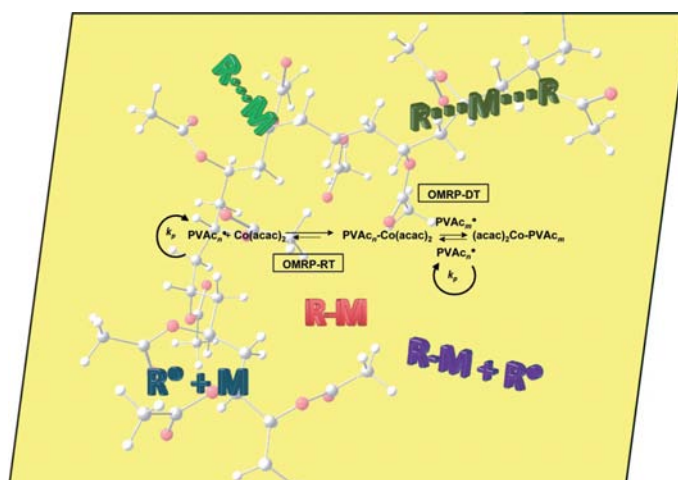


EurJIC is a journal of ChemPubSoc Europe, a union of 16 European chemical societies formed for the purpose of publishing high-quality science. All owners merged their national journals to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*.

Other ChemPubSoc Europe journals are *Chemistry – A European Journal*, *ChemBioChem*, *ChemPhysChem*, *ChemMedChem*, *ChemSusChem* and *ChemCatChem*.

COVER PICTURE

The cover picture shows two different and interplaying processes involving a metal complex and organic radicals, which play a key role in the controlled radical polymerization of vinyl acetate by what has been termed “Organometallic Mediated Radical Polymerization” (OMRP). Bis(acetylacetonato)cobalt(II), $\text{Co}(\text{acac})_2$, reversibly adds the growing radical chain (symbolized by “ $\text{M} + \text{R}^\bullet$ ”) to form a dormant metal-capped $(\text{acac})_2\text{-Co-PVAc}$ chain (“ $\text{M}-\text{R}$ ”), which contains a thermally fragile metal–carbon bond. The latter, however, in addition to the reversible radical chain dissociation, can also undergo an associative radical-chain exchange through a transition state symbolized as “ $\text{R}^\bullet \cdots \text{M} \cdots \text{R}$ ”. This is just one example of how one-electron processes involving metal complexes and radicals play a fundamental role in radical polymerization. It is the topic of the Microreview by R. Poli on p. 1513ff, covering the coordination chemistry of organic radicals and its relevance to metal-mediated radical polymerization. The background image represents a random conformation of a poly(vinyl acetate) chain segment.



MICROREVIEW

Radical Coordination Chemistry

R. Poli* 1513–1530

Radical Coordination Chemistry and Its Relevance to Metal-Mediated Radical Polymerization

Keywords: Radicals / Electron transfer / Atom transfer / Radical reactions / Polymerization / Transition metals



Radicals react with transition-metal complexes in many different ways. The type of reaction, when reversible, is relevant to the outcome of metal-mediated radical polymerizations. This article analyses all these reactivity patterns and their relevance to radical polymerization processes, attempting to identify trends and principles of general use.

SHORT COMMUNICATIONS

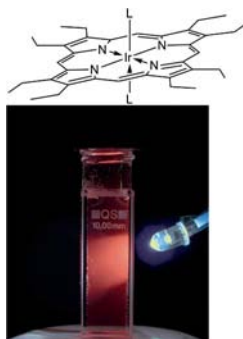
Phosphorescent Oxygen Indicators

K. Koren, S. M. Borisov,* R. Saf,
I. Klimant 1531–1534

Strongly Phosphorescent Iridium(III)–Porphyrins – New Oxygen Indicators with Tuneable Photophysical Properties and Functionalities



Keywords: Porphyrinoids / Iridium / Phosphorescence / Optical sensors / Oxygen



New Ir^{III}–porphyrin complexes were synthesized and characterized. They possess high phosphorescence quantum yields (up to 30%). Axial ligands influence their solubility and photophysical properties. Furthermore, functional groups were introduced and used for covalent coupling. Application of these dyes for designing advanced optical oxygen sensing materials is demonstrated.

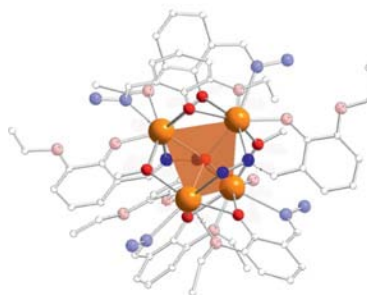
Chiral SMMs

P.-H. Lin, I. Korobkov, W. Wernsdorfer,
L. Ungur, L. F. Chibotaru,
M. Murugesu* 1535–1539

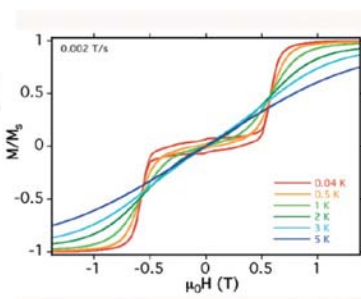
A Rare μ_4 -O Centred Dy₄ Tetrahedron with Coordination-Induced Local Chirality and Single-Molecule Magnet Behaviour



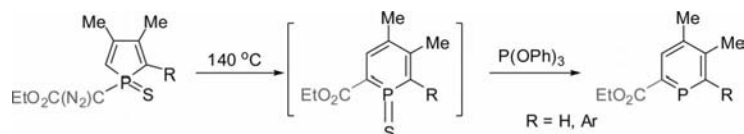
Keywords: Clusters / Magnetic properties / Single-molecule magnets / Chirality / Lanthanides



Coordination-induced chirality was achieved in a unique tetrahedral [Dy₄(μ_4 -O)(μ -OMe)₂(beh)₂(esh)₄·3MeOH] complex through a twisted diazine bridge from a Schiff base ligand. Magnetic measurements



reveal weak intramolecular antiferromagnetic interactions ($J = -0.3 \text{ cm}^{-1}$) with single-molecule magnet behaviour ($U_{\text{eff}} = 23.42 \text{ K}$).



Upon heating, 1-diazoalkylphosphole sulfides are converted into phosphinine sulfides whose in situ reduction by triphenylphosphite affords the dicoordinate

phosphanes. The corresponding trivalent phospholes easily decompose but do not give phosphinines.

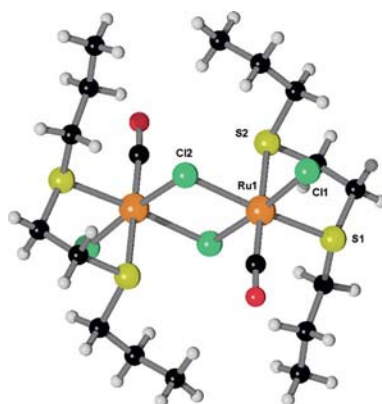
H. Chen, J. Li, H. Wang, H. Liu,
Z. Duan,* F. Mathey* 1540–1543

Investigating the Phospholylcarbene to Phosphinine Conversion

Keywords: Heterocycles / Phosphorus / Arsenic / Carbenes / Density functional calculations

FULL PAPERS

Irradiation of $[\text{Ru}_3(\text{CO})_{12}]$ in THF in the presence of thioether ligands yields ruthenium–carbonyl compounds $[\text{Ru}_4(\text{CO})_{13}(\mu_2\text{-R}_2\text{S})]$ in the case of monodentate ligands, but $[\text{Ru}_3(\text{CO})_{10}(\text{RS}\cap\text{SR})]$ and $[\text{Ru}_3(\text{CO})_8(\text{RS}\cap\text{SR})_2]$ if bidentate thioether ligands are used. The latter may be oxidatively cleaved by CHCl_3 to produce the dinuclear complex $[\text{Ru}_2(\text{CO})_2(\mu_2\text{-Cl})_2\text{Cl}_2(\text{RS}\cap\text{SR})_2]$.

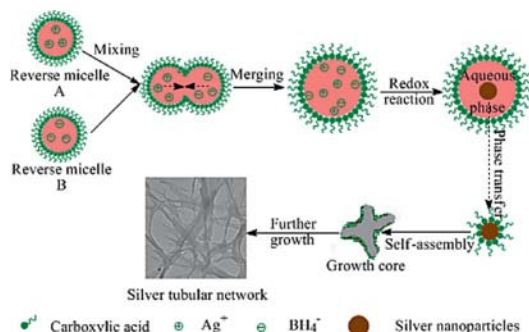


Ruthenium–Thioether Complexes

B. K. Maiti, H. Görls, O. Klobes,
W. Imhof* 1545–1552

Photochemical Synthesis of Ruthenium–Carbonyl Compounds with Thioether Ligands and Subsequent Oxidative Cleavage of Trinuclear Complexes by Chlorinated Solvents

Keywords: Ruthenium / Carbonyl ligands / Thioether ligands / Photochemistry / X-ray diffraction



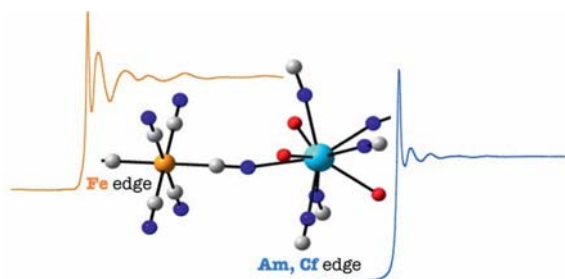
A novel tubular network assembled from silver nanoparticles was fabricated from a

lauric acid-assisted reverse micellar solution.

G. Yan, L. Wang,* H. Yu, L. Zhang,
J. Gao, J. Wang, L. Ma, Y. Zhao, Q. Wu,
A. M. Amin 1553–1559

A Tubular Network Assembled from Silver Nanoparticles

Keywords: Silver / Nanotubes / Nanoparticles / Tubular network / Conducting materials / Micelles



Two new members of hexacyanoferrate molecular solids were synthesized with the elements americium and californium. The local atomic order around the actinide

atoms was characterized by EXAFS and also compared with lanthanide parent structures.

Am and Cf Hexacyanoferrates

G. Dupouy, I. Bonhoure, S. D. Conradson,
T. Dumas, C. Hennig, C. Le Naour,
P. Moisy, S. Petit, A. C. Scheinost,
E. Simoni, C. Den Auwer* 1560–1569

Local Structure in Americium and Californium Hexacyanoferrates – Comparison with Their Lanthanide Analogues

Keywords: Actinides / Americium / Californium / X-ray absorption spectroscopy / EXAFS spectroscopy

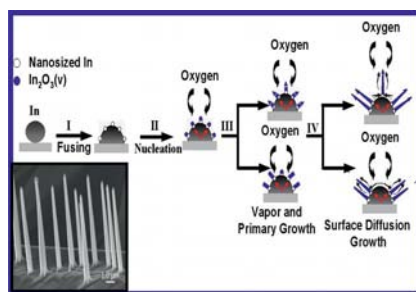
CONTENTS

Indium Oxide Nanowire Arrays

W. Yin, M. Doty, C. Ni, C. Hu,*
M. Cao,* B. Wei* 1570–1576

Vertically Well-Aligned In_2O_3 Cone-Like Nanowire Arrays Grown on Indium Substrates

Keywords: Indium / Nanostructures / Chemical vapor deposition / Arrays / Luminescence



Cone-like In_2O_3 nanowire (NW) arrays were synthesized on the surface of indium grains by using a simple chemical vapor deposition method and a possible mechanism was proposed for their formation. The indium grains served both as the indium source and the substrate for the growth of the cone-like In_2O_3 NW arrays. Their emission properties in a wide visible/infrared range indicate their potential applications in optoelectronics and phototherapy.

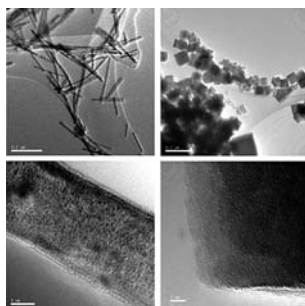
Nanophosphors

Y. Yoshida, S. Fujihara* 1577–1583



Shape-Controlled Synthesis and Luminescent Properties of $\text{CeO}_2\text{:Sm}^{3+}$ Nanophosphors

Keywords: Rare earths / Samarium / Cerium / Nanoparticles / Nanomaterials / Luminescence



$\text{CeO}_2\text{:Sm}^{3+}$ nanorods and nanocubes were selectively synthesized by hydrothermal treatments of aqueous solutions. The nanocubes exhibited much better photoluminescent properties than the nanorods, which can be explained by shape-induced structural defects.

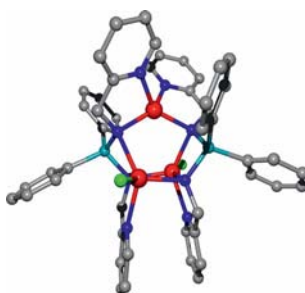
Ligand Degradation at Iron

A. Malassa, B. Schulze, B. Stein-Schaller,
H. Görls, B. Weber,
M. Westerhausen* 1584–1592



Influence of *N*-Substitution on the Oxidation of 2-Pyridylmethylamines with Bis(trimethylsilyl)amides of Iron(III) – Synthesis of Heteroleptic Iron(II) 2-Pyridylmethylamides

Keywords: Iron / Oxidation / Pyridylmethylamide ligands / Magnetic properties



Complexes of 3d metals with substituted 2-pyridylmethylamide ligands show rich protonation/deprotonation and redox chemistry. Diphenylphosphanyl substituents add also ligand degradation reactions leading to the formation of phosphonium moieties in $[(\text{ClFe})_2\{\text{Ph}_2\text{P}(\text{N-CH}_2\text{-2-Py})_2\}-\{\mu\text{-N}(\text{SiMe}_3)_2\}]$; Fe (red), Cl (green), N (blue), P (light blue), (grey) C.

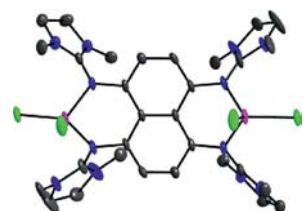
Redox-Active Guanidines

V. Vitske, P. Roquette, S. Leingang,
C. Adam, E. Kaifer, H. Wadepohl,
H.-J. Himmel* 1593–1604

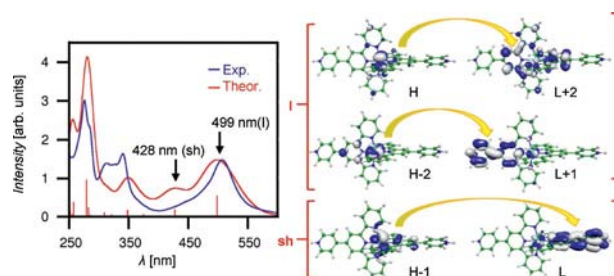


Donor-Acceptor Couples and Late Transition Metal Complexes of Oxidation-Labile 1,4,5,8-Tetrakis(guanidino)naphthalene Superbases

Keywords: Nickel / Cobalt / Copper / Dinuclear complexes / Donor-acceptor systems / Redox chemistry / Magnetic properties / Superbases / Guanidines



Redoxactive and superbasic are the two guanidine ligands ttmgm and tdmgn, the chemistry of which is analysed in this article.



A DFT/TDDFT study has been carried out to examine the pH-dependent photophysical properties of $[\text{Ru}(\text{tpy-py})_2]^{2+}$. The pH dependence is due to the presence of the basic nitrogen atom on the terminal

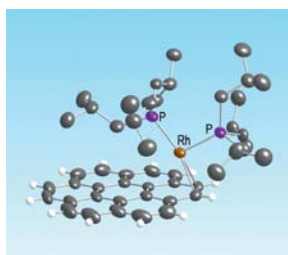
pyridyl groups. A good agreement between theory and experiment was found, reproducing the redshift of the absorption spectrum and rationalizing the emission upon increasing pH.

M. G. Lobello, S. Fantacci, A. Credi,
F. De Angelis* 1605–1613

pH-Sensitive Bis(2,2':6',2''-terpyridine)ru-
thenium(II) Complexes – A DFT/TDDFT
Investigation of Their Spectroscopic
Properties

Keywords: Photophysics / Density func-
tional calculations / Protonation / UV/Vis
spectroscopy / Luminescence / Ruthenium

A range of polyaromatic hydrocarbons of increasing size (naphthalene through corone) have been prepared and their solid-state and solution structures investigated.

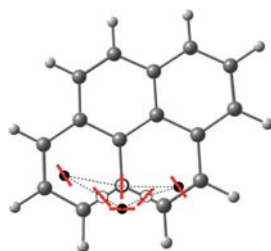


A. Woolf, A. B. Chaplin, J. E. McGrady,
M. A. M. Alibadi, N. Rees, S. Draper,
F. Murphy, A. S. Weller* 1614–1625

$\{\text{Rh}(\text{PiBu}_3)_2\}^+$ Fragments Ligated to
Arenes: From Benzene to Polyaromatic
Hydrocarbons, Part I – An Experimental
Approach

Keywords: Rhodium / Arenes / Arene li-
gands / Pi interactions / Hydrocarbons /
Polyaromatic hydrocarbons

Unavoidable compromises between the electronic demands of the $\{\text{Rh}(\text{PiBu}_3)_2\}^+$ fragment and the aromatic ligand lead to low barriers to haptotropic shifts in complexes of pyrene and coronene.

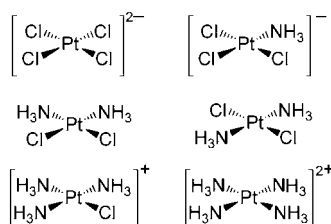


A. Woolf, M. A. M. Alibadi,
A. B. Chaplin, J. E. McGrady,*
A. S. Weller 1626–1634

$\{\text{Rh}(\text{PiBu}_3)_2\}^+$ Fragments Ligated to
Arenes: From Benzene to Polyaromatic
Hydrocarbons, Part II – Computational
Analysis of Pathways for Haptotropic
Migration

Keywords: Density functional calculations /
Rhodium / Arene ligands / Arenes / Pi in-
teractions / Hydrocarbons / Polyaromatic
hydrocarbons

The interaction between double-stranded DNA (ds-DNA) and six neutral, anionic or cationic Pt complexes $[\text{PtCl}_n(\text{NH}_3)_{4-n}]^{(2-n)}$ ($n = 0-4$) was evaluated by using an electrochemical DNA biosensor. This interaction was measured as a function of the variation in the guanine oxidation signal of the metal–DNA adduct deposited onto the electrode.



M. Ravera, E. Gabano, M. Sardi,
M. Alessio, D. Osella* 1635–1639

Electrochemical Biosensor Assay of the In-
teraction between $[\text{PtCl}_n(\text{NH}_3)_{4-n}]^{(2-n)}$
($n = 0-4$) Complexes and ds-DNA

Keywords: Platinum / DNA / Biosensors /
Drug design / Electrochemistry

CONTENTS

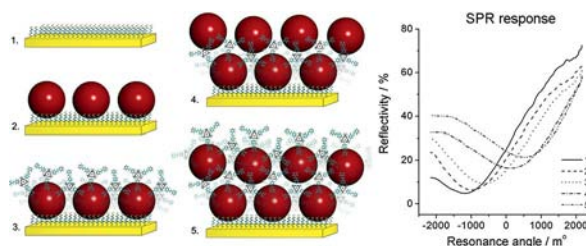
Au/Ru Hybrid Materials

S. H. Toma, J. J. Santos, K. Araki,*
H. E. Toma 1640–1648



Supramolecular Approach to Gold Nanoparticle/Triruthenium Cluster Hybrid Materials and Interfaces

Keywords: Gold / Ruthenium / Nanoparticles / Cluster compounds / Raman spectroscopy



A coordinative layer-by-layer approach has been exploited to fabricate hybrid films of gold nanoparticles and $[\text{Ru}_3(\text{CH}_3\text{COO})_6(\text{L})_3]^+$ triruthenium cluster complexes [L = 4-cyanopyridine, 4,4'-bipyridine, 4,4'-bis-

(pyridyl)ethylene] as bridging ligands. The binding constants and stabilities depend upon the ligands L as follows: $\text{bpe} > 4,4'\text{-bpy} \gg 4\text{-CNpy}$. Their electrocatalytic properties have been evaluated.

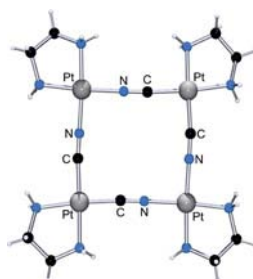
Metallacycles

A. Galstyan, P. J. Sanz Miguel, J. Wolf,
E. Freisinger, B. Lippert* 1649–1656



Discrete Molecular Squares $\{[(\text{en})\text{M}(\text{CN})_4]^{4+}\}$ Derived from $[(\text{en})\text{M}(\text{CN})_2]$ (M = Pt^{II} , Pd^{II})

Keywords: Cyanides / Platinum / Palladium / Metallacycles / Model nucleobases



Cationic molecular squares composed of $(\text{en})\text{M}$ (M = Pt^{II} , Pd^{II}) corners and cyanide bridges have been prepared and details of their formation and reactivity have been studied.

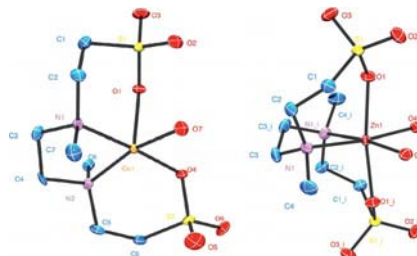
Antiviral Transition-Metal Complexes

S. García-Gallego, M. J. Serramía,
E. Arnaiz, L. Díaz,
M. A. Muñoz-Fernández,*
P. Gómez-Sal, M. F. Ottaviani,
R. Gómez,* F. J. de la Mata* ... 1657–1665



Transition-Metal Complexes Based on a Sulfonate-Containing N-Donor Ligand and Their Use as HIV Antiviral Agents

Keywords: Inhibitors / Antiviral agents / Transition metals / N,O ligands / HIV



A sulfonate-containing N-donor ligand readily forms complexes with transition metals (Ni , Co , Cu and Zn). All of them have been tested as HIV anti-viral agents both in pre- and post-infected cells and show dual preventive and therapeutic behaviour.

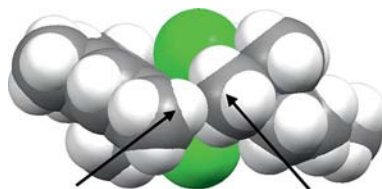
Radical Polymerization

S. Gulli, J.-C. Daran, R. Poli* ... 1666–1672



Synthesis and Structure of Four-Coordinate Copper(II) Complexes Stabilized by β -Ketiminato Ligands and Application in the Reverse Atom-Transfer Radical Polymerization of Styrene

Keywords: Copper / Functionalized ligands / Radical reactions / Polymerization / Polystyrene



Neutral monochlorido- Cu^{II} complexes with (dialkylamino)ethyl-functionalized β -ketiminato ligands have been synthesized, structurally characterized, and shown to control the radical polymerization of styrene under reverse atom-transfer radical polymerization (ATRP) conditions.

* Author to whom correspondence should be addressed.

Supporting information on the WWW (see article for access details).

This article is available online free of charge (Open Access).

If not otherwise indicated in the article, papers in issue 9 were published online on March 14, 2011