

IN THIS ISSUE

ISSN 1144-0546 CODEN NJCHES 29(1) 1-252 (2005)

In this issue...

Contributions from members of the *NJC* Editorial and Advisory Boards.



Chemical biology articles published in this journal also appear in the *Chemical Biology Virtual Journal*: www.rsc.org/chembiol



Cover

See Luca Prodi, page 20.

The front cover shows the enhancement in fluorescence with increasing concentration of Cd^{2+} ions (from left to right) in methanol solutions of a crown ether receptor linked with an 8-hydroxyquinoline derivative, irradiated with UV light.

A good understanding of luminescent chemosensors and the mechanisms involved in translating analyte recognition into luminescent signal modulation is essential in the development of macroscopic sensing devices.

CHEMICAL SCIENCE

C1

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

January 2005/Volume 2/Issue 1

www.rsc.org/chemicalscience

EDITORIALS

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NJC set to strengthen further

Professor Jean-Pierre Majoral, the new Editor-in-Chief, reflects on recent developments and looks forward to further strengthening the position of *NJC* as an "International Journal of the Chemical Sciences".



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Editorial

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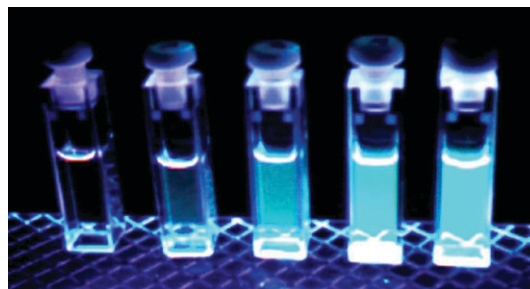
PERSPECTIVES

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Luminescent chemosensors: from molecules to nanoparticles

Luca Prodi

Luminescent chemosensors are finding applications in many fields of great social and economical importance. Through the discussed compounds the reader will be able to follow our step-by-step approach towards this fascinating research field, in which, we believe, a very important role will be played by nanoparticles.

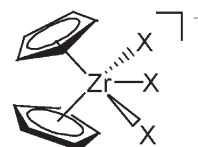


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Zirconate complexes: multifaceted reagents

Jean-Pierre Majoral* and Maria Zablocka*

Design, characterization and versatile behaviour of zirconocene-ate complexes are reviewed.

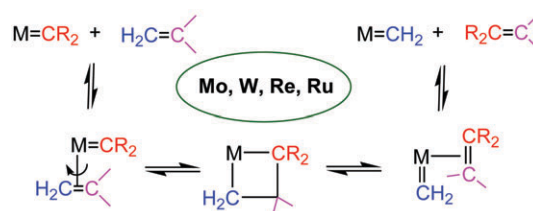


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The metathesis reactions: from a historical perspective to recent developments

Didier Astruc

The development of the metathesis reactions is reviewed from a historical perspective and the latest developments and perspectives are given.



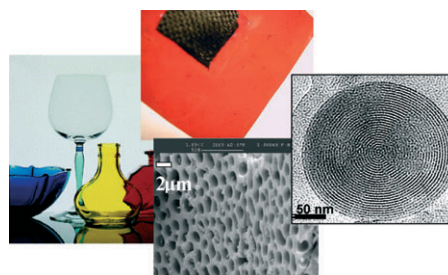
OPINION

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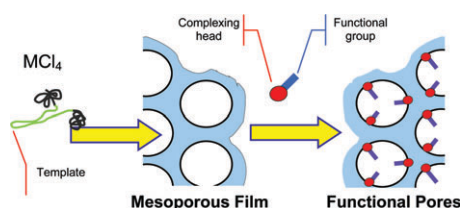
Hybrid materials. Functional properties. From Maya Blue to 21st century materials

Pedro Gómez-Romero and Clément Sanchez

The field of hybrid organic-inorganic nanocomposites is quickly evolving towards functional materials and applications while broadening spectacularly the variety of hybrid combinations explored. Improved understanding and control of the chemistry, processing and microstructure of these versatile systems leads to new opportunities in dealing with increasingly complex chemistries and materials.



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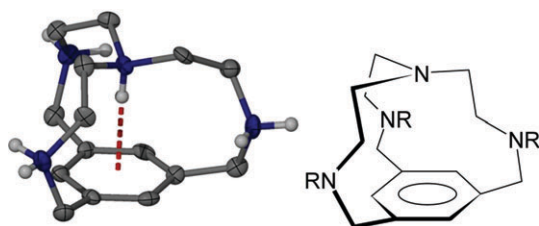


Hybrid non-silica mesoporous thin films

Paula C. Angelomé, Sara Aldabe-Bilmes, Mauricio E. Calvo, Eduardo L. Crepaldi, David Grosso, Clément Sanchez* and Galo J. A. A. Soler-Illia*

Mesoporous hybrid TiO₂ and ZrO₂ thin films with organic functions attached to the walls are produced by evaporation-induced self-assembly (EISA) followed by pore post-functionalisation.

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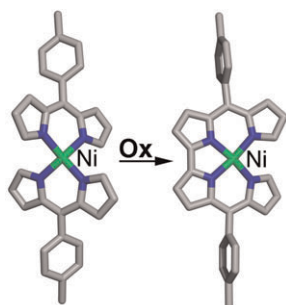


Hydrogen bonds between ammonium ions and aromatic rings exist and have key consequences on solid-state and solution phase properties

Christos A. Ilioudis, Michael J. Bearpark and Jonathan W. Steed*

An azacyclophane binds strongly to H⁺ via a charge-assisted NH...π interaction.

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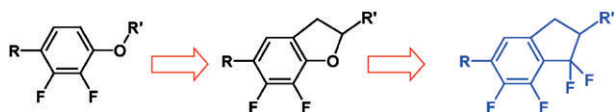


Preparation of α,β-unsubstituted meso-arylbidipyrins via metal-templated, oxidative coupling of dipyrins

Hubert S. Gill, Isaac Finger, Ivana Božidarević, Florence Szydło and Michael J. Scott*

New meso-aryl-α,β-unsubstituted bisdipyrinato nickel complexes, prepared from a one-pot procedure, give easy access to an unprecedented class of meso-aryl-α,β-unsubstituted bidipyrins.

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1,1,6,7-Tetrafluoroindanes: improved liquid crystals for LCD-TV application

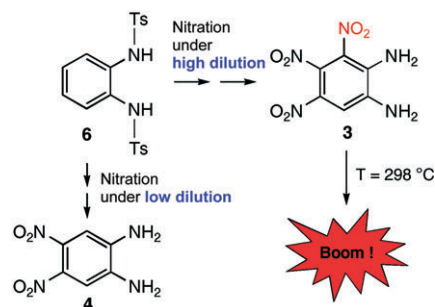
Matthias Bremer* and Lars Lietzau

A synthesis involving *ortho*-metallation, intramolecular Heck reaction and oxidative fluorination as key steps yielded tetrafluoroindanes whose highly negative values for dielectric anisotropies found experimentally were not expected based on quantum chemical calculations.

Tuning the synthesis of a dinitroaromatic towards a new trinitroaromatic stabilized energetic material

Olivier Siri* and Pierre Braunstein*

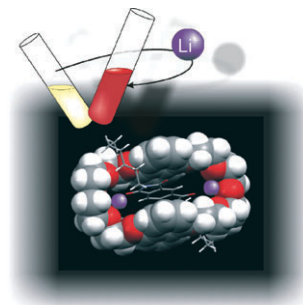
Depending on experimental conditions, nitration of **6** affords either a new isomer of diaminotrinitrobenzene **3**, whose deflagration temperature of 298 °C is of interest for heat-resistant explosives, or **4** whose crystal structure determination reveals an interesting hydrogen-bonding network in the solid-state.



Cation-reinforced donor-acceptor pseudorotaxanes

Sofia I. Pascu, Thibaut Jarrosson, Christoph Naumann, Sijbren Otto, Guido Kaiser and Jeremy K. M. Sanders*

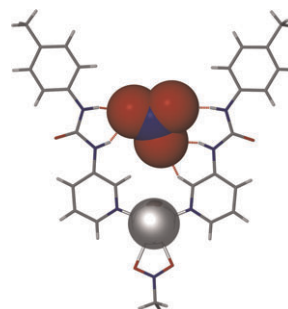
Li^+ is a remarkable template for the formation of pseudorotaxanes from an electron-rich crown ether and a pyromellitic diimide.



Anion binding by Ag(I) complexes of urea-substituted pyridyl ligands

David R. Turner, Benjamin Smith, Elinor C. Spencer, Andres E. Goeta, Ivana Radosavljevic Evans, Derek A. Tocher, Judith A. K. Howard and Jonathan W. Steed*

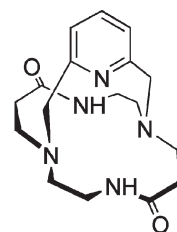
Reaction of a *meta*-ureidopyridyl ligand with AgNO_3 results in a discrete, self-assembled cooperative anion pair binding system in solution. In contrast, other combinations give hydrogen-bonded polymers.



Synthesis, characterization and X-ray crystal structures of cyclam derivatives. Part VI. Proton binding studies of a pyridine-strapped 5,12-dioxocyclam based macrobicycle

Michel Meyer, Laurent Frémond, Alain Tabard, Enrique Espinosa, Guy Yves Vollmer, Roger Guilard* and Yves Dory

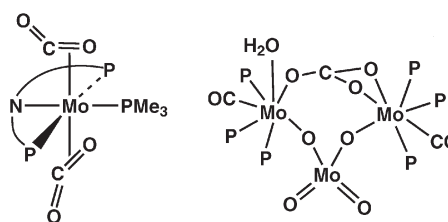
A combination of NMR, potentiometric, spectrophotometric, and DFT results enabled us to unravel the solution structure and unusual acid-base properties of the title compound, which displays slow proton-transfer kinetics.



Novel carbon dioxide and carbonyl carbonate complexes of molybdenum. The X-ray structures of *trans*-[Mo(CO₂)₂{HN(CH₂CH₂PMe₂)₂}(PMe₃)] and [Mo₃(μ₂-CO₃)(μ₂-O)₂(O)₂(CO)₂(H₂O)(PMe₃)₆] · H₂O

Leopoldo Contreras, Margarita Paneque, Murielle Sellin, Ernesto Carmona,* Pedro J. Pérez, Enrique Gutiérrez-Puebla, Angeles Monge and Caridad Ruiz

Bis(carbon dioxide) and carbonyl carbonate complexes of molybdenum stabilized by PMe_3 and $\text{HN}(\text{CH}_2\text{CH}_2\text{PMe}_2)_2$ ligands have been prepared and structurally characterized by X-ray crystallography.



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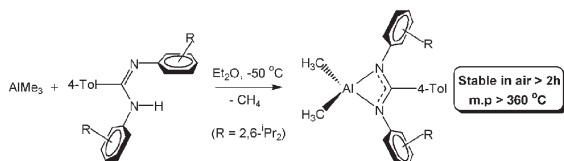


Weak interactions between resorcinarenes and quaternary alkyl ammonium cations

Heidi Mansikkamäki, Christoph A. Schalley, Maija Nissinen and Kari Rissanen*

An analysis of the interactions of resorcin[4]arenes with alkyl ammonium cations reveals a remarkable structural variety of the complexes due to subtle effects from the cation size and charge, the nature of the counterions and the presence of solvents.

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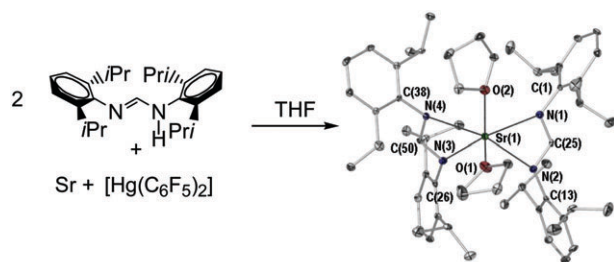


The syntheses and structures of some main group complexes of the sterically hindered *N,N'*-bis(2,6-diisopropylphenyl)-4-toluamidine ligand

René T. Boéré, Marcus L. Cole and Peter C. Junk*

The reaction of the bulky benzamidine *N,N'*-bis(2,6-diisopropylphenyl)-4-toluamidine (HDippAm) with metal alkyls of lithium, magnesium and aluminium is reported. The three compounds generated: [Li(DippAm)(THF)₂] (**1**), [Mg(DippAm)₂] (**2**) and [Al(DippAm)Me₂] (**3**), the latter also obtained *via* the reaction of **1** with Me₂AlCl, exhibit rigid geometries that, as evidenced by VT ¹H NMR, are maintained at increased temperatures.

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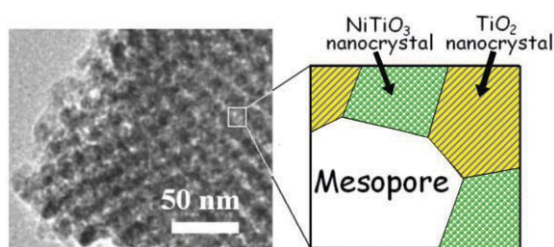


N,N'-Bis(2,6-diisopropylphenyl)formamidinate complexes of the heavy alkaline earths

Marcus L. Cole and Peter C. Junk*

The reaction of heavy alkaline earth metals with two equivalents of a bulky formamidine in the presence of bis(pentafluorophenyl)mercury affords the bis(formamidinate) species in good to moderate yield. These species serve as a model for the synthesis and composition of targeted divalent lanthanoid compounds.

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Preparation of multi-nanocrystalline transition metal oxide (TiO₂-NiTiO₃) mesoporous thin films

David Ortiz de Zárate, Cédric Boissière, David Grosso, Pierre-Antoine Albouy, Heinz Amenitsch, Pedro Amoros and Clément Sanchez*

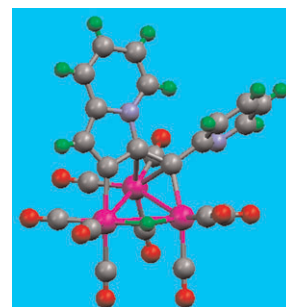
Ordered mesoporous thin films with crystalline walls made of TiO₂ anatase and NiTiO₃ ilmenite nanocrystals have been prepared by the evaporation induced self-assembly process and a carefully controlled thermal treatment.

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**Molecular rearrangements of diynes coordinated to triosmium carbonyl clusters: reactions of $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$ and $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ with 1,4-dipyridylbuta-1,3-diyne**

Lionel P. Clarke, Jacqueline M. Cole, John E. Davies, Alexandra French, Olivia F. Koentjoro, Paul R. Raithby* and Gregory P. Shields

Reaction of $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$ with 1,4-dipyridylbuta-1,3-diyne yields two new clusters, $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}\{\mu\text{-}\eta^1:\eta^1\text{-}(\text{C}_8\text{H}_5\text{N})\text{-C}(\text{C}_5\text{H}_4\text{N})\}]$ and $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}\{\mu_3\text{-}\eta^1:\eta^1:\eta^1\text{-}(\text{C}_5\text{H}_4\text{N})\text{-C-C}(\text{C}_8\text{H}_6\text{N})\}]$, in which the diyne has rearranged to form a substituted indolizine ring system.

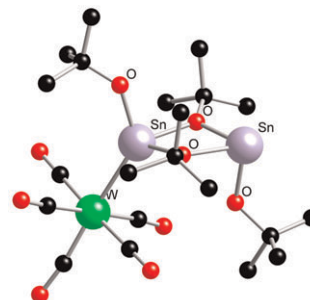


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**Synthesis, solid-state molecular structure and solution dynamics of new alkoxy stannylene-transition metal complexes**

Michael Veith,* Markus Ehses and Volker Huch

X-Ray crystallography shows systematic changes in the structure of the dimeric alkoxy stannylene $[\text{Sn}(\text{O}^t\text{Bu})_2]_2$ on complexation with group 6 pentacarbonyl fragments. Temperature variable heteronuclear NMR spectroscopy reveals a stepwise exchange of the terminal and bridging substituents for the trinuclear complexes.



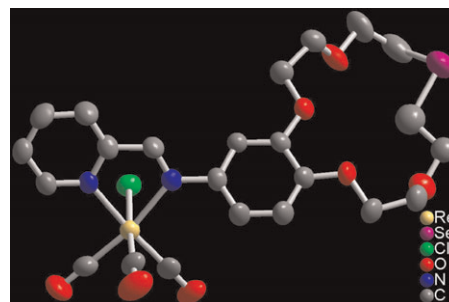
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**Synthesis, photophysics, electrochemistry and metal ion-binding studies of rhenium(i) complexes with crown ether pendants: selective and specific binding properties for various metal ions**

Keith Man-Chung Wong, Wei-Ping Li, Kung-Kai Cheung and Vivian Wing-Wah Yam*

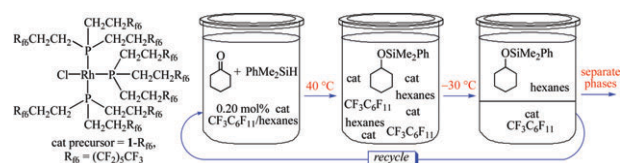
Unlike the oxacrown ether containing complexes, the thia- and selenacrown ether analogues show high binding affinity towards silver ions; selective and specific binding properties have also been studied for various metal cations of different sizes and different degrees of hardness and softness.

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**Monophasic and biphasic hydrosilylations of enones and ketones using a fluorous rhodium catalyst that is easily recycled under fluorous-organic liquid-liquid biphasic conditions**

Long V. Dinh and John A. Gladysz*

Rate studies of the title reactions confirm that the active catalysts generated from $\text{ClRh}[\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_n - 1\text{CF}_3)_3]_3$ ($n = 6, 8$) can be efficiently recovered and used for at least four cycles.

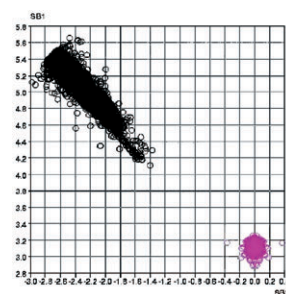


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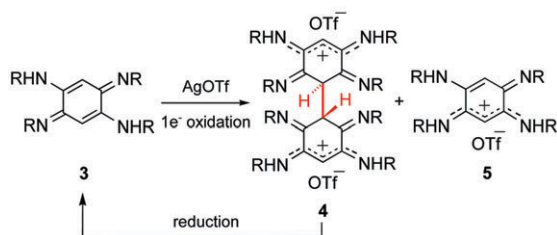
New light on the mechanism of the solid state $[2 + 2]$ cycloaddition of alkenes: a database analysis

Frank H. Allen,* Mary F. Mahon, Paul R. Raithby,* Gregory P. Shields and Hazel A. Sparkes

Knowledge mining techniques have been applied to an analysis of the mechanism of solid state $[2 + 2]$ cycloaddition reactions of alkenes. The alkenes do not have to be parallel for the reaction to occur, and a large twist angle of the reacting species can lead to a puckered cyclobutane reaction product.



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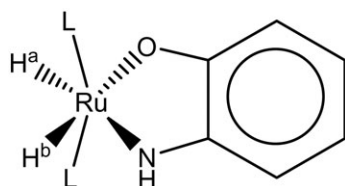


One-electron oxidation-induced dimerising C–C coupling of a 2,5-diamino-1,4-benzoquinonediimine: a chemical and electrochemical investigation

Jean-philippe Taquet, Olivier Siri, Jean-Paul Collin, Abdellatif Messaoudi and Pierre Braunstein*

The one-electron oxidation of **3** leads to the formation of the benzoquinonemonoimineminoiminium salt **5** and of the new dimer **4**, which provides the first non-dehydrogenative C–C coupling in quinonoid chemistry. Chemically induced reduction of **4** reverses the process and regenerates **3**.

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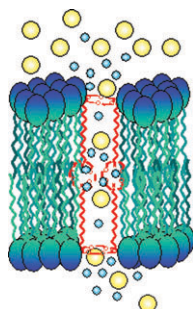


New d⁴ dihydrides of Ru(IV) and Os(IV) with π -donor ligands: $M(H)_2(chelate)(P^iPr_3)_2$ with chelate = *ortho*-XYC₆H₄ with X, Y = O, NR; R = H or CH₃

German Ferrando-Miguel, Peng Wu, John C. Huffman and Kenneth G. Caulton*

The pictured molecules are non-octahedral species with dianionic, not quinoid chelate ligands.

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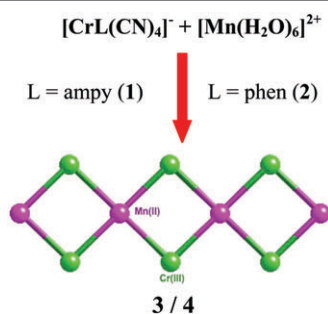


Structure and medium effects on hydrphile synthetic ion channel toxicity to the bacterium *E. coli*

W. Matthew Leevy, Michael R. Gokel, George B. Hughes-Strange, Paul H. Schlesinger and George W. Gokel*

The toxicity of synthetic hydrphile channels with various side arms against *E. coli* is pH-dependent and is enhanced in the presence of hydrophobic side chains.

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$[Cr^{III}(L)(CN)_4]^-$: a new building block in designing cyanide-bridged 4,2-ribbon-like chains $\{[Cr^{III}(L)(CN)_4]_2Mn(H_2O)_2\} \cdot nH_2O$ [L = 2-aminomethylpyridine ($n = 6$) and 1,10-phenanthroline ($n = 4$)]

Luminita Toma, Rodrigue Lescouëzec, Jacqueline Vaissermann, Patrick Herson, Valérie Marvaud, Francesc Lloret and Miguel Julve*

The use of stable tetracyanochromate(III) species as a complex ligand towards fully hydrated manganese(II) ions provides new cyanide-bridged crossed double bimetallic chains exhibiting metamagnetic properties.

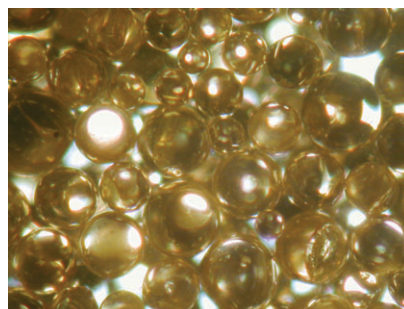
PAPERS

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Solid-phase synthesis of peptide-platinum complexes using platinum-chelating building blocks derived from amino acids

Marc S. Robillard, Sophie van Alphen, Nico J. Meeuwenoord, Bart A. J. Jansen, Gijs A. van der Marel, Jacques H. van Boom and Jan Reedijk*

To expand the diversity of platinum structures available through a solid-phase combinatorial or parallel synthesis approach, amino acids are employed as precursors in the synthesis of platinum-chelating building blocks.

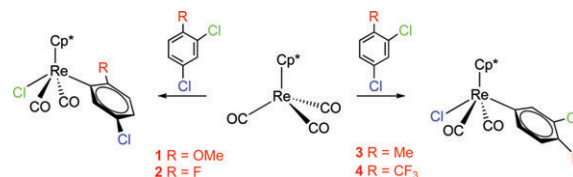


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**Selectivity in C–Cl bond activation of dichloroarenes by photogenerated $\text{Cp}^*\text{Re}(\text{CO})_2$: combined experimental and DFT studies**

Alvaro Aballay, Eric Clot, Odile Eisenstein,* Maria Teresa Garland, Fernando Godoy, A. Hugo Klahn,* Juan Carlos Muñoz and Beatriz Oelckers

$\text{Cp}^*\text{Re}(\text{CO})_2$ inserts selectively into the C–Cl bond of 1-R-2,4- $\text{C}_6\text{Cl}_2\text{H}_3$; insertion occurs at the 2-position for R = OMe and F, but at the 4-position for R = Me and CF_3 .

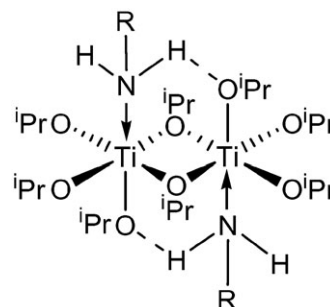


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**Amine adducts of titanium tetraalkoxides**

Helmut Fric and Ulrich Schubert*

The formation of Lewis base–Lewis acid adducts must be taken into account when Lewis basic nitrogen compounds are co-reacted with titanium alkoxides (and metal alkoxides in general), especially in sol-gel processes.

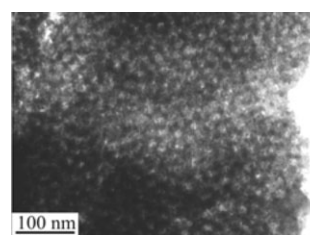


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**The generation of mesostructured crystalline CeO_2 , ZrO_2 and CeO_2 – ZrO_2 films using evaporation-induced self-assembly**

Torsten Brezesinski, Markus Antonietti,* Matthijs Groenewolt, Nicola Pinna and Bernd Smarsly

Mesostructured thin films of CeO_2 , ZrO_2 and CeO_2 – ZrO_2 with highly crystalline pore walls and well-ordered arrays of mesopores are obtained by EISA and a controlled temperature procedure.



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**Multiple ionic interactions for noncovalent synthesis of molecular capsules in polar solvents**

Francesca Corbellini, Fijis W. B. van Leeuwen, Hans Beijleveld, Huub Kooijman, Anthony L. Spek, Willem Verboom, Mercedes Crego-Calama* and David N. Reinhoudt*

Schematic representation of the molecular capsules resulting from the self-assembly of oppositely charged (thia)calix[4]arenes *via* multiple ionic interactions.



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