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ISSN 1144-0546 CODEN NJCHES 30(11) 1513-1684 (2006)



Cover

See Roser Pleixats *et al.*, p. 1586. 15-Membered triolefinic macrocycles featuring fluorous and polyoxyethylenated chains stabilize palladium(0) nanoparticles instead of only forming discrete palladium(0) complexes.

Image reproduced by permission of Anna Serra-Muns, Roger Soler, Elena Badetti, Paula de Mendoza, Marcial Moreno-Mañas, Roser Pleixats, Rosa M. Sebastián and Adelina Vallribera, New J. Chem., 2006, **30**, 1586.

CHEMICAL SCIENCE

C81

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November 2006/Volume 3/Issue 11 www.rsc.org/chemicalscience

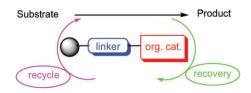
PERSPECTIVES

1525

Recoverable and recyclable chiral organic catalysts

Maurizio Benaglia

A few selected, significant works reported in the field of supported chiral organic catalysts will be presented, with a special attention to the papers that appeared after 2002. A few considerations on the methodologies, the future and the problems related to the immobilization of chiral organic catalysts will also be briefly discussed.



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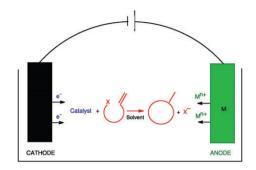
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PERSPECTIVES

1534

Intramolecular reductive cyclisations using electrochemistry: development of environmentally friendly synthetic methodologies

Elisabet Duñach,* Maria José Medeiros and Sandra Olivero This review summarises electrochemical reductive intramolecular cyclisations, including transition-metal catalysed reactions.



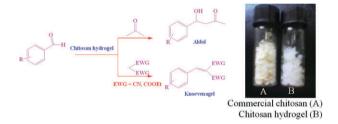
LETTERS

1549

Chitosan hydrogel: A green and recyclable biopolymer catalyst for aldol and Knoevenagel reactions

K. Rajender Reddy,* K. Rajgopal, C. Uma Maheswari and M. Lakshmi Kantam

Chitosan hydrogel is prepared and efficiently utilized as an organocatalyst for aldol and Knoevenagel reactions, providing the products in high yields with a high chemoselectivity under biphasic conditions.

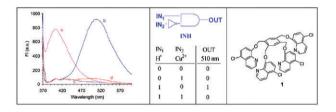


1553

Photonic logic gates based on metal ion and proton induced multiple outputs in 5-chloro-8-hydroxyquinoline based tetrapod

Prabhpreet Singh and Subodh Kumar*

Tetrapod 1 shows opportunities for OR, NOR and INHIBIT logic gates based on fluorescence enhancement (FE) $(Zn^{2+}, Cd^{2+}; 435-445 \text{ nm})$, fluorescence quenching (FQ) $(Cu^{2+}, Ni^{2+}, Co^{2+}; 402 \text{ nm})$ and dual FQ (402 nm)—FE (510 nm) (H $^+$) outputs.

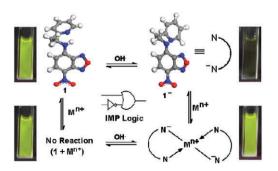


1557

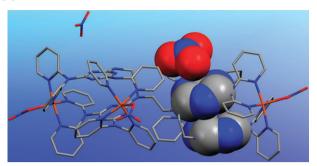
pH-Regulated "Off-On" fluorescence signalling of d-block metal ions in aqueous media and realization of molecular IMP logic function

Moloy Sarkar, Sandip Banthia, Aditi Patil, Mohd. Bismillah Ansari and Anunay Samanta*

Efficient sensing of d-block metal ions in aqueous media by employing an anionic binding site in the ICT sensor system has been explored and the optical event leads to the implementation of the molecular IMP logic gate.



1561

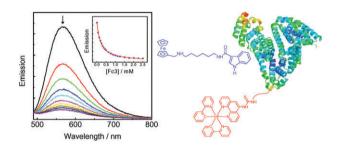


Crystallographic evidence of theoretically novel anion– π interactions

Héléne Casellas, Chiara Massera, Francesco Buda, Patrick Gamez* and Jan Reedijk*

The crystallographic evidence of anion- π - π supramolecular interactions is reported, supported by theoretical calculations.

1567

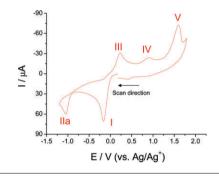


Synthesis, crystal structures, electrochemical and proteinbinding properties of ferrocene—indole conjugates

Kenneth Kam-Wing Lo,* Jason Shing-Yip Lau and Nianyong Zhu

Two redox-active ferrocene-indole compounds can be recognized by indole-binding proteins; the spacer arm in one reduces the steric hindrance between the protein and the ferrocene.

1576

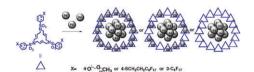


Electrochemical studies of gold and chloride in ionic liquids

Leigh Aldous, Debbie S. Silvester, Constanza Villagrán, William R. Pitner, Richard G. Compton, M. Cristina Lagunas* and Christopher Hardacre*

The electrochemistry of Na[AuCl₄] is investigated for the first time in a 'second generation' ionic liquid, [C₄mim][NTf₂]. [AuCl₄] is reduced to [AuCl₂] (I) followed by deposition of Au(0) (IIa). Stripping of gold (V) requires the presence of Cl , Cl₃ (III) or Cl₂ (IV).

1584



15-Membered triolefinic macrocycles as stabilizers of palladium(0) nanoparticles

Anna Serra-Muns, Roger Soler, Elena Badetti, Paula de Mendoza, Marcial Moreno-Mañas, Roser Pleixats,* Rosa M. Sebastián* and Adelina Vallribera*

Triolefinic macrocycles featuring fluorinated and polyoxyethylenated stabilizing chains form palladium(0) nanoparticles.



Combination of fluorescent switch and electrochemical switch based on a photochromic diarylethene

Nan Xie and Yi Chen*

Compound 1a, a diarylethene with oligothiophene side arms, behaved as a fluorescent and electrochemical switch based on ring-opening and ring-closing photoisomerization. In addition, 1a exhibited interesting photoelectrochromic properties.

1599

Behaviour of dimeric methylrhenium(vI) oxides in the presence of hydrogen peroxide and its consequences for oxidation catalysis

Alexandra M. J. Rost, Andrea Scherbaum, Wolfgang A. Herrmann* and Fritz E. Kühn*

An alternative synthetic pathway to methyltrioxorhenium (MTO), replacing the toxic methyl tin precursors with dimethyl zinc, is investigated. The behaviour of the by-products is examined in detail.

1606

Analogs of Michler's ketone for two-photon absorption initiation of polymerization in the near infrared: synthesis and photophysical properties

Gilles Lemercier,* Cécile Martineau, Jean-Christophe Mulatier, Irène Wang, Olivier Stéphan, Patrice Baldeck and Chantal Andraud*

Synthesis and photophysical properties of conjugated Michler's ketone analogs are described. These molecules appear as efficient initiators for polymerization by TPA.

$$C_{d}H_{0} \xrightarrow{C_{d}H_{0}} G$$

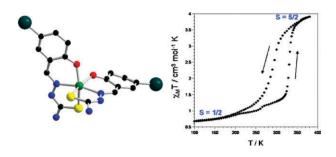
1614

Structure and reactivity of tautomeric forms of zwitterionic species from the reaction of phosphorus(III) compounds with electron deficient alkenes and alkynes

N. N. Bhuvan Kumar, Manab Chakravarty and K. C. Kumara Swamy*

Tautomeric forms (3–5) of zwitterionic intermediates proposed in the phosphine-catalysed reactions of electron-deficient alkenes/alkynes, a novel heterocycle (6) and the phenol addition product (7 · PhOH ··· OPh) are described.

1621

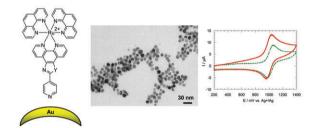


The crystallographic phase transition for a ferric thiosemicarbazone spin crossover complex studied by X-ray powder diffraction

Sébastien Floquet,* Nathalie Guillou, Philippe Négrier, Eric Rivière and Marie-Laure Boillot*

This study reports the structural investigation of a thiosemicarbazone ferric complex that exhibits a discontinuous spin transition associated with a large hysteresis loop near room temperature.

1628



Polypyridyl ruthenium complexes as coating agent for the formation of gold and silver nanocomposites in different media. Preliminary luminescence and electrochemical studies

C. R. Mayer,* E. Dumas, F. Miomandre, R. Méallet-Renault, F. Warmont, J. Vigneron, R. Pansu, A. Etcheberry and F. Sécheresse

Control of the size, shape and stability of Au and Ag nanoparticles stabilized by fully conjugated polypyridyl ruthenium complexes.

1638

 $(-2.303R)\log K$

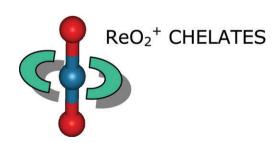
$$= (\alpha_{H}/T - \alpha_{S}) + (\beta_{H}/T - \beta_{S})(pKa' + 4)$$
$$+ (\phi_{H}/T - \phi_{S}) pKa'\pi + (\gamma_{H}/T - \gamma_{S})\theta$$

Multi-mechanism linear free energy relationships and isoequilibrium or isokinetic temperatures

Kevin A. Bunten and Anthony J. Poë*

The linear free energy (LFER) equation shown describes the temperature dependence of the individual modulating terms in a multi-mechanism LFER, and implies that isoequilibrium temperatures (IETs) are merely a consequence of the combination of enthalpic and entropic contributions to the modulation, thus removing any anxiety over the physical significance of negative IETs *etc*.

1650



 $\mbox{ReO_2}^+$ chelates with aliphatic diamines. Structural and proton transfer properties

Jorge S. Gancheff, Carlos Kremer,* Oscar N. Ventura, Sixto Domínguez, Carla Bazzicalupi, Antonio Bianchi,* Leopoldo Suescun and Alvaro W. Mombrú

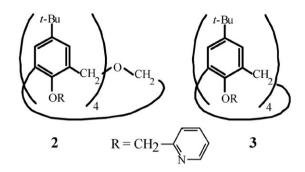
By appropriately selecting the equatorial ligands for chelation of ReO₂⁺ it is possible to perform a rather fine tuning of the complex proton transfer properties.

1655

Binding properties of *p-tert*-butyldihomooxacalix[4]arene tetra(2-pyridylmethoxy) derivative towards alkali, alkaline earth, transition and heavy metal cations

Paula M. Marcos,* Besma Mellah, José R. Ascenso, Sylvia Michel, Véronique Hubscher-Bruder and Françoise Arnaud-Neu

The binding properties of 2, in the cone conformation, have been assessed by extraction studies of metal picrates and stability constant measurements in methanol and acetonitrile.

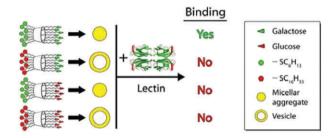


1662

Probing specific protein recognition by size-controlled glycosylated cyclodextrin nanoassemblies

Antonino Mazzaglia,* Antonio Valerio, Valentina Villari, Anna Rencurosi, Luigi Lay, Salvatore Spadaro, Luigi Monsù Scolaro and Norberto Micali*

The recognition of lectin by amphiphilic glycosylated cyclodextrins is driven by their morphology and the specificity of cyclodextrins with shorter hydrophobic groups towards a receptor is assessed in water solution by the presence of small micelles able to interact efficiently with the lectin binding site.

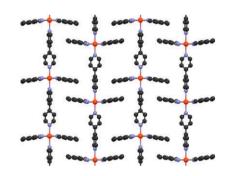


1669

A spin-crossover iron(II) coordination polymer with the 8-aminoquinoline ligand: synthesis, crystal structure and magnetic properties of [Fe(aqin)₂(4,4'-bpy)](ClO₄)₂ · 2EtOH (aqin = 8-aminoquinoline, 4,4'-bpy = 4,4'-bipyridyl)

Caroline Genre, Galina S. Matouzenko,* Erwann Jeanneau and Dominique Luneau

A new spin-crossover iron(II) polymer was synthesised and magnetically and structurally characterised. It has a linear chain structure and displays a rather abrupt HS \leftrightarrow LS transition with $T_{1/2} = 220$ K.



1675

Catalysed low temperature H₂ release from nitrogen heterocycles

Audrey Moores, Macarena Poyatos, Yi Luo* and Robert H. Crabtree*

Potentially relevant to hydrogen storage, the introduction of heteroatoms into a series of organic molecules progressively facilitates hydrogen release, both thermodynamically and kinetically.

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