

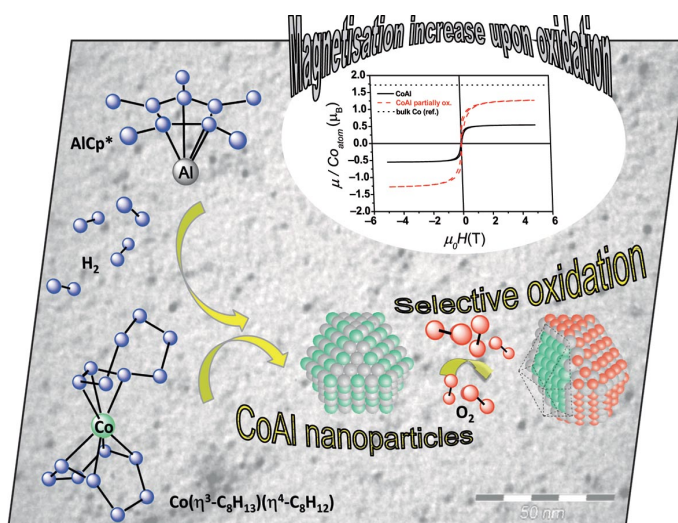


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COVER PICTURE

The cover picture shows the reaction path followed to produce bimetallic CoAl nanoparticles (background image). Organometallic precursors such as AlCp^* and $\text{Co}(\eta^3\text{-C}_8\text{H}_{13})(\eta^4\text{-C}_8\text{H}_{12})$ offer the unique advantage of being easily reduced under dihydrogen, thus enabling access to alloyed β -CoAl nanoparticles as evidenced by X-ray absorption and diffusion techniques. As expected, these nanoparticles are highly reactive towards oxygen. The reaction starts with the selective oxidation of Al, with simultaneous segregation of Co. Known in the bulk, this phenomenon is studied for the first time on the nanometer scale. It is clearly evidenced by SQUID measurements: an increase in the ratio of segregated Co atoms is accompanied by an increase in the magnetization of the nanoparticles. To passivate the system, excess aluminum must be decomposed on top of the CoAl nanoparticles. This study evidences the relevance of organometallic chemistry for nanoalloy engineering. Details are discussed in the Short Communication by C. Amiens et al. on p. 1599.



SHORT COMMUNICATIONS

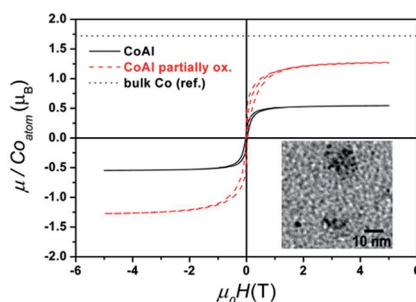
Nano-Alloy Engineering

M. Cokoja, H. Parala, A. Birkner,
R. A. Fischer, O. Margeat, D. Ciuculescu,
C. Amiens,* B. Chaudret, A. Falqui,
P. Lecante 1599–1603



Organometallic Synthesis of β -CoAl Nanoparticles and β -CoAl/Al Nanoparticles and Their Behaviour upon Air Exposure

Keywords: Nanoparticles / Alloys / Synthetic methods / Core-shell nanoparticles / Passivation



β -CoAl nanoparticles have been prepared by a soft organometallic route. The alloy character of the bimetallic nanoparticles was demonstrated by wide-angle X-ray scattering and X-ray absorption techniques. Upon air exposure, the magnetisation of these nanoparticles first increases suggesting the formation of a $\text{Co}/\text{Al}_2\text{O}_3$ nanocomposite, then collapses upon full oxidation of the material. Core/shell CoAl/Al nanoparticles, of increased air stability, were also prepared by a seed-mediated growth process.

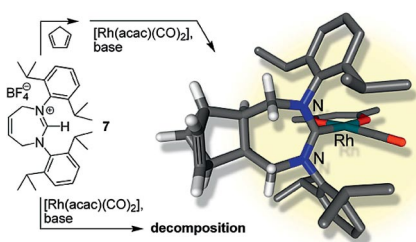
N-Heterocyclic Carbenes

M. Iglesias, D. J. Beetstra, K. J. Cavell,*
A. Dervisi,* I. A. Fallis,* B. Kariuki,
R. W. Harrington, W. Clegg, P. N. Horton,
S. J. Coles,
M. B. Hursthouse 1604–1607



Expanded-Ring and Backbone-Functionalised N-Heterocyclic Carbenes

Keywords: Carbene ligands / Cycloaddition / Rhodium / Ligand design / Isomers



Although the direct reaction of the unsaturated amidinium salt **7** with metal precursors results in decomposition, **7** undergoes a facile Diels-Alder cycloaddition with cyclopentadiene to afford a sterically encumbered amidine salt from which Rh^{I} complexes may be prepared. Thus, in a short versatile synthesis, it is possible to prepare sterically crowded NHC complexes bearing a peripheral alkene functionality.

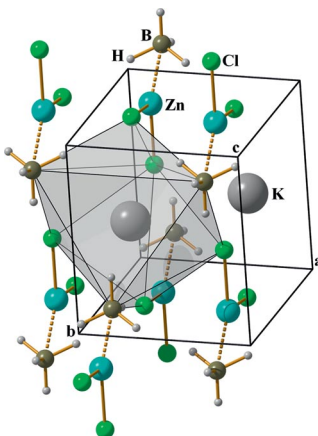
Mixed Anion/Cation Borohydrides

D. B. Ravnsbæk, L. H. Sørensen,
Y. Filinchuk, D. Reed, D. Book,
H. J. Jakobsen, F. Besenbacher,
J. Skibsted, T. R. Jensen* 1608–1612



Mixed-Anion and Mixed-Cation Borohydride $\text{KZn}(\text{BH}_4)\text{Cl}_2$: Synthesis, Structure and Thermal Decomposition

Keywords: Hydrides / X-ray diffraction / Solid-state structures / Solid-phase synthesis / Transition metals



An addition reaction between ZnCl_2 and KBH_4 yields $\text{KZn}(\text{BH}_4)\text{Cl}_2$, which is synthesized for the first time. The structure of this compound contains the complex anion $[\text{Zn}(\text{BH}_4)\text{Cl}_2]^-$, extending the structural diversity of mixed alkali and d-block metal borohydrides. This class of materials also reveals low decomposition temperatures.

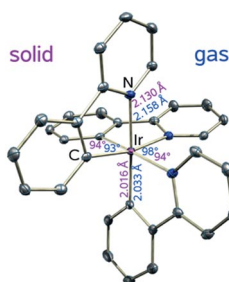
OLED Basis Compound

R. J. F. Berger,* H.-G. Stammer,
B. Neumann, N. W. Mitzel* 1613–1617



fac- $\text{Ir}(\text{ppy})_3$: Structures in the Gas-Phase and of a New Solid Modification

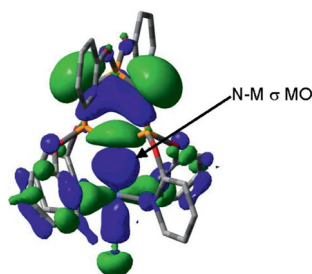
Keywords: Iridium / OLED / Structure determination / Gas electron diffraction



The gas-phase structure of the classical OLED triplet emitter compound *fac*- $\text{Ir}(\text{ppy})_3$ was determined and a hitherto unknown, second modification of the compound was obtained by sublimation. Possible implications for an accurate quantum-chemical description of the electronic structure and some results from prior investigations are discussed in the light of the new results.

FULL PAPERS

DFT calculations show that the phosphazene ring nitrogen acts as a σ donor towards divalent transition metal ions. The lengthening of the PN bonds flanking the metal coordination site can be explained as a result of electron density that is transferred from ring PN bonding orbitals to the 4s orbital of the metal ion rather than a decrease in the extent of π -bonding as suggested by earlier models.



Metal–Phosphazene Bonding

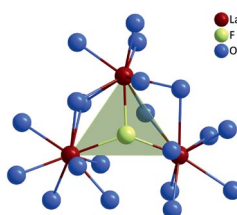
R. J. Davidson, E. W. Ainscough,*
A. M. Brodie,* J. A. Harrison,
M. R. Waterland 1619–1625

The Nature of the Phosphazene Nitrogen–Metal Bond: DFT Calculations on 2-(Pyr-idyloxy)cyclophosphazene Complexes



Keywords: Phosphazenes / Transition metals / Density functional calculations / Metal–ligand bonds

Coordination environment of oxygen atoms around the triangular $[\text{FLa}_3]^{8+}$ units in the crystal structure of $\text{La}_3\text{FMo}_4\text{O}_{16}$. The triangles are arranged according to a two-dimensional hexagonally close-packed layer within the (100) plane. All oxygen atoms belong either to three tetrahedral $[\text{MoO}_4]^{2-}$ anions or to dimers $[\text{Mo}_2\text{O}_8]^{4-}$ consisting of two edge-sharing quadrangular pyramids.



Lanthanum Oxomolybdates

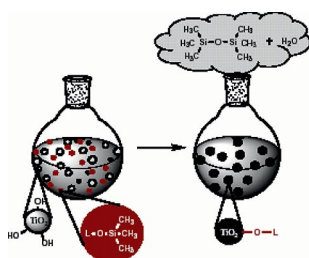
I. Hartenbach,* S. Strobel, T. Schleid,
B. Sarkar, W. Kaim, P. Nockemann,
K. Binnemans, P. K. Dorhout ... 1626–1632

Synthesis, Structure, and Spectroscopic Properties of the New Lanthanum(III) Fluoride Oxomolybdate(VI) $\text{La}_3\text{FMo}_4\text{O}_{16}$



Keywords: Lanthanum / Fluorine / Molybdates / Solid-state structures / Luminescence

The direct covalent bonding of an OH-bearing molecule onto a metal oxide surface can easily be achieved by *O*-trimethylsilylation. This group reacts with OH on the solid matrix, thus resulting in the grafting of the organic molecule onto the surface. Trimethylsilanol is formed and can easily be eliminated as volatile hexamethyldisiloxane and water.



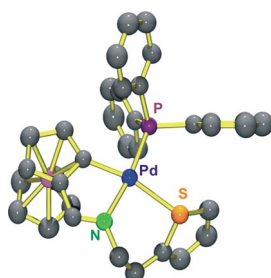
Covalent Grafting

H. Arzoumanian,* N. J. Castellanos,
F. O. Martínez, E. A. Pérez-Mozo,
F. Ziarelli 1633–1641

Silicon-Assisted Direct Covalent Grafting on Metal Oxide Surfaces: Synthesis and Characterization of Carboxylate $\text{N,N}'$ -Li-gands on TiO_2

Keywords: Titanium oxide / Ligand grafting / Molybdenum / Oxidation

Novel palladium(II) complexes with $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{S}(\text{thienyl})]^-$ ligands have been prepared and characterized. The study of their reactivity in front of PPh_3 under different experimental conditions reveals that the $\sigma(\text{Pd}-\text{S})$ bond is more labile than in their analogue with a $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{S}(\text{thioether})]^-$ ligand.



Palladacycles with Polydentate Ligands

D. Pou, C. López,* Sonia Pérez,
X. Solans, M. Font-Bardía,
P. W. N. M. van Leeuwen,
G. P. F. van Strijdonck 1642–1648

Study on the Lability of the $\sigma(\text{Pd}-\text{S})$ Bond of Novel Palladacycles with $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{S}(\text{thienyl})]^-$ Pincer Ligands



Keywords: Palladium / Palladacycles / Sandwich complexes / Ferrocene derivatives / Pincer ligands

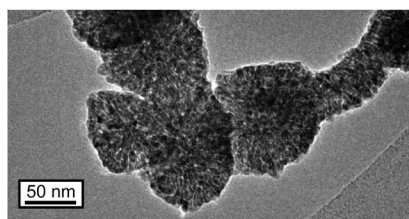
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Zinc Oxide Nanoparticles

M. Estruga,* C. Domingo,
J. A. Ayllón* 1649–1654

Mild Synthetic Routes to High-Surface
Zinc Oxide Nanopowders

Keywords: Zinc / Mesoporous materials /
Nanoparticles / Synthesis design / Semi-
conductors



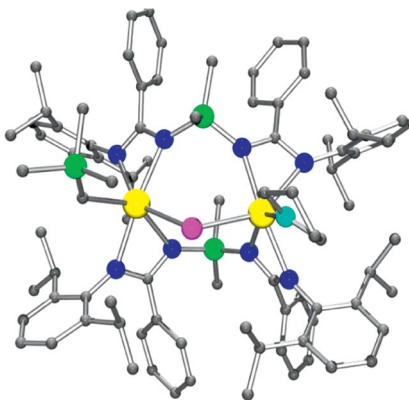
High-surface wurtzite ZnO nanopowders were obtained by thermal decomposition of two different precursors at 90 °C for 150 h: (i) commercial zinc acetate dihydrate and (ii) a solid mixture obtained after evaporation of a solution of zinc acetate in aqueous ammonia. The proposed methods are mild and involve very simple equipment.

Rare Earth Hydrides

G. G. Skvortsov, A. O. Tolpyguin,
G. K. Fukin, A. V. Cherkasov,
A. A. Trifonov* 1655–1662

Dinuclear Chlorido-, Alkyl(chlorido)-, and
Hydrido-tertrium Complexes Supported by
 μ -Bridging-Silyl-Linked Bis(amidinate)
Ligands

Keywords: Rare earths / N ligands / Alkyl
complexes / Hydrido complexes / Structure
elucidation



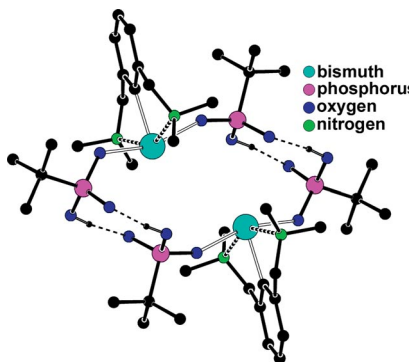
Dinuclear chlorido-, alkyl(chlorido)-, and hydrido-tertrium complexes, featuring “spanning” coordination modes of silyl-bridged bis(amidinate) ligands, were synthesized.

Sb and Bi Organophosphonates

T. Svoboda, R. Jambor, A. Růžicka,
Z. Padělková, M. Erben, R. Jirásko,
L. Dostál* 1663–1669

NCN-Chelated Organoantimony(III) and
Organobismuth(III) Phosphonates: Syn-
theses and Structures

Keywords: Antimony / Bismuth / Phos-
phorus / Chelates / X-ray diffraction



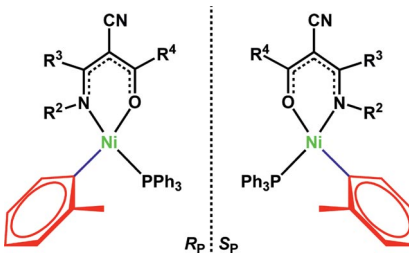
The synthesis of molecular organoantimony and organobismuth phosphonates, where the central antimony or bismuth atom is stabilized by the NCN pincer-type ligand $[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]^-$, is described. The structures of the studied compounds were determined both in solution and in the solid state.

Planar Chirality

U. Beckmann,* G. Hägele,
W. Frank 1670–1678

Square-Planar 2-Toluenido(triphenylphos-
phane)nickel(II) Complexes Containing Bi-
dentate N,O Ligands: An Example of
Planar Chirality

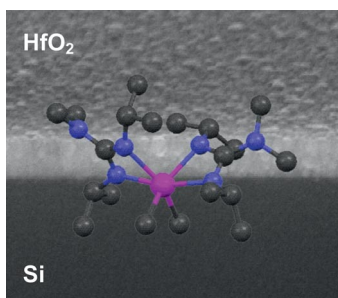
Keywords: Nickel / Chirality / N,O ligands /
Homogeneous catalysis / Polyketones



Several arenidonickel(II) complexes of different β -enaminonic *N,O*-chelating ligands are presented. Rotation around the Ni–C bond is hindered, and thus planar chirality is introduced. Such complexes are active catalysts in the copolymerisation of ethene and CO.

Hafnium Precursors for MOCVD

Two new guanidinate- and amidinate-based hafnium compounds were characterized in detail and evaluated for their use in metalorganic chemical vapor deposition (MOCVD) of HfO_2 thin films. Stoichiometric HfO_2 thin films with a preferred orientation were grown on Si(100) substrates.



K. Xu, A. P. Milanov, M. Winter,
D. Barreca, A. Gasparotto, H.-W. Becker,
A. Devi* 1679–1688

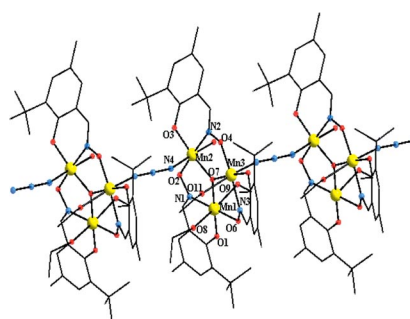
Heteroleptic Guanidinate- and Amidinate-Based Complexes of Hafnium as New Precursors for MOCVD of HfO_2



Keywords: Hafnium oxide / Chemical vapor deposition / Thin films / Precursors

Mn(III) Single-Chain Magnets

Two homospin manganese single-chain magnets were synthesized, in which $[\text{Mn}^{\text{III}}_3\text{O}]$ clusters are bridged by formate or azide ligands. Both complexes show slow relaxation of their magnetizations associated with single-chain magnet behavior.



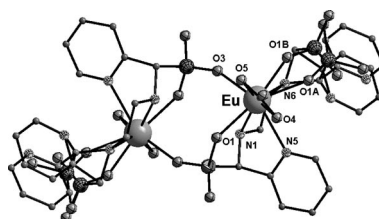
X. Song, P. Yang, X. Mei, L. Li,*
D. Liao 1689–1695

1D Chains Constructed from Oxido-Centered $[\text{Mn}_3\text{O}]$ Units Exhibiting Single-Chain Magnet Behavior

Keywords: Magnetic properties / Manganese / Chain structures / Structure elucidation

Lanthanide Complexes

Coordination studies involving {ethane-1,2-diylbis[imino(pyridin-2-ylmethanediyl)]}-bis(phosphonic acid) and a series of Ln^{III} ions revealed rarely observed differences in the solid-state and solution binding-mode of the metal ion.



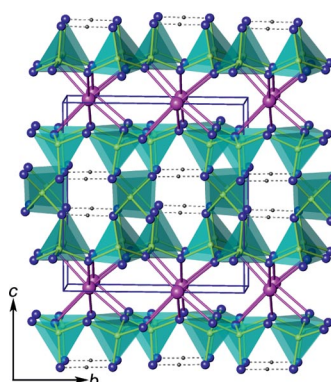
J. Gałęzowska,* R. Janicki,*
H. Kozłowski, A. Mondry, P. Młynarz,
Ł. Szyrwił 1696–1702

Unusual Coordination Behaviour of a Phosphonate- and Pyridine-Containing Ligand in a Stable Lanthanide Complex

Keywords: Lanthanides / N,P ligands / Stability constants / Coordination modes

Borate Networks

The structure of $\text{H}_2\text{InB}_5\text{O}_{10}$ is made up of InO_6 octahedra layers and 2D tetrahedrally four-connected borate layers. The 2D borate network, formed by two 6^3 borate layers combined with additional BO_4 groups in a spiro-5 mode, exhibits a new pentaborate fundamental building block, B_5O_{14} . The strong hydrogen bonds that cross-link oxygen atoms inside the 2D borate layer help to stabilize the network.



R. H. Cong, T. Yang, H. M. Li,
F. H. Liao, Y. X. Wang,*
J. H. Lin* 1703–1709

$\text{H}_2\text{InB}_5\text{O}_{10}$: A New Pentaborate Constructed from 2D Tetrahedrally Four-Connected Borate Layers and InO_6 Octahedra



Keywords: Borates / Indium / X-ray diffraction / Network structures / Hydrogen bonds

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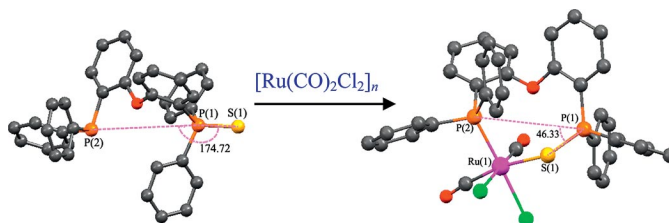
Functionalized Chelating Diphosphanes

B. Deb, P. P. Sarmah,
D. K. Dutta* 1710–1716



Synthesis of Dicarbonylruthenium(II) Complexes of Functionalized P,S-Chelating Diphosphane Ligands and Their Catalytic Transfer Hydrogenation

Keywords: Ruthenium / P ligands / S ligands / Hydrogenation / Carbonyl ligands



Two new Ru^{II} complexes of P,S-chelating diphosphane ligands [bis(2-diphenylphosphanylphenyl)ether monosulfide] (**a**) and [9,9-dimethyl-4,5-bis(diphenylphosphanyl)-xanthene monosulfide] (**b**) have been syn-

thesized. The complex with **a** exhibits a significantly higher catalytic activity in transfer hydrogenation reactions than that of ligand **b**, which has a rigid backbone.

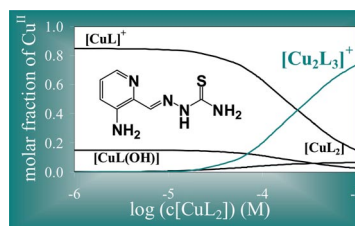
Thiosemicarbazone Complexes

É. A. Enyedy,* N. V. Nagy, É. Zsigó,
C. R. Kowol,* V. B. Arion, B. K. Keppler,
T. Kiss 1717–1728



Comparative Solution Equilibrium Study of the Interactions of Copper(II), Iron(II) and Zinc(II) with Triapine (3-Aminopyridine-2-carbaldehyde Thiosemicarbazone) and Related Ligands

Keywords: Antitumor agents / Stability constants / EPR spectroscopy / Transition metals / Thiosemicarbazones



Complex formation of Triapine and two N-terminally dimethylated derivatives with Cu^{II}, Fe^{II} and Zn^{II} was studied by pH potentiometry, UV/Vis, EPR, and ¹H NMR spectroscopy and ESI-MS in aqueous solution. pK_a and log β values were determined. N-terminally dimethylated thiosemicarbazones were found to be much more potent chelators than Triapine for these divalent metal ions.

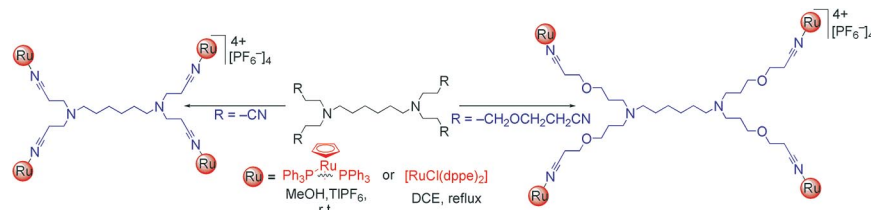
Ruthenium Dendrimers

M. G. Jardim, K. Rissanen,*
J. Rodrigues* 1729–1735



Preparation and Characterization of Novel Poly(alkylidenamine) Nitrile Ruthenium Metallo dendrimers

Keywords: Ruthenium / Dendrimers / Sandwich complexes / Polynuclear complexes / N ligands



A new family of nitrile-functionalized poly(alkylidenamine) dendrimer cores with an extended inner chain and extended lateral

branches was prepared and fully functionalized with the ruthenium moieties [Ru(η⁵-C₅H₅)(PPh₃)₂]⁺ and [RuCl(dppe)₂]⁺.

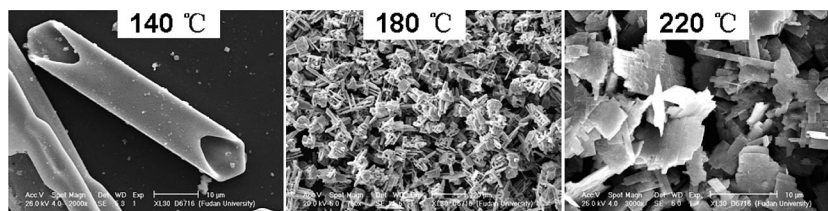
Superstructure Growth

X. Guo,* J. Yang, Y. Deng, H. Wei,
D. Zhao* 1736–1742



Hydrothermal Synthesis and Photoluminescence of Hierarchical Lead Tungstate Superstructures: Effects of Reaction Temperature and Surfactants

Keywords: Lead / Tungsten / Self-assembly / Surfactants / Morphology



Lead tungstate (PbWO₄) crystals with distinct hierarchical superstructures, including flat tubular and rod-shaped arrays, as well as complex slab structures, have been successfully synthesized in the presence of tri-

block copolymer poly(ethylene oxide)poly(propylene oxide)poly(ethylene oxide) (PEO₂₀PPO₇₀PEO₂₀, P₁₂₃) under mild hydrothermal conditions.

* Author to whom correspondence should be addressed.

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

If not otherwise indicated in the article, papers in issue 10 were published online on March 22, 2010