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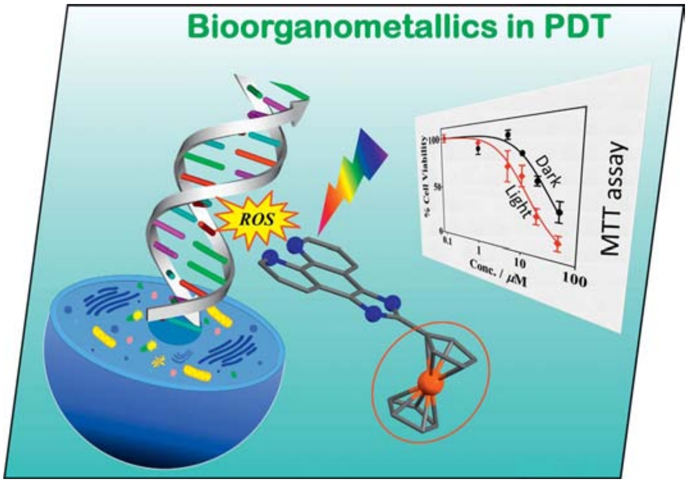
COVER PICTURE

The cover picture shows "bioorganometallics in PDT" in which a ferrocene-conjugated imidazophenanthroline derivative exhibits significant photocytotoxic effects in human cervical cancer HeLa cells in visible light, while being less cytotoxic in the unexposed state. The compound is also an efficient DNA snapper in visible light. Details are discussed in the article by A. R. Chakravarty et al. on p. 1379ff.



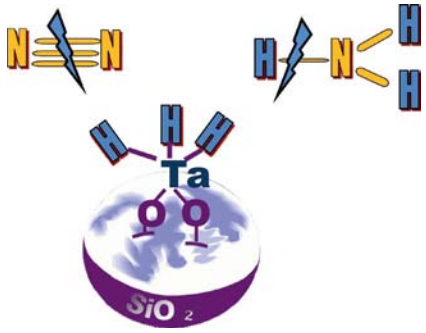
MICROREVIEW

Ammonia and Dinitrogen Activation

C. Chow, M. Taoufik,
E. A. Quadrelli* 1349–1359

Ammonia and Dinitrogen Activation by Surface Organometallic Chemistry on Silica-Grafted Tantalum Hydrides

Keywords: Dinitrogen / Ammonia / Tantalum / Hydrides / Surface chemistry



Isolated Ta^{III} and Ta^{V} hydride centres $[(\equiv SiO)_2TaH]$ and $[(\equiv SiO)_2TaH_3]$ supported on a silica surface cleave N_2 with H_2 at 250 °C and atmospheric pressure and activate NH_3 at room temperature to yield the Ta^{V} amido imido product $[(\equiv SiO)_2Ta(=NH)(NH_2)]$. Their synthesis by surface organometallic chemistry (SOMC), reactivity toward C–H and C–C bonds of alkanes and this new reactivity toward the N≡N and N–H bonds are reviewed from a mechanistic point of view.

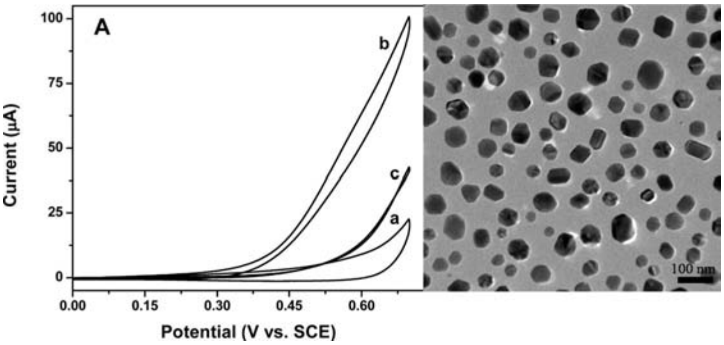
SHORT COMMUNICATION

Nanoelectrocatalysts

L. Xu, J. X. Xia, H. M. Li,* H. N. Li,
K. Wang, S. Yin 1361–1365

Ionic Liquid Assisted Solvothermal Synthesis of Cu Polyhedron-Pattern Nanostructures and Their Application as Enhanced Nanoelectrocatalysts for Glucose Detection

Keywords: Copper / Ionic liquids / Solvothermal synthesis / Nanostructures / Non-enzymatic electrocatalysis



A new synthesis of Cu polyhedron-pattern stable and small-sized nanocrystals by ethylene glycol solvothermal reduction in the presence of an ionic liquid is reported. Moreover, the electrocatalytic activity of electrodes modified with these Cu nanostructures towards glucose oxidation was investigated by cyclic voltammetry. They exhibited good non-enzymatic electrocatalytic response to glucose in alkaline media.

Silica-Grafted Lanthanum Species

B. Revel, L. Delevoye,
G. Tricot, M. Rastätter,
M. Kuzdrowska, P. W. Roesky,*
R. M. Gauvin* 1366–1369

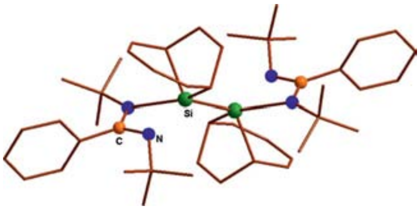
A Well-Defined Silica-Supported Lanthanum Bis(phosphinimino)methanide

Keywords: Lanthanum / P ligands / Silica / Surface chemistry / Solid-state NMR spectroscopy

The bis(phosphinimino)methanide complex $[La\{L\}\{N(SiHMe_2)_2\}_2]$ {L = $CH(PPh_2NSiMe_3)_2$} has been grafted onto dehydroxylated silica (SiO_2-700), affording a material decorated with $[(\equiv SiO)La\{L\}\{N(SiHMe_2)_2\}]$ surface species along with $[\equiv SiOSiHMe_2]$ sites.

Silicon Chemistry

Treatment of bis(silylene) LSi–SiL [L = PhC(N*t*Bu)$_2$] with cyclooctatetraene in toluene afforded a complex with intact Si–Si bond, whereas the Si–N(ligands) bonds are cleaved. The product was characterized by multinuclear NMR spectroscopy and single-crystal X-ray diffraction studies. This is one of the rare reactions with bis(silylene) without cleavage of the central Si–Si bond.

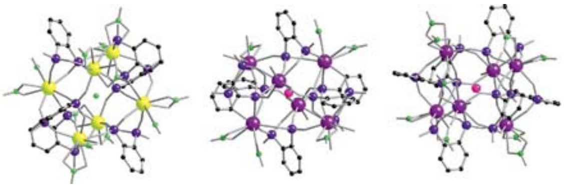


S. S. Sen, S. Khan, D. Kratzert, H. W. Roesky,* D. Stalke 1370–1373

Reaction of a Base-Stabilized Bis(silylene) [PhC(N*t*Bu)$_2$Si]$_2$ with Cyclooctatetraene without Cleavage of the Si–Si Bond

Keywords: Silicon / Alkynes / Cyclooctatetraene / Cycloaddition / N ligands

4f and 5f Clusters



Six hexanuclear anionic clusters of Ce^{IV}, Th^{IV}, and Pu^{IV} were prepared by room-temperature slow concentration. The change in ionic radius from Pu^{IV} to Th^{IV} of approximately 0.0§ allows for the cavity size to be tuned, and the clusters to preferentially bind cations that are best suited to the size of the cavities.

J. Diwu, J. J. Good, V. H. DiStefano, T. E. Albrecht-Schmitt* 1374–1377

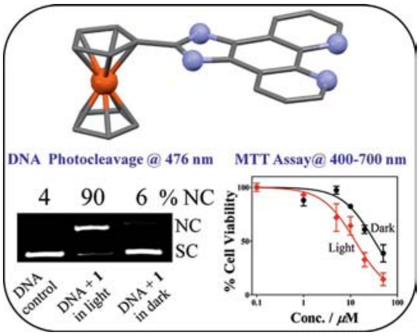
Self-Assembly of Hexanuclear Clusters of 4f and 5f Elements with Cation Specificity

Keywords: Self-assembly / Cluster / Cerium / Thorium / Plutonium

FULL PAPERS

Cytotoxic Ferrocene Conjugates

2-Ferrocenylimidazophenanthroline is a potent bioorganometallic photodynamic therapy (PDT) agent that shows plasmid DNA photocleavage activity and cytotoxicity in HeLa cancer cells under visible light with moderate dark toxicity. Nuclear staining experiments suggest an apoptotic cell death mechanism.



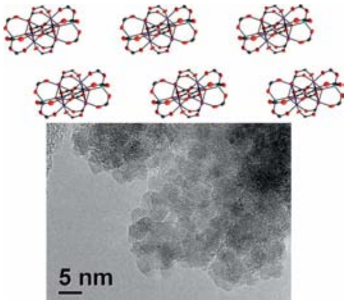
B. Maity, B. V. S. K. Chakravarthi, M. Roy, A. A. Karande, A. R. Chakravarty* 1379–1386

DNA Photocleavage and Cytotoxic Properties of Ferrocene Conjugates

Keywords: Metallocenes / Iron / DNA cleavage / Cytotoxicity / Photodynamic therapy

Heterobimetallic Carbamates

The void in a new heterobimetallic Mn/Zn carbamate complex can be filled with oxygen. The complex in its oxidized and reduced form is a precursor to magnetic oxide nanoparticles (ZnMn$_2$O$_4$/MnO) under mild conditions.



D. Domide, O. Hübner, S. Behrens, O. Walter, H. Wadepohl, E. Kaifer, H.-J. Himmel * 1387–1394

Synthesis and Reactivity of a New Oxidation-Labile Heterobimetallic Mn$_6$Zn$_2$ Carbamate Cluster and Precursor to Nanosized Magnetic Oxide Particles

Keywords: Zinc / Manganese / Cluster compounds / Magnetic properties / Oxido ligands / Oligonuclear complexes / Carbamates

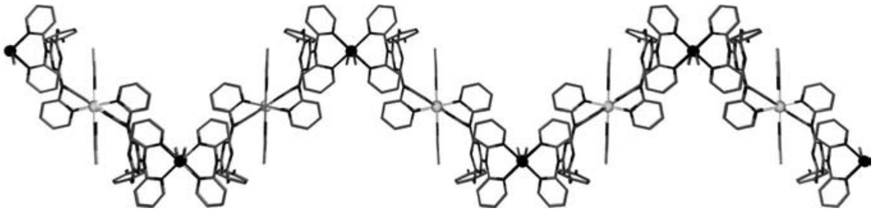
CONTENTS

Spin Crossover Polymers

T. M. Ross, B. Moubaraki, D. R. Turner, G. J. Halder, G. Chastanet, S. M. Neville, J. D. Cashion, J.-F. Létard, S. R. Batten, K. S. Murray* **1395–1417**

Spin Crossover and Solvate Effects in 1D Fe^{II} Chain Compounds Containing Bis(dipyridylamine)-Linked Triazine Ligands

Keywords: Iron / Spin crossover / 1D coordination polymers / Magnetic properties / LIESST / Mössbauer effect / Solvates



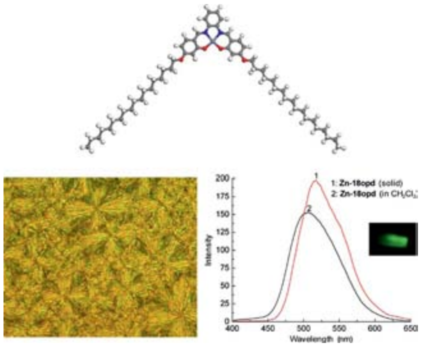
New polymeric spin crossover compounds of type *trans*-[Fe^{II}(NCX)$_2$(L)]·Solvent have been synthesised and characterised. In some cases ordered HS-LS Fe^{II} sites are observed at low temperatures, and LIESST and Mössbauer effect measurements have been made. Powder and single-crystal X-ray data are used to draw magnetostructural correlations.

Photoluminescent Metallomesogen

C. R. Bhattacharjee,* G. Das, P. Mondal, S. K. Prasad, D. S. S. Rao **1418–1424**

Novel Green Light Emitting Nondiscoid Liquid Crystalline Zinc(II) Schiff-Base Complexes

Keywords: Zinc / Metallomesogens / Luminescence / Density functional calculations



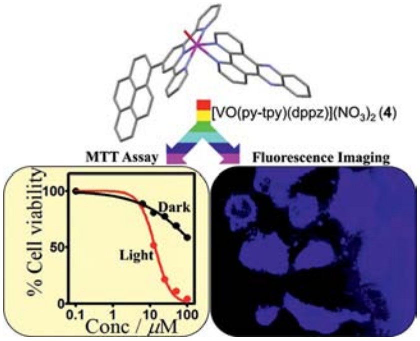
A series of novel photoluminescent Zn^{II} complexes of [N$_2$O$_2$] donor Schiff base have been synthesised. The ligands are nonmesogenic but their complexes exhibit columnar mesomorphism showing a crossover from primitive rectangular to a thermally stable monoclinic oblique type.

Oxovanadium Complexes

B. Banik, P. K. Sasmal, S. Roy, R. Majumdar, R. R. Dighe, A. R. Chakravarty* **1425–1435**

Terpyridine Oxovanadium(IV) Complexes of Phenanthroline Bases for Cellular Imaging and Photocytotoxicity in HeLa Cells

Keywords: Medicinal chemistry / Vanadium / DNA cleavage / Antitumor agents / Imaging agents / Photodynamic therapy / Cytotoxicity



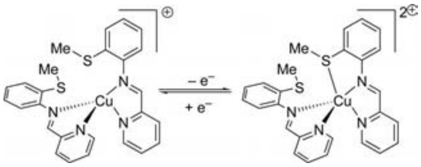
Terpyridine oxovanadium(IV) complexes of planar phenanthroline bases are potent metal-based PDT agents showing plasmid DNA cleavage activity in near-IR light of 785 nm and photocytotoxicity in HeLa cancer cells in visible light with low dark toxicity. The pyrenyl-terpyridine (py-tpy) VO^{2+} complex of dppz is used for cellular imaging.

Copper Complexes

J. Schnödt, J. Manzur, A.-M. García, I. Hartenbach, C.-Y. Su, J. Fiedler, W. Kaim* **1436–1441**

Coordination of a Hemilabile N,N,S Donor Ligand in the Redox System [CuL$_2$]$^{+/2+}$, L = 2-Pyridyl-*N*-(2′-alkylthiophenyl)methyleneimine

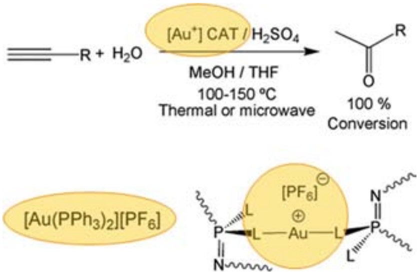
Keywords: Copper / Diimines / Ligand effects / S ligands / Redox chemistry



Fully reversible electron transfer was observed (spectro)electrochemically for a Cu^{I}/Cu^{II} complex redox system containing a tridentate (2N+S donor) ligand.

Supported Gold(I) Catalysts

The complex [Au(PPh$_3$)$_2$]PF$_6$ (**C1**) catalyses the specific hydration of different terminal alkynes in the presence of H$_2$SO$_4$, specially using microwave radiation. The phosphazene polymeric framework (**C2**), and the cyclomatrix material (**C3**), both having cationic [-Ph$_2$P-Au$^+$-PPh$_2$-] cross-linking sites, catalysed the complete hydration of terminal alkynes.



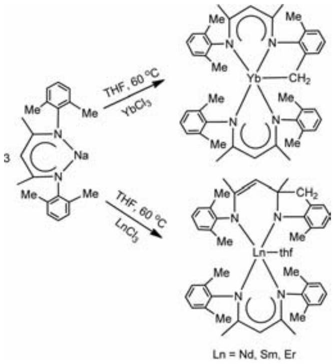
G. A. Carriedo,* S. López,
S. Suárez-Suárez, D. Presa-Soto,
A. Presa-Soto 1442–1447

Covalently Bonded Bis(phosphane)gold(I) Cations in a Cross-Linked Phosphazene Polymeric Matrix as Recyclable Supported Catalysts for Thermal and Microwave-Assisted Hydration of Alkynes

Keywords: Alkynes / Supported catalysts / Gold / Phosphane ligands / Hydration of alkynes / Polyphosphazene

Sterically Induced Deprotonation

The attempted synthesis of sterically demanding tris(β-diketiminato)lanthanide complexes led to the deprotonation of the β-diketiminato ligand with the formation of novel complexes, depending on the lanthanide metal used.



R. Jiao, M. Xue, X. Shen, Y. Zhang,
Y. Yao, Q. Shen* 1448–1453

Deprotonation of β-Diketiminate in Sterically Demanding β-(Diketiminato)lanthanide Complexes: Influence of Lanthanide Metals

Keywords: Lanthanide complexes / N ligands / Diketiminato ligand / Deprotonation / Metalation / Steric hindrance

Lithiosilanes

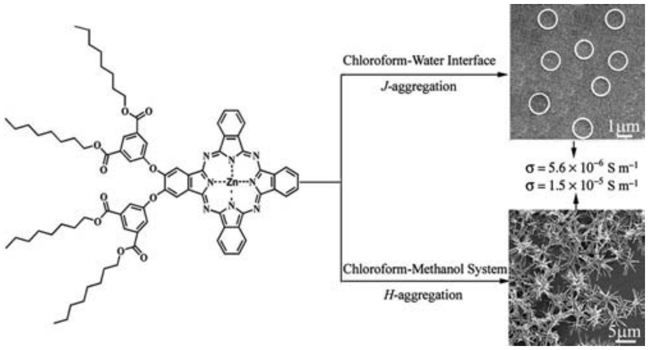
On the basis of detailed experimental and supporting quantum chemical studies, the reaction of enantiomerically pure lithiosilanes and halo electrophiles has been investigated. It was found that the obtained product composition and enantiomeric ratio is strongly influenced by both the organic group as well as the halide of the used trapping reagent as a result of competing reaction mechanisms.

C. Däschlein, S. O. Bauer,
C. Strohmann* 1454–1465

Mechanistic Insights into the Reaction of Enantiomerically Pure Lithiosilanes and Electrophiles: Understanding the Differences between Aryl and Alkyl Halides

Keywords: Silicon / Lithium / Silanes / Lithiosilanes / Substituent effects / Reaction mechanisms / Chirality

Phthalocyanine Nanostructures



An unsymmetrical (phthalocyaninato)zinc complex has been synthesized and, through a self-assembly process, converted into *J*- and *H*-type nanostructures with ring- and star-shaped morphologies, respectively. Current–voltage (*I*–*V*) measurements revealed the star-shaped nanostructures to have better semiconducting properties than the ring-shaped nanostructures.

N. Tian, P. Ma, Q. Wang, X. Zhang,
J. Jiang,* M. Bai* 1466–1472

Ring-Shaped *J*-Type and Star-Shaped *H*-Type Nanostructures of an Unsymmetrical (Phthalocyaninato)zinc Complex

Keywords: Phthalocyanines / Self-assembly / Nanostructures / Aggregation

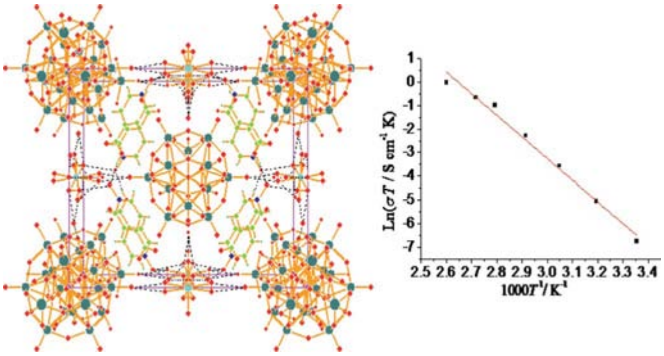
CONTENTS

Protonic Conductivity

M.-L. Wei,* P.-F. Zhuang, H.-H. Li, Y.-H. Yang 1473–1478

Crystal Structures and Conductivities of Two Organic–Inorganic Hybrid Complexes Based on Poly-Keggin-Anion Chains

Keywords: Organic-inorganic hybrid composites / Conducting materials / Polyoxometalates / Structure elucidation



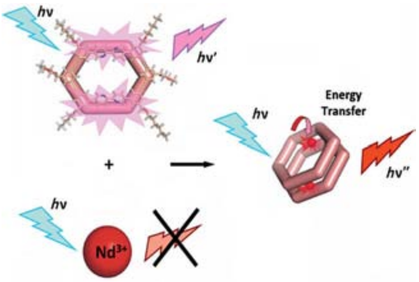
Two molecular hybrids with hydrogen-bonding networks have been constructed by the self-assembly of ionized water clusters and poly-Keggin-anion chains and their structures were determined by single-crystal X-ray diffraction. Both complexes showed high proton conductivities of 10^{-3} S cm^{-1} in the temperature range of 85–100 °C under 98% relative humidity.

Luminescent Macrocycles

M. E. Gallina, C. Giansante, P. Ceroni,* M. Venturi, J. Sakamoto, A. D. Schlüter 1479–1486

Shape-Persistent Macrocycles as Ligands and Sensitisers of Nd^{3+} Ions

Keywords: Lanthanides / NIR emitters / Light-harvesting antenna / Macrocycles



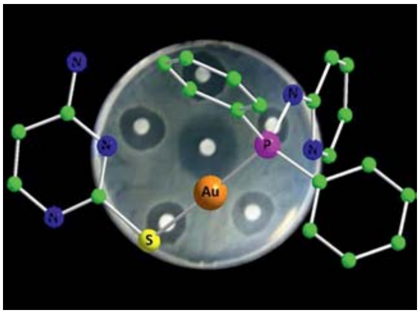
Shape-persistent macrocycles with a hexagonal backbone and incorporating two bipyridine moieties bind Nd^{3+} ions with formation of complexes with 1:2, 1:1 and 2:1 metal to ligand stoichiometries. The NIR emission of the lanthanide is efficiently sensitised by the macrocycle shown aside even in air-equilibrated solution and the resultant system shows a high brightness.

Gold Thiolate Complexes

M. F. Fillat, M. C. Gimeno,* A. Laguna, E. Latorre, L. Ortego, M. D. Villacampa* 1487–1495

Synthesis, Structure and Bactericide Activity of (Aminophosphane)gold(I) Thiolate Complexes

Keywords: Gold / Biological activity / P ligands / Thiols / X-ray diffraction



Gold(I) complexes with aminophosphane and thiolato ligands have been prepared, and the susceptibility of several Gram-positive and Gram-negative bacteria towards these complexes has been evaluated. Some of the complexes show excellent activity towards Gram-positive microorganisms.

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* Author to whom correspondence should be addressed.

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