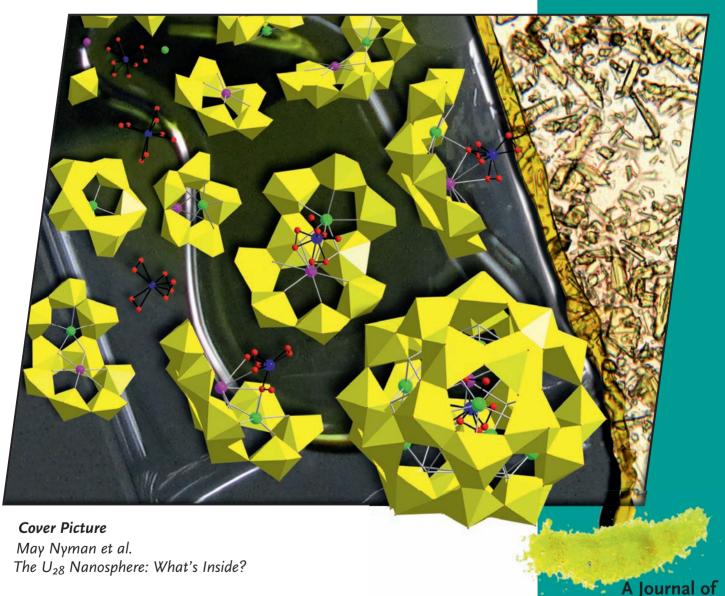


14/2011 2nd May Issue



ChemPubSoc





www.eurjic.org

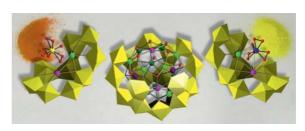
# **FULL PAPERS**

#### **Uranium Cluster**

M. Nyman,\* M. A. Rodriguez, T. M. Alam ...... 2197–2205

 $\square$  The  $U_{28}$  Nanosphere: What's Inside?

**Keywords:** Cluster compounds / Peroxides / Polyanions / Polyoxometalates / Uranium

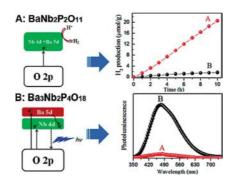


Reproducible, high-yield syntheses of uranyl peroxide polyoxometalates have been developed by strategic choice of internal templating cations and anions. We demonstrate irrefutably these clusters can be redissolved intact: a key point to fully developing the chemistry of actinide polyoxometalates.

## Ba-Nb- Phosphate Compounds

Electronic Band Structure, Optical Properties, and Photocatalytic Hydrogen Production of Barium Niobium Phosphate Compounds (BaO-Nb<sub>2</sub>O<sub>5</sub>-P<sub>2</sub>O<sub>5</sub>)

**Keywords:** Solid-phase synthesis / Ceramics / Electronic structure / Luminescence / Water splitting



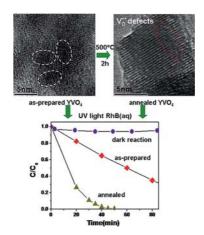
Two barium niobium phosphate compounds ( $BaNb_2P_2O_{11}$  and  $Ba_3Nb_2P_4O_{18}$ ) were prepared by a conventional solid-state reaction method. Although both compounds have similar optical band gaps (ca. 3.6 eV), their optical and photocatalytic behavior differs due to their different conduction band constructions, which results from their different crystal structure environments.

#### **Yttrium-Vanadate Nanocrystals**

L. Yang, G. Li, W. Hu, M. Zhao, L. Sun, J. Zheng, T. Yan, L. Li\* ........ 2211-2220

Control Over the Crystallinity and Defect Chemistry of YVO<sub>4</sub> Nanocrystals for Optimum Photocatalytic Property

**Keywords:** Vanadium / Yttrium / Nanoparticles / Crystal engineering / Photocatalysis



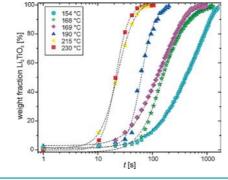
YVO<sub>4</sub> nanocrystals with controlled crystallinity and surface chemical states were successfully prepared. It is demonstrated that YVO<sub>4</sub> nanocrystals with high crystallinity and sufficient oxygen vacancies show optimum photocatalytic performance.

# **In-situ Synchrotron Diffraction**

A. Laumann, K. M. Ørnsbjerg Jensen, C. Tyrsted, M. Bremholm, K. T. Fehr, M. Holzapfel, B. B. Iversen\* ... 2221–2226

In-situ Synchrotron X-ray Diffraction Study of the Formation of Cubic Li<sub>2</sub>TiO<sub>3</sub> Under Hydrothermal Conditions

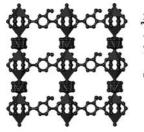
**Keywords:** Kinetics / Reaction mechanisms / Hydrothermal synthesis / Titanium / Lithium / Synchrotron diffraction

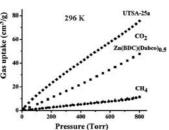


Hydrothermal syntheses, following the reaction  $TiO_2(s) + 2 LiOH(aq) \rightarrow Li_2-TiO_3(s) + H_2O(l)$ , are studied in-situ by synchrotron powder X-ray diffraction at varying temperatures. The formation of cubic  $Li_2TiO_3$  shows increasing reaction rates at higher temperatures, which enables the determination of the activation energy.



## Metal-Organic Frameworks





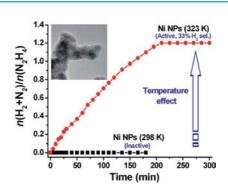
The 3D microporous metal—organic framework (MOF) Zn(BDC-OH)(DABCO)<sub>0.5</sub> (UTSA-25a; H<sub>2</sub>BDC-OH = 2-hydroxybenzenedicarboxylic acid, DABCO = 1,4-diazabicyclo[2.2.2]octane) with func-

tional -OH groups on the pore surfaces exhibits much higher selective  $CO_2/CH_4$  separation than the original MOF  $Zn(BDC)(DABCO)_{0.5}$  at ambient temperatures

Significantly Enhanced  ${\rm CO_2/CH_4}$  Separation Selectivity within a 3D Prototype Metal-Organic Framework Functionalized with OH Groups on Pore Surfaces at Room Temperature

**Keywords:** Zinc / Microporous materials / Adsorption / Immobilization / Gas separation / Carbon dioxide

A drastic enhancement in the catalytic performance of Ni nanoparticles, which are inactive for the decomposition of hydrous hydrazine to hydrogen at room temperature, was observed with an increase of reaction temperature to 323 K. This temperature effect has been exploited to achieve  $100\%~H_2$  selectivity from hydrous hydrazine decomposition by alloying Ni and Pt with a Pt content as low as 1 mol-%.

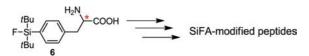


## **Hydrogen Generation**

Temperature-Induced Enhancement of Catalytic Performance in Selective Hydrogen Generation from Hydrous Hydrazine with Ni-Based Nanocatalysts for Chemical Hydrogen Storage

**Keywords:** Nickel / Hydrogen / Hydrazine / Nanostructures / Temperature effects

## <sup>18</sup>F-Labelled Peptides



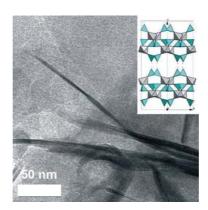
Both enantiomers of the SiFA-modified phenylalanine were synthesized and characterized. They are key compounds for the efficient synthesis of a large variety of SiFA-modified peptides, which, in turn, hold great potential for the development of novel <sup>18</sup>F-labelled radiopharmaceuticals.

SiFA-Modified Phenylalanine: A Key Compound for the Efficient Synthesis of <sup>18</sup>F-Labelled Peptides

**Keywords:** Fluorine / Silicon / Radiopharmaceuticals / Synthesis design / Enantioselectivity / Amino acids

#### Intercalations

The synthesis of lamellar microporous titanosilicate AM-4 has been improved by varying the Ti source, autoclave time, and seeding. UZAR-S2 has been obtained by swelling and exfoliation of small crystals of AM-4.



C. Casado, D. Ambroj, Á. Mayoral, E. Vispe, C. Téllez,

J. Coronas\* ...... 2247-2253

Synthesis, Swelling, and Exfoliation of Microporous Lamellar Titanosilicate AM-4

**Keywords:** Intercalations / Layered compounds / Adsorption / Organic—inorganic hybrid composites / Zeolite analogues

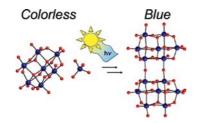
# **CONTENTS**

#### Photoreduction



Synthesis, Structure, and Photochemistry of an Organic Heptamolybdate-Monomolybdate

**Keywords:** Photochemistry / Polyoxometalates / Molybdenum / Reduction



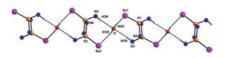
 $\label{eq:colorless} \begin{array}{ll} Colorless & (BuNH_3)_8[(Mo_7O_{24})(MoO_4)] \\ 3H_2O \ (BuNH_3 = butan-1-aminium), which contains heptamolybdate and monomolybdate anions, is easily transformed to the blue dimer & (BuNH_3)_{10}[(Mo_7O_{22})(\mu_2-O)_2-(Mo_7O_{22})] \\ \cdot 5.5H_2O \ under \ sun \ irradiation. \end{array}$ 

## **Selenium Hydrogen Bonding**

P. Chandrasekaran, J. T. Mague, M. S. Balakrishna\* ...... 2264–2272

Synthesis and Derivatization of the Bis-(amido)- $\lambda^3$ -cyclodiphosphazanes cis-[R'-(H)NP( $\mu$ -NR)]<sub>2</sub>, Including a Rare Example, trans-[tBu(H)N(Se)P( $\mu$ -NCy)]<sub>2</sub>, Showing Intermolecular Se···H-O Hydrogen Bonding

**Keywords:** Chalcogens / Selenium / Phosphorus / Heterocycles / Hydrogen bonds



Bis(amido)- $\lambda^3$ -cyclodiphosphazanes, *cis*-[R'(H)NP( $\mu$ -NR)]<sub>2</sub>, were prepared and converted into their P<sup>V</sup> derivatives of the type *cis*-[R'(H)N(E)P( $\mu$ -NR)]<sub>2</sub> [E = O, S, Se, N=P(O)(OPh)<sub>2</sub>]. An intermolecular Se···H-O hydrogen bond between *trans*-[tBu(H)N(Se)P( $\mu$ -NCy)]<sub>2</sub> and H<sub>2</sub>O was observed.

## **Schiff Base Complexes**

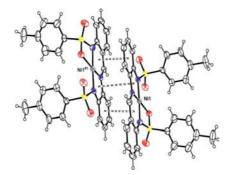
A. Sousa-Pedrares, J. A. Viqueira, J. Antelo, E. Labisbal, J. Romero, A. Sousa, O. R. Nascimento,

J. A. García-Vázquez\* ...... 2273-2287



Synthesis and Characterization of Homoleptic and Heteroleptic Cobalt, Nickel, Copper, Zinc and Cadmium Compounds with the 2-(Tosylamino)-*N*-[2-(tosylamino)-benzylidene]aniline Ligand

**Keywords:** Copper / Cobalt / Nickel / Zinc / Cadmium / Transition metals / Schiff bases / Structure elucidation / Hydrogen bonds / Stacking interactions / Electrochemistry



Homo- and heteroleptic metal(II) complexes (Co, Ni, Cu, Zn and Cd) containing the 2-(tosylamino)-N-[2-(tosylamino)benzylidene]aniline ligand have been synthesized by an electrochemical procedure and characterized by various spectroscopic techniques and single-crystal X-ray diffraction.

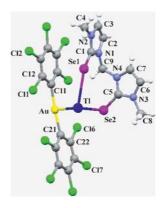
## **Organodiselone Ligands**

M. Arca, T. Aroz, M. Concepción Gimeno, M. Kulcsar, A. Laguna, T. Lasanta, V. Lippolis,\* J. M. López-de-Luzuriaga,\* M. Monge, M. E. Olmos ....... 2288–2297



Homopolynuclear Tl<sup>I</sup> and Heteropolynuclear Au<sup>I</sup>-Tl<sup>I</sup> Complexes with Organodiselone Ligands: Activation of Luminescence by Intermetallic Interactions

**Keywords:** Gold / Thallium / Selenium ligands / Luminescence / Density functional calculations

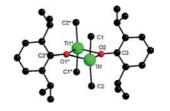


Homopolynuclear  $Tl^I$  and heteropolynuclear  $Au^I - Tl^I$  complexes that bear organodiselone ligands have been synthesized. The luminescence of the Au - Tl derivatives has been analyzed experimentally and theoretically through DFT calculations.



## Thallium-Chalcogen Interactions

X-ray structural analysis of dimeric  $[Me_2TIO(2,6-R_2C_6H_3)]_2$  (R=H,Me,iPr,Ph) shows significant structural changes due to the increased steric bulk of the phenoxide ligand. Sufficient steric bulk is present when R=tBu to facilitate isolation of a monomeric species. DFT calculations were employed to rationalize the observed structures.

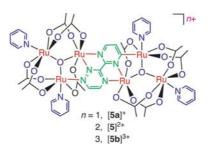


Structural Effects of Varied Steric Bulk in 2,(4),6-Substituted Dimethylthallium(III) Phenoxides

**Keywords:** Thallium / O ligands / Density functional calculations / Structure elucidation

## Mixed-Valence Chemistry

Dimeric species of triruthenium cluster moieties exhibit six reversible one-electron redox processes and rich mixed-valence chemistry with strong cluster—cluster interactions across the asymmetric bis(tridentate) triazine ligand.



Spectroscopic, Electrochemical, and DFT Studies of Oxo-Centered Triruthenium Cluster Complexes with a Bis(tridentate) Triazine Ligand

**Keywords:** Ruthenium / Cluster compounds / N ligands / Redox chemistry / Density functional calculations

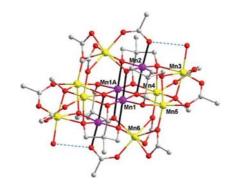
# **Modifiable Magnetic Anisotropy**

J.-D. Leng, L.-Y. Dian, J.-L. Liu, M.-L. Tong\* ...... 2317–2326

A Series of  ${\rm Mn^{III}_4Mn^{II}_8}$  Single-Molecule Magnets Mediated by Intra- and Intermolecular Interactions

**Keywords:** Manganese / Tripodal ligands / Molecular interactions / Magnetic properties / Single-molecule magnets

A series of valence-sandwich-type Mn<sup>III</sup><sub>4</sub>Mn<sup>III</sup><sub>8</sub> clusters were synthesized by solvothermal reaction. Magnetization studies reveal that they all behave as single-molecule magnets (SMMs) and the ground-state anisotropy of four clusters are effectively modified by intra- and intermolecular interactions by substituting tripodal ligands and terminal ligands.

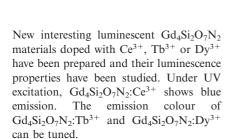


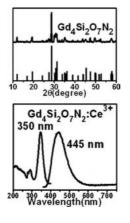
## **Tunable Phosphors**

Y. Song, N. Guo, H. You\* ..... 2327-2332

Synthesis and Luminescent Properties of Cerium-, Terbium-, or Dysprosium-Doped  $Gd_4Si_2O_7N_2$  Materials

**Keywords:** Cerium / Terbium / Dysprosium / Luminescence





<sup>\*</sup> 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 13 were published online on April 20, 2011