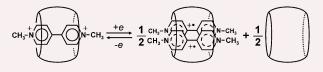
Jian-Ping Ge, Ya-Dong Li* and Guo-Qiang Yang

A novel sonochemical method was found to prepare amorphous CdSe cluster and hexagonal nanocrystalline CdSe in aqueous solution. An interfacial mechanism was confirmed and the exploration for luminescence properties of the as-prepared CdSe nanoparticles revealed its wide application in many fields.



Control of the stoichiometry in host-guest complexation by redox chemistry of guests: Inclusion of methylviologen in cucurbit[8]uril

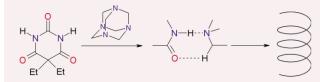
Woo Sung Jeon, Hee-Joon Kim, Chongmok Lee and Kimoon Kim*



The binding stoichiometry of a host–guest complex can be effectively controlled by the redox chemistry of the guest: a 1:1 inclusion complex of methylviologen dication (MV $^{2+}$) in cucurbit[8]uril (CB[8]) converts completely and reversibly to a 2:1 inclusion complex of cation radical (MV $^{+}$ ·) in CB[8] upon the reduction of the guest.



Supramolecular synthons based on N–H···N and C–H···O hydrogen bonds. Crystal engineering of a helical structure with 5,5-diethylbarbituric acid

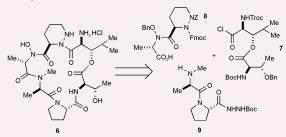


Peddy Vishweshwar, Ram Thaimattam, Mariusz Jaskólski* and Gautam R. Desiraju*

A new strong/weak synthon, N–H···N/C–H···O, is reported and shown to arise from the molecular precursor, barbital. By using urotropine as the co-crystallising agent a helix structure is obtained.

(1832)

Synthesis of an L-proline modified mimetic of the A83586C antitumour cyclodepsipeptide



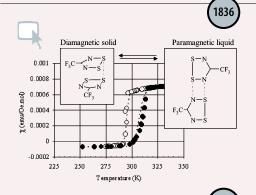
Karl J. Hale* and Linos Lazarides

A mimetic **6** of the A83586C cyclodepsipeptide has been synthesised by a three-segment coupling protocol involving dipeptides **9**, **8** and **7**.

Coordination polymers of gold(I) with dithiolate and diphosphine ligands

William J. Hunks, Michael C. Jennings and Richard J. Puddephatt*

The first hybrid organic—inorganic coordination polymers with linear gold(I) centres in the backbone are easily formed on crystallization from the macrocyclic isomers.



Thermal hysteresis in dithiadiazolyl and dithiazolyl radicals induced by supercooling of paramagnetic liquids close to room temperature: a study of $F_3CCNSSN$ and an interpretation of the behaviour of $F_3CCSNSCCF_3$

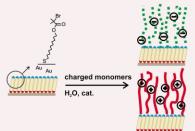
Hongbin Du, Robert C. Haddon, Ingo Krossing, Jack Passmore,* Jeremy M. Rawson* and Melbourne J. Schriver

The trifluoromethyl-substituted dithiadiazolyl and dithiazolyl radicals, $F_3CCNSSN$ (1) and $F_3CCSNSCCF_3$ (2) associate through $\pi^*-\pi^*$ covalent and electrostatic $S^{\delta^+}...N^{\delta^-}$ interactions in the solid state, but melt with a dramatic volume increase to generate paramagnetic liquids.

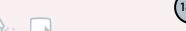
Controlled growth of triblock polyelectrolyte brushes

Vicky L. Osborne, Darren M. Jones and Wilhelm T. S. Huck*

A significant breakthrough in the synthesis of polyelectrolyte brushes of controlled thickness and density is reported, demonstrated by the synthesis of triblock copolymer brushes composed of cationic, neutral, and anionic segments.



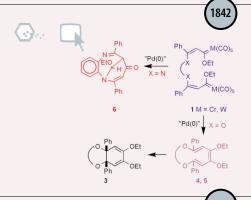




Isocyanate and carbodiimide synthesis by nitrene-group-transfer from a nickel(II) imido complex

Daniel J. Mindiola and Gregory L. Hillhouse*

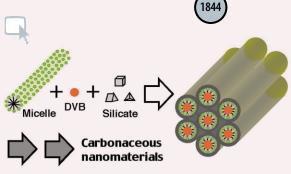
Carbon monoxide and benzyl isocyanide add across the Ni=NR bond of the imido complex (dtbpe)Ni=N(2,6- i Pr₂C₆H₃) to give nickel isocyanate and carbodiimide complexes which react further with CO to liberate O=C=N(2,6- i Pr₂C₆H₃) and PhCH₂N=C=N(2,6- i Pr₂C₆H₃) with formation of (dtbpe)Ni(CO)₂.



New Pd-catalyzed tandem cyclization processes on group 6 bis-carbene complexes

Miguel A. Sierra,* Juan C. del Amo, María J. Mancheño, Mar Gómez-Gallego and M. Rosario Torres

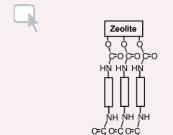
The reaction of bis-carbene complexes **1a,b** derived from catechol and Pd-catalysts gave product **3** derived from an intramolecular coupling–electrocyclization process, while nucleophilic attack–*NH*-carbene insertion product **6** was obtained from complexes **1c,d** derived from 1,2-diaminobenzene.



Novel synthesis of polymer and carbonaceous nanomaterials *via* a micelle/silicate nanostructured precursor

Isamu Moriguchi,* Yasuhiro Koga, Ryosuke Matsukura, Yasutake Teraoka and Masaya Kodama

Mesoporous carbonaceous materials have been synthesized by a new method composed of *in situ* polymerization of divinylbenzene (DVB) in the hydrophobic phase of a micelle/silicate nanocomposite and a carbonization process.



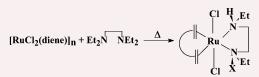
Diisocyanates as novel molecular binders for monolayer assembly of zeolite crystals on glass

Yu Sung Chun, Kwang Ha, Yun-Jo Lee, Jin Seok Lee, Hyun Sung Kim, Yong Soo Park and Kyung Byung Yoon*

Isocyanate groups readily form urethane linkages with surface hydroxy groups on glass and zeolites and this phenomenon was utilized in the assembly of monolayers of zeolite microcrystals on glass by employing diisocyanates as novel molecular binders.

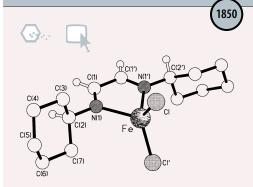
1848

Intramolecular dealkylation of chelating diamines with Ru(II) complexes



M. Esther Morilla, Galanda Morfes, M. Carmen Nicasio, Tomás R. Belderrain, M. Mar Díaz-Requejo, Claudia Graiff, Antonio Tiripicchio, Roberto Sánchez-Delgado* and Pedro J. Pérez*

Ruthenium(II) centres mediate the intramolecular dealkylation of tertiary chelating dimines.



Four-coordinate iron complexes bearing α -diimine ligands: efficient catalysts for Atom Transfer Radical Polymerisation (ATRP)

Vernon C. Gibson,* Rachel K. O'Reilly, Warren Reed, Duncan F. Wass, Andrew J. P. White and David J. Williams

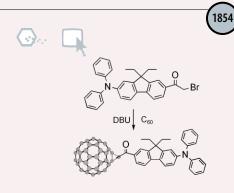
Four-coordinate iron(II) complexes bearing α -diimine ligands with alkyl substituents are shown to be efficient catalysts for the well-controlled atom transfer radical polymerisation of styrene; catalysts containing aryldiimine ligands support competitive β -hydrogen chain transfer processes.

Determine quantita $J = 7.4 \pm 0.1 \text{Hz}$ N_1 N_2 N_3

Determining hydrogen-bond strengths in the solid state by NMR: the quantitative measurement of homonuclear J couplings

S. P. Brown, M. Pérez-Torralba, D. Sanz, R. M. Claramunt and L. Emsley*

Hydrogen-bonding strengths in solids are quantified through the accurate determination ($\pm 0.2~{\rm Hz}$) of hydrogen-bond mediated J couplings using a straightforward 2D spin-echo magic-angle spinning approach.



Synthesis of C_{60} -diphenylaminofluorene dyad with large 2PA cross-sections and efficient intramolecular two-photon energy transfer

Long Y. Chiang,* Prashant A. Padmawar, Taizoon Canteenwala, Loon-Seng Tan,* Guang S. He, Ramamurthi Kannan, Richard Vaia, Tzu-Chau Lin, Qingdong Zheng and Paras N. Prasad

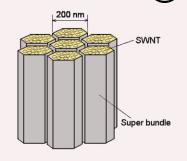
The first, highly two-photon active C_{60} derivative comprised of a A-sp³-D conjugate structure was synthesized showing effective two-photon absorption cross-sections ($\sigma_2' = 196 \times 10^{-48} \text{ cm}^4 \text{ sec}^{-1} \text{ molecule}^{-1}$) in the nanosecond regime.



Lewis acid-promoted Baylis–Hillman-type reaction of α,β -unsaturated ethyl thioester with aldehydes without the use of a Lewis base

Wei Pei, Han-Xun Wei and Guigen Li*

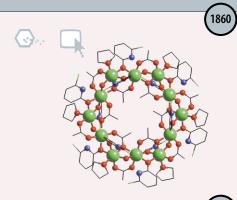
The Baylis–Hillman-type reaction between α,β -ethyl thioacrylate and aldehydes was achieved by using diethylaluminium iodide as the promoter without the direct use of any Lewis bases.



Long super-bundles of single-walled carbon nanotubes

Hongwei Zhu,* Bin Jiang, Cailu Xu and Dehai Wu

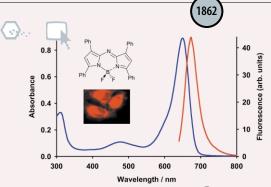
A novel densely bundled structure (200 nm-thick super bundles) consisting of long single-walled carbon nanotubes showing a novel polygonization and densely aligned arrangement is reported.



Synthetic and magnetic studies of a dodecanuclear cobalt wheel

Euan K. Brechin, Olivier Cador, Andrea Caneschi,* Cyril Cadiou, Steven G. Harris, Simon Parsons, Michele Vonci and Richard E. P. Winpenny*

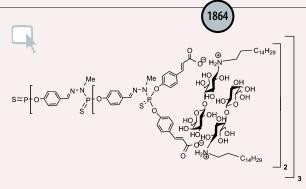
The cyclic $\{Co_{12}\}$ cage shown has a highly anisotropic S=6 ground state.



Synthesis of BF₂ chelates of tetraarylazadipyrromethenes and evidence for their photodynamic therapeutic behaviour

John Killoran, Lorcan Allen, John F. Gallagher, William M. Gallagher and Donal F. O'Shea*

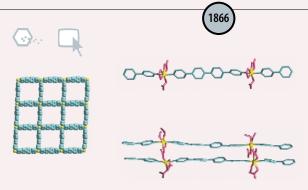
A new, non-porphyrin, class of therapeutic window photosensitiser is described with potential as photodynamic therapeutic agents.



Phosphorus-containing dendrimers bearing galactosylceramide analogs: Self-assembly properties

Muriel Blanzat, Cédric-Olivier Turrin, Emile Perez, Isabelle Rico-Lattes,* Anne-Marie Caminade and Jean-Pierre Majoral*

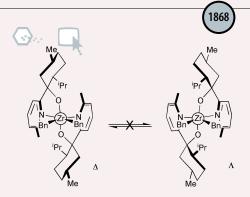
Proton transfer between carboxylic acid capped phosphorus dendrimers and $\text{gal}\beta_1\text{cer}$ analogs leads to catanionic dendrimers. These versatile amphiphilic supra-assemblies spontaneously form vesicles in water.



A 'three-in-one' crystal of coordination networks

Kumar Biradha and Makoto Fujita*

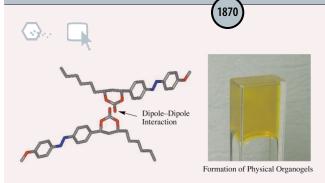
Square grid, linear chain and double linear chain coordination polymers crystallized together in one crystal consistently in the presence of three different solvents.



Efficient predetermination of chirality-at-zirconium

Ian J. Munslow, Adam J. Clarke, Robert J. Deeth,* Ian Westmoreland and Peter Scott*

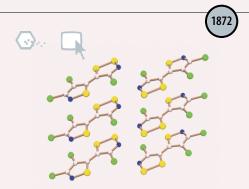
Metal centered helicity in a stereochemically labile zirconium dialkyl complex is controlled at equilibrium by exploiting strongly the expressed chirality of a new and readily available pyridine alcohol ligand.



A rodlike organogelator: fibrous aggregation of azobenzene derivatives with a *syn*-chiral carbonate moiety

Jun-ichi Mamiya, Kiyoshi Kanie, Tamejiro Hiyama, Tomiki Ikeda* and Takashi Kato*

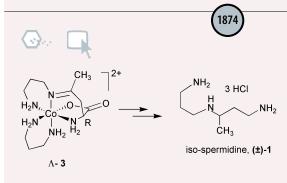
A rodlike azobenzene derivative containing a cyclic *syn*-carbonate moiety functions as a new type of organogelator; the dipole–dipole interactions of the chiral carbonate moieties drive the fibrous self-assembly of the azobenzene organogelator.



A π -stacked 1,2,3-dithiazolyl radical. Preparation and solid state characterization of (Cl₂C₃NS)(ClC₂NS₂)

Leanne Beer, A. Wallace Cordes, Robert C. Haddon, Mikhail E. Itkis, Richard T. Oakley,* Robert W. Reed and Craig M. Robertson

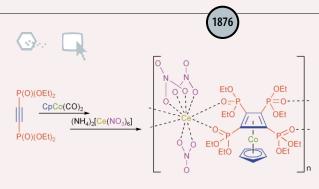
A 5-isothiazolo-1,2,3-dithiazolylium cation can be prepared in a one-step synthesis from glutaronitrile. Reduction affords the corresponding dithiazolyl radical, the structure of which consists of undimerized radical π -stacks, with $\sigma_{RT} = 2 \times 10^{-7} \ S \ cm^{-1}$.



Assembly of polyamines *via* amino acids from three components using cobalt(III) template methodology

Gilles Laval, William Clegg, Christopher G. Crane, Anders Hammershøi, Alan M. Sargeson and Bernard T. Golding*

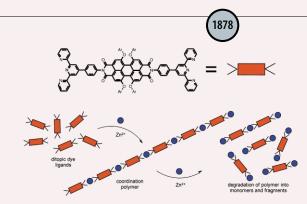
A versatile and efficient template synthesis has been developed to synthesise novel polyamines [$e.g.\ rac-N^3$ -(3-aminopropyl)butane-1,3-diamine, isospermidine 1] via amino acids [$e.g.\ (2R,4S/2S,4R)-N^4$ -(3-aminopropyl)-2,4-diaminopentanoic acid] using cobalt(III) to assemble the three precursor components in a biomimetic manner.



$(\eta^5\text{-Cyclopentadienyl})(\eta^4\text{-di-}$ and tetraphosphorylcyclobutadiene)cobalt(I): Synthesis, structure, and formation of 1-D coordination polymer

Shigeru Sasaki,* Yoshihiro Tanabe and Masaaki Yoshifuji*

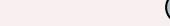
 $(\eta^5$ -Cyclopentadienyl) $(\eta^4$ -di- and tetraphosphorylcyclobutadiene)cobalt(I) complexes were synthesized by the reaction of phosphorylacetylenes with $CpCo(CO)_2$. The tetraphosphoryl derivative has proved to work as a bis-bidentate ligand affording a one-dimensional coordination polymer with Ce(III).



Photoluminescent supramolecular polymers: metal-ion directed polymerization of terpyridine-functionalized perylene bisimide dyes

Rainer Dobrawa and Frank Würthner*

Terpyridine ligands attached to a perylene bisimide chromophore can be complexed by Zn²⁺ to spontaneously form highly fluorescent dimers or coordination polymers which are characterized by ¹H NMR and fluorescence spectroscopy.



Bimolecular rate constants for diffusion in ionic liquids

1880

Andrew J. McLean,* Mark J. Muldoon, Charles M. Gordon* and Ian R. Dunkin

The temperature dependence of the bimolecular rate constants for a diffusion controlled reaction involving neutral reactants have been directly determined in five room temperature ionic liquids.



Synthesis of CoFe₂O₄ nanowire in carbon nanotubes. A new use of the confinement effect

C. Pham-Huu,* N. Keller, C. Estournès, G. Ehret and M. J. Ledoux

Cobalt ferrite nanowires with an average diameter of 50 nm and lengths up to several micrometers were synthesized inside carbon nanotubes under mild reaction conditions using the confinement effect provided by the carbon tubular template.



Silylstannation of terminal alkynes using a recyclable palladium(0) catalyst immobilised in an ionic liquid

Ivan Hemeon and Robert D. Singer*

$$R-C \equiv CH \qquad \begin{array}{c} Bu_3SnSiMe_3 \\ Pd(PPh_3)_4 \\ \hline \\ [bmim]PF_6/Et_2O \\ 70^\circ C/reflux \end{array} \qquad \begin{array}{c} R \\ Bu_3Sn \\ SiMe_3 \end{array}$$

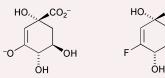
Silylstannanes can be regioselectively added across terminal alkynes in a quantitative fashion in the presence of a palladium(0) catalyst immobilised in the [bmim]PF₆ ionic liquid which can be recycled without loss of activity.



Vinyl fluoride as an isoelectronic replacement for an enolate anion: Inhibition of type II dehydroquinases

Martyn Frederickson, John R. Coggins and Chris Abell*

A potent inhibitor of type II dehydroquinases has been prepared using a vinyl fluoride as a molecular replacement for reactive enolate functionality.



Enolate mimic Enolate intermediate K_i 10 μM

3',4'-trans-Linked bicyclic nucleosides locked in S-type conformations

Helena Thomasen, Michael Meldgaard, Morten Freitag, Michael Petersen, Jesper Wengel and Poul Nielsen*

This communication presents a new synthetic concept in the construction of conformationally restricted oligonucleotide analogues. Two bicyclic nucleosides perfectly locked in S-type conformations are presented.

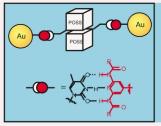


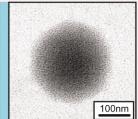
Inhibition and acceleration of deuterium exchange in amidefunctionalized monolayer-protected gold clusters

Cheryl Briggs, Tyler B. Norsten and Vincent M. Rotello*

Radially-dependent catalysis and inhibition of H/D exchange is observed with amide-functionalized monolayers on gold nanoparticles.





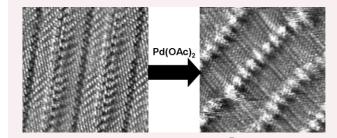


Self-assembly of gold nanoparticles through tandem hydrogen bonding and polyoligosilsequioxane (POSS)-POSS recognition processes

Joseph B. Carroll, Benjamin L. Frankamp and Vincent M. Rotello

Diaminopyridine-functionalized polyhedral oligomeric silsesquioxanes (**POSS-DAP**) self-assemble with complementary thymine-functionalized Au nanoparticles (**Thy-Au**) into well-defined spherical aggregates, providing highly structured nanocomposites.

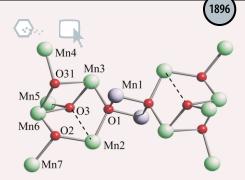




Submolecular visualisation of palladium acetate complexation with a bipyridine derivative at a graphite surface

Mohamed M. S. Abdel-Mottaleb, Norbert Schuurmans, Steven De Feyter,* Jan Van Esch,* B. L. Feringa and Frans C. De Schryver*

Self-assembly of a monolayer of a bipyridine derivative and its complexation with palladium acetate at a graphite/liquid surface is described; its stability in air is demonstrated.



Synthesis and studies of a tetradecanuclear manganese(II)/(III) cage

Guillem Aromí, Aidan Bell, Simon J. Teat, A. Gavin Whittaker and Richard E. P. Winpenny*

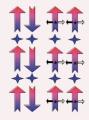
The first $\{Mn_{14}\}$ cage is reported, which has a core consisting of linked $\{Mn_3O_4\}$ cubanes.

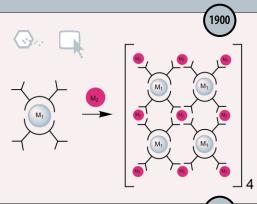


Non-centrosymmetric packing of 1-D coordination networks based on chirality

Abdelaziz Jouaiti, Mir Wais Hosseini* and Nathalie Kyritsakas

A C_2 chiral tecton possessing a monodentate and a tridentate coordination pole leads in the presence of $CoCl_2$ to the formation of a directional 1-D coordination network. The packing of the latter in parallel fashion generates a polar solid.





A sponge-like luminescent coordination framework *via* an *Aufbau* approach

Brett D. Chandler, Adrien P. Ĉoté, David T. Cramb, Josephine M. Hill and George K. H. Shimizu*

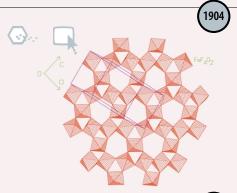
A mixed Eu/Ba coordination framework is generated *via* a stepwise assembly. The solid is luminescent with a flexible structure for sorbing guest molecules.



Encapsulation of diquats by resorcinarenes: a novel staggered anion-solvent mediated hydrogen bonded capsule

Heidi Mansikkamäki, Maija Nissinen and Kari Rissanen*

X-Ray structural studies of encapsulation of diquats by ethyl resorcinarene resulted in anion and/or solvent mediated capsules in which both staggered and eclipsed orientations of capsule forming hosts is observed



An organically templated iron sulfate with a distorted Kagome lattice exhibiting unusual magnetic properties

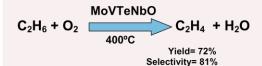
Geo Paul, Amitava Choudhury and C. N. R. Rao*

A layered iron sulfate of the composition $[H_3N(CH_2)_2NH_2(CH_2)_2NH_3][Fe^{II}_3F_6(SO_4)_2]$, possessing a distorted Kagome lattice, prepared hydrothermally, is found to exhibit magnetic hysteresis like a ferrimagnet besides the characteristics of a frustrated system, like those of a spin glass.

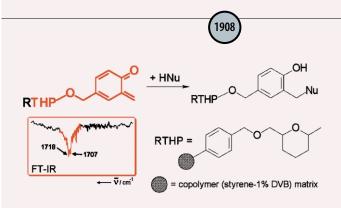


The selective oxidative dehydrogenation of ethane over hydrothermally synthesised MoVTeNb catalysts

J. M. López Nieto,* P. Botella, M. I. Vázquez and A. Dejoz



MoVTeNbO mixed oxide catalysts are active and selective in the oxidative dehydrogenation of ethane to ethene in the 350–400 $^{\circ}$ C temperature interval with a yield of ethene of about 75%.

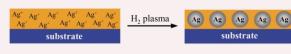


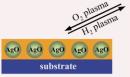
Synthesis, spectroscopic characterization and chemical reactions of stable *o*-QM on solid phase

Riccardo Zanaletti and Mauro Freccero*

A novel approach towards quinone methide stabilization has been achieved by anchoring the reactive *o*-QM intermediate on a solid phase. Supported *o*-QM maintains its reactivity with nucleophiles.







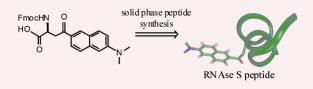
Reversible conversion of nanoparticles of metallic silver and silver oxide in ultrathin ${\rm TiO_2}$ films: a chemical transformation in nano-space

Junhui He, Izumi Ichinose, Shigenori Fujikawa, Toyoki Kunitake* and Aiko Nakao

Interconversion of silver and silver oxide nanoparticles was achieved by H₂ and O₂ plasma treatments in ultrathin TiO₂ films. This *in-situ* approach is useful for the preparation of nano-sized materials that are not readily accessible by other means.



Enantioselective synthesis and application of the highly fluorescent and environment-sensitive amino acid 6-(2-dimethylaminonaphthoyl) alanine (DANA)



Mark Nitz, Adam R. Mezo, Mayssam H. Ali and Barbara Imperiali*

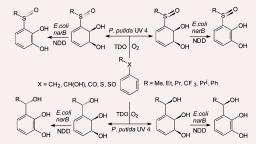
The amino acid DANA was prepared *via* enantioselective alkylation of glycine benzophenone imine. The spectroscopic properties of DANA were demonstrated by incorporation into the RNase S model system.



Tandem enzyme-catalysed oxidations of alkyl phenyl sulfides and alkyl benzenes: enantiocomplementary routes to chiral phenols

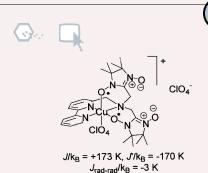
Derek R. Boyd,* Narain D. Sharma, Vera Ljubez, Breige E. Byrne, Steven D. Shepherd, Christopher C. R. Allen, Leonid A. Kulakov, Michael J. Larkin and Howard Dalton

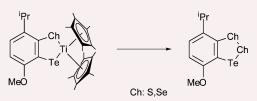
Sulfoxide *cis*-dihydrodiols and triols have been produced and converted to enantiopure catechols *via* enzyme-catalysed and chemoenzymatic methods.



Christophe Stroh and Raymond Ziessel*

An unusually high ferromagnetic and a strong antiferromagnetic copper(II)-nitroxide exchange interaction has been obtained by coordinating a ligand bearing flexible nitronyl nitroxide radicals.





Novel multi-chalcogen ring systems with three different chalcogen atoms: synthesis, structure and redox property of five-membered trichalcogenaheterocycles

Satoshi Ogawa,* Satoko Yoshimura, Noriyoshi Nagahora, Yasushi Kawai, Yuji Mikata and Ryu Sato*

The molecular structure of novel five-membered trichalcogenaheterocycles with sulfur, selenium and tellurium, has been determined by crystallographic studies.

Syntheses and structures of structurally diverse potassium β -diketiminates derived from the ligand [$\{N(SiMe_3)C(Ph)\}_2CH\}^-$

Peter B. Hitchcock, Michael F. Lappert,* Diang-Sheng Liu and Rafaël Sablong

A new family of potassium β -diketiminates has been synthesised and crystallographically characterised, including **1–4**.

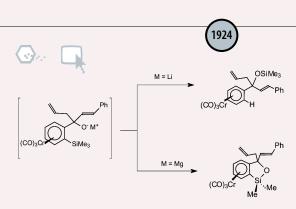
1922

β-Replacement reaction of serine-O-carbonate derivatives with thiols catalyzed by a pyridoxal model having an ionophore side-chain

MeOCOO X NH₂ X (5 mol%), RSH, MeCN NH₂ X = OBn, NHBn and amino esters

Kazuyuki Miyashita, Hidenobu Murafuji, Hiroshi Iwaki, Eito Yoshioka and Takeshi Imanishi*

Serine-*O*-carbonate derivatives, including peptides having a serine-*O*-carbonate residue at the N-terminal position, are catalytically transformed into *S*-substituted cysteine derivatives.



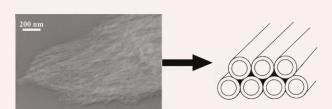
Cleavage of Si-Ar bond vs Si-Me bond: a remarkable counterion effect on reactivity

Suresh Kumar Tipparaju, Sunil K. Mandal, Surojit Sur, Vedavati G. Puranik and Amitabha Sarkar

Formation of distinctly different products from the same alkoxide intermediate indicates a strong dependence of reaction pathways on counterions.

1926

Synthesis of a mesoporous composite material prepared by the self-assembly of mineral liquid crystals



Franck Camerel,* Jean-Christophe P. Gabriel and Patrick Batail

A novel route toward mesoporous composite materials with large pores based on the direct assembly and the immobilization of $[\mathrm{Nb}_6\mathrm{O_{17}}^{4-}]_n$ hollow tubular inorganic building blocks.

1928

Spontaneous deposition of horseradish peroxidase into polyelectrolyte multilayer capsules to improve its activity and stability

Changyou Gao,* Xingyu Liu, Jiacong Shen and Helmuth Möhwald

MF/PSS complex containing PEM microcapsules HRP deposition

Horseradish peroxidase (HRP) was encapsulated in the pre-formed polyelectrolyte multilayer (PEM) microcapsules by spontaneous deposition with remarkably improved stability and catalytic activity.

1930 R CO₂· O CO

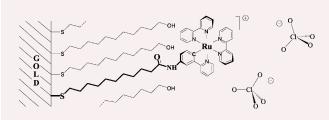
Ratiometric probes for hydrogencarbonate analysis in intracellular or extracellular environments using europium luminescence

Yann Bretonnière, Martin J. Cann, David Parker* and Rachel Slater

In a cell lysate medium, a 69% change in the 618/588 nm intensity ratio signals reversible hydrogenearbonate binding over the range 5 to 15 mM.

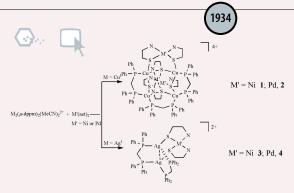
1932

A new redox site as an alternative to ferrocene to study electron transfer in self-assembled monolayers



Cédric Hortholary, Freddy Minc, Christophe Coudret,* Jacques Bonvoisin* and Jean-Pierre Launay

Easily functionalized, highly soluble and undergoing very fast redox processes, the cyclometallated ruthenium complex $[Ru(bpy)_2(pp))]^+$, embedded into Self-Assembled Monolayers, is an attractive redox center to study heterogeneous electron transfer, as confirmed by impedance spectroscopy.



Self-assembly luminescent heteroheptanuclear complexes with metal diphosphine and metal thiolate as components

Hong-Wu Xu, Zhong-Ning Chen,* Shoji Ishizaka, Noboru Kitamura* and Ji-Gui Wu*

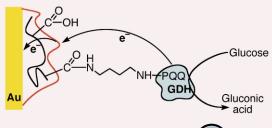
Self-assembly between $[M_2(\mu\text{-dppm})_2(MeCN)_2]^{2+}$ (M = Cu or Ag; dppm = bis(diphenylphosphino)methane) and M'(aet)₂ (M' = Ni or Pd, aet = 2-aminoethanethiolate) afforded photoluminescent heteroheptanuclear (M = Cu^I) and heterotrinuclear complexes (M = Ag^I).

1936

Electrical contacting of glucose dehydrogenase by the reconstitution of a pyrroloquinoline quinone-functionalized polyaniline film associated with an Au-electrode: an *in situ* electrochemical SPR study

Oleg A. Raitman, Fernando Patolsky, Eugenii Katz and Itamar Willner*

The reconstitution of apo-glucose dehydrogenase on a PQQ-functionalized polyaniline film associated with an electrode resulted in an electrically contacted enzyme. The bioelectrocatalytic functions of the enzyme-electrode are elucidated by cyclic voltammetry and *in situ* electrochemical surface plasmon resonance experiments.



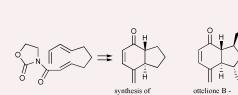
Synthesis and structural analysis of dehydrophenylalanine cyclophanes

Susan E. Gibson (née Thomas),* Jerome O. Jones, S. Barret Kalindjian, Jamie D. Knight, Jonathan W. Steed and Matthew J. Tozer

The syntheses and structures of three cyclophanes containing two (Z)-dehydrophenylalanine residues are reported; the distance between the two amino acid residues is easily altered and changing this parameter has a significant effect on the solid state structures of the cyclophanes.

Synthesis of the bicyclic dienone core of the antitumor agent ottelione B

Derrick L. J. Clive* and Stephen P. Fletcher

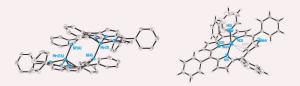


The synthesis of the unusual core of the powerful antitumor agent ottelione B is described; the compound shows little tendency to isomerize to the *cis*-fused isomer or to the aromatic tautomer.



Dimeric and monomeric forms of manganese N-confused porphyrin

John D. Harvey and Christopher J. Ziegler*

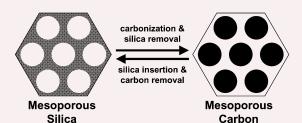


The synthesis and structural characterization of dimeric and monomeric manganese adducts of N-confused tetraphenylporphyrin (NCTPP) are presented; this dimeric form represents the first structural characterization of a new binding mode for this macrocycle, and both complexes exhibit agostic CH interactions as seen in other first row transition metal NCTPP compounds.



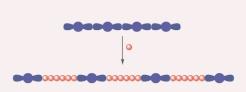
1948

Reversible replication between ordered mesoporous silica and mesoporous carbon



Min Kang, Seung Hwan Yi, Hyung Ik Lee, Jae Eui Yie and Ji Man Kim*

Highly ordered 2-D hexagonal mesoporous silica can be regenerated from a mesoporous carbon CMK-3 that is a negative replica of mesoporous silica SBA-15, indicating reversible replication between carbon and inorganic materials.

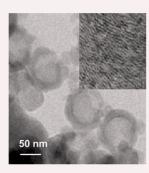


Controlled monomer insertion into polymer main chain: synthesis of sequence ordered polystyrene containing thiourethane and trithiocarbonate units by the RAFT process

Suguru Motokucho, Atsushi Sudo, Fumio Sanda and Takeshi Endo

An easy process for synthesizing regularly nano-structured polymers was developed by controlled insertion polymerization into a polymeric precursor having a trithiocarbonate group in the main chain.

4



Direct synthesis of uniform hollow carbon spheres by a self-assembly template approach

Gang Hu, Ding Ma, Mojie Cheng, Lin Liu and Xinhe Bao

Hollow carbon spheres (50–100 nm) have been synthesized by a self-assembly approach using hexachlorobenzene and Na. NaCl which generated during the reaction has been successfully exploited as a template for the direct synthesis of porous carbon materials.



Enhanced cooperative binding of oligonucleotides to form DNA duplexes mediated by metal ion chelation

Imogen Horsey, Yamuna Krishnan-Ghosh and Shankar Balasubramanian*

Metal chelating iminodiacetic acid moieties were appended to abutting ends of two 9-mer oligonucleotides that were designed to hybridize contiguously on an



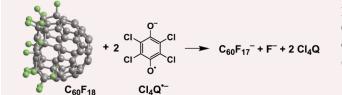


18-mer target. The inclusion of 1 equivalent of Gd^{III} resulted in a 15 °C increase in $T_{\rm m}$ for the complex. Metal chelation has been shown to be effective in cooperatively increasing affinities of oligonucleotides to single stranded DNA targets.

1952

Electron transfer reduction of a highly electron-deficient fullerene, $C_{60}F_{18}$

Kei Ohkubo, Roger Taylor,* Olga V. Boltalina, Seiji Ogo and Shunichi Fukuzumi*



Electron transfer reduction of $C_{60}F_{18}$ to the defluorinated anion, $C_{60}F_{17}^-$ occurs efficiently by the *p*-chloranil radical anion. The one-electron reduction potential of $C_{60}F_{18}$ is evaluated as 0.04 V (*vs.* SCE).

1954

1956

Solution-phase electroluminescence

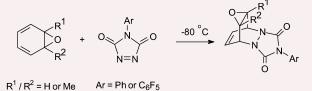
Joshua B. Edel, Andrew J. deMello* and John C. deMello*

We report emissive devices exhibiting electroluminescence in the solution phase. The principle operating mechanism—direct electronic carrier injection from the electrodes into the carrier bands of the polymer—resembles that of conventional solid-state organic light-emitting diodes.



).. 「

Trapping of benzene oxide-oxepin and methyl-substituted derivatives with 4-phenyl- and 4-pentafluorophenyl-1,2,4-triazoline-3,5-dione



Alistair P. Henderson, Esra Mutlu, Amélie Leclercq, Christine Bleasdale, William Clegg, Richard A. Henderson and Bernard T. Golding*

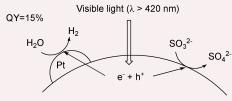
4-Phenyl-1,2,4-triazoline-3,5-dione and its pentafluoro analogue are efficient reagents for trapping arene oxides, *e.g.* benzene oxideoxepin, affording crystalline adducts that can be quantitatively analysed by HPLC and MS techniques.

1958

$AgInZn_7S_9$ solid solution photocatalyst for H_2 evolution from aqueous solutions under visible light irradiation

Akihiko Kudo,* Issei Tsuji and Hideki Kato

The $AgInZn_7S_9$ solid solution with a 2.3 eV band gap showed high photocatalytic activity for H_2 evolution from an aqueous solution under visible light irradiation.



AgInZn₇S₉ solid solution photocatalyst Band gap = 2.3 eV



Oxygen abstraction by laser pyrolysis of $W(CO)_6$; a mild route to gasphase carbene chemistry

Grant R. Allen and Douglas K. Russell*

$$W(CO)_n \xrightarrow{(CH_3)_2CO} W(CO)_nO + (CH_3)_2C: \xrightarrow{CH_2=CH(CH_3)} CH_3 = CH$$

Gas phase carbenes may be generated by O-atom abstraction from organic carbonyls by $W(CO)_n$, produced by laser pyrolysis of $W(CO)_6$. Dimerisation products of carbenes such as $(CH_3)_2C$: have been detected for the first time.

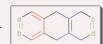


Synthesis of polycyclic compounds utilizing the nickel-catalysed alkynylstannylation of 1,2-dienes



•the Diels-Alder reaction

 $\begin{array}{l} \bullet \textit{Ni-catalysed cyclization with alkynes} \\ \bullet \textit{Zr-mediated cyclization with o-} I_2C_6H_4 \end{array}$

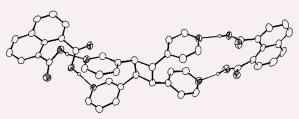


Eiji Shirakawa,* Yoshiaki Nakao, Teruhisa Tsuchimoto and Tamejiro Hiyama*

Polycyclic compounds having linearly-fused six-membered rings can be readily prepared by various modes of cyclization from dienediynes, which were synthesized through the nickel-catalysed alkynylstannylation of 1,2-dienes followed by the palladium-catalysed oxidative homocoupling of the resulting alkenylstannanes.



Site-directed regiocontrolled synthesis of a 'head-to-head' photodimer *via* a single-crystal-to-single-crystal transformation involving a linear template

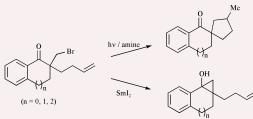


Dushyant B. Varshney, Giannis S. Papaefstathiou and Leonard R. MacGillivray*

A linear template is used to direct the synthesis of a 'head-to-head' photodimer in the solid state, which occurs *via* a single-crystal-to-single-crystal transformation.

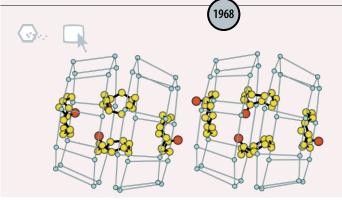


Changeable reactivity of ketyl radicals derived from 2-bromomethyl-2-(3-butenyl)benzocyclic-1-alkanones depending on electron transfer conditions employed



Eietsu Hasegawa,* Shinya Takizawa, Kazuki Iwaya, Miyuki Kurokawa, Naoki Chiba and Keiko Yamamichi

Photoinduced electron transfer reaction of 2-bromomethyl-2-(3-butenyl)benzocyclic-1-alkanones with amines afforded 5-exo radical cyclization products while electron transfer reaction with samarium diiodide produced cyclopropanols.



X-Ray structure of the $\delta\text{-cyclodextrin}$ complex with cycloundecanone

Kazuaki Harata,* Hiroaki Akasaka, Tomohiro Endo, Hiromasa Nagase and Haruhisa Ueda

The crystal structure of the δ -cyclodextrin complex with cycloundecanone shows a channel-type structure consisting of head-to-head dimer units that include four guest molecules.

A regio- and stereoselective α -methylation of γ , δ -epoxy- α , β -unsaturated esters with a Me₂Zn–CuCN reagent

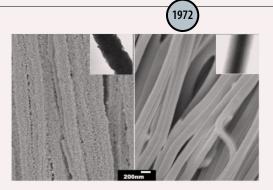
*

Me CO₂Et OH **2**-anti

> up to 99% yield up to >99:1 α-selectivity

Atsushi Hirai, Atsushi Matsui, Kei Komatsu, Keiji Tanino and Masaaki Miyashita*

A highly regio- and stereoselective $\alpha\text{-methylation}$ reaction of $\gamma\text{-}\delta\text{-}$ epoxy- $\alpha\text{-}\beta\text{-}\text{unsaturated}$ esters was achieved by using a Me $_2Zn\text{-}CuCN$ reagent.



Binary hydrogel nanowires of invertible core/shell phases prepared in porous alumina membranes

Zhenzhong Yang* and Zhongwei Niu

Poly(*N*,*N*-dimethylacrylamide)/poly(acrylic ammonium) binary hydrogel nanowires with invertible core/shell phases were made by a radical polymerization in the nanosized cylinder pores of alumina membranes, where the pore surface wettability is controlled by chemical modification.

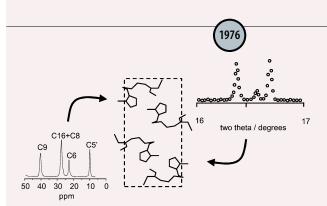


Carbonyl olefination utilizing an alkyl halide-titanocene(II) system

Takeshi Takeda,* Keiko Shimane, Kenji Ito, Naoko Saeki and Akira Tsubouchi

 $R^{1} \xrightarrow{R^{2}} R^{2} \xrightarrow{R^{3} \times X} X \xrightarrow{R^{1} \times R^{3}} R^{2}$

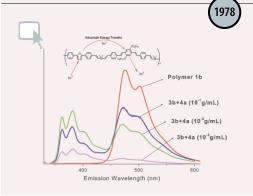
Ketones, aldehydes, esters and lactones are transformed into olefins when treated with the organotitanium species formed from alkyl halides and titanocene(II).



Conformational analysis by solid-state NMR and its application to restrained structure determination from powder diffraction data

David A. Middleton,* Xin. Peng, David Saunders, Kenneth Shankland, William I. F. David and Anders J. Markvardsen

Solid-state NMR is used to dramatically improve the efficiency and reliability of molecular crystal structure determination from X-ray powder diffraction data.

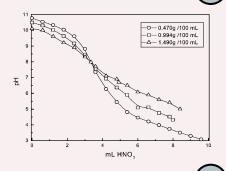


Intrachain energy transfer in silylene-spaced alternating donor-acceptor divinylarene copolymers

Yen-Ju Cheng, Tsyr-Yuan Hwu, Jui-Hung Hsu and Tien-Yau Luh*

Silylene-spaced donor–acceptor divinylarene copolymers are synthesized by hydrosilylation of bisalkynes 7 with bisvinylsilanes 3; efficient intrachain energy transfer between donor–acceptor chromophores is observed.





Potentiometric mass titrations: a quick scan for determining the point of zero charge

John Vakros, Christos Kordulis and Alexis Lycourghiotis*

The points of zero charge of four oxidic catalytic carriers have been determined as the intersection points of four sets of three potentiometric titration curves. These curves have been plotted using three suspensions for each oxide having the same ionic strengths but containing different masses of the oxides.



Self-assembly of a stereoselective trinuclear sodium/lithium triple helix

Magdalena Capó,* José M. Saá and Angel Alvarez

Synthesis and characterisation of the stereoselective triple-stranded helicate complexes M_3L_3 self-assembled quantitatively by means of MOTf (M = Na, Li) and a BINOL-derivative.

1984

Co"TPP + Cr CI CI CO"TPP]+ $(CO^{\parallel}TPP)$ + $(CO^{\parallel}$

Activation of electron transfer reduction of *p*-benzoquinone derivatives by intermolecular regioselective hydrogen bond formation

Shunichi Fukuzumi,* Hironori Kitaguchi, Tomoyoshi Suenobu and Seiji Ogo

Electron transfer reduction of p-benzoquinones by cobalt tetraphenylporphyrin is enhanced significantly by the presence of o-bis(phenylcarbamoylmethyl)benzene (o- \mathbf{L}) due to the regioselective hydrogen bond formation between the corresponding semiquinone radical anions and o- \mathbf{L} .

1986

1988

Suzuki cross-coupling reactions of aryl halides in phosphonium salt ionic liquid under mild conditions

James McNulty,* Alfredo Capretta, Jeff Wilson, Jeff Dyck, George Adjabeng and Al Robertson

The Suzuki cross-coupling of aryl boronic acids with aryl halides, including aryl chlorides, proceeds in the phosphonium salt ionic liquid tetradecyltrihexylphosphonium chloride under mild conditions.

ADDITIONS AND CORRECTIONS

Béatrice Quiclet-Sire, Benoît Sortais

and Samir Z. Zard

A convergent approach to 2-substituted-5-methoxyindoles. Application to the synthesis of melatonin



Dates, venues and contact details of forthcoming events.

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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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