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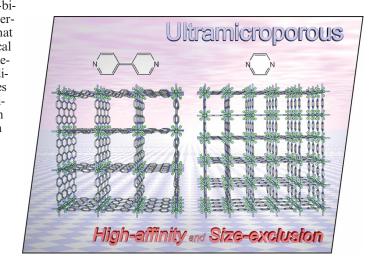




A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further members of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the two journals.

# COVER PICTURE

The cover picture shows two crystal structures of porous coordination polymers, [Cu(SiF<sub>6</sub>)(4,4'- $[Zn(SiF_6)(pyz)_2]_n$  (4,4'-bpy = 4,4'-bipyridine, pyz = pyrazine), which have been generated from square-grid coordination polymers that are cross-linked by μ-SiF<sub>6</sub> anions. Although typical bridging ligands such as 4,4'-bpy and 1,4-benzenedicarboxylate produce open octahedral coordination polymers with micropores, such micropores need to be further narrowed to become ultramicropores (< 7 Å) for separation and purification of smaller gas molecules. We have succeeded in obtaining the ultramicroporous coordination polymer  $[\text{Zn}(\text{SiF}_6)(\text{pyz})_2]_n$  with  $4.5 \pm 4.5 \text{ Å}^2$ pores by simply replacing 4,4'-bpy in  $[M(SiF_6)(4,4'-bpy)_2]_n$  (M =  $Zn^{2+}$ ,  $Cu^{2+}$ ) with pyz. The ultramicropores of  $[Zn(SiF_6)(pyz)_2]_n$ adsorb Me<sub>2</sub>CO rather than iPrOH, showing the size-exclusive effect. Additionally, this compound shows a sharp uptake in H<sub>2</sub> adsorption at 77 K, because the interaction potential is expected to be strong as a result of the synergistic effect of the neighbouring pore walls. Details are discussed in the article by K. Uemura et al. on p. 2329ff.



# **MICROREVIEW**

## Ion-Pairing

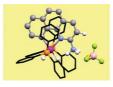
E. Clot\* ...... 2319-2328

Ion-Pairing in Organometallic Chemistry: Structure and Influence on Proton Transfer from a Computational Perspective

**Keywords:** Ion pairs / Density functional calculations / Anions / Cations / Proton transfer









Ion-pairing is not solely the result of electrostatic interaction between a positive and a negative charge. Specific geometries for ion pairs may result from H-bonding inter-

actions and could influence the thermodynamics and/or kinetics in organometallic chemistry.

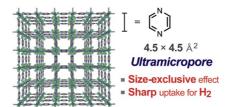
# **FULL PAPERS**

#### **Porous Coordination Polymers**



Syntheses, Crystal Structures and Adsorption Properties of Ultramicroporous Coordination Polymers Constructed from Hexafluorosilicate Ions and Pyrazine

**Keywords:** Microporous materials / Metal—organic frameworks / Adsorption / Copper / Zinc



Hexafluorosilicate/pyrazine bridging porous coordination polymers with  $4.5 \times 4.5^2$  ultramicropores were synthesized and characterized. They show a size-exclusive effect and a sharp uptake in  $H_2$  adsorption.

## Metal-Organic Frameworks

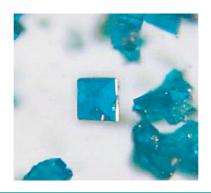
C. G. Carson, K. Hardcastle, J. Schwartz, X. Liu, C. Hoffmann, R. A. Gerhardt,

R. Tannenbaum\* ...... 2338-2343



Synthesis and Structure Characterization of Copper Terephthalate Metal-Organic Frameworks

**Keywords:** Microporous materials / Coordination polymers / Crystal engineering / Magnetic properties / Carboxylate ligands / Metal-organic frameworks



Gram quantities of copper terephthalate can be synthesized solvothermally in dmf in a matter of hours. The resulting product has crystallizes in the *C2/m* space group. When thermally activated, it exhibits the high surface area and magnetic properties associated with similar frameworks.

#### Windmill Copper(II) Complexes

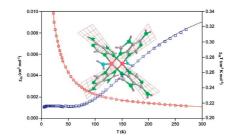
J. Cepeda, O. Castillo,\* J. P. García-Terán, A. Luque,\* S. Pérez-Yáñez,

P. Román ...... 2344-2353



Supramolecular Architectures and Magnetic Properties of Self-Assembled Windmill-Like Dinuclear Copper(II) Complexes with Purine Ligands

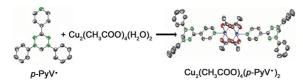
**Keywords:** Nitrogen heterocycles / Copper / Magnetic properties / Density functional calculations / Supramolecular chemistry



Three dimeric  $[Cu_2(\mu\text{-purine derivative})_4]$  entities were employed in the construction of supramolecular architectures from their self-assembly process. DFT calculations were carried out to evaluate the correlation of the exchange value with several structural parameters and the nature of the bridging ligand.



#### **Copper-Verdazyl Complex**



Pyridyl-substituted verdazyl (*p*-PyV) and the binuclear copper complex [Cu<sub>2</sub>-(OCOCH<sub>3</sub>)<sub>4</sub>(*p*-PyV)<sub>2</sub>] are synthesized and structurally characterized. Their magnetic properties are studied by ESR spectroscopy and by measuring their temperature-dependent magnetic susceptibility. Structure, Spectral and Magnetic Properties of 3-(*p*-Pyridyl)-1,5-diphenylverdazyl (*p*-PyV) and the Binuclear Copper(II) Radical Complex [Cu<sub>2</sub>(OCOCH<sub>3</sub>)<sub>4</sub>(*p*-PyV)<sub>2</sub>]

**Keywords:** Radicals / Copper / X-ray diffraction / EPR spectroscopy / Magnetic properties

# Di(pyridin-2-yl) ligands form with the $V^{IV}O^{2+}$ ion mono- and bis-chelated complexes with $(N_{pyr}, N_{pyr})$ , $(N_{pyr}, CO)$ and $(N_{pyr}, O^-)$ coordination. The amino acid derivatives promote the deprotonation and coordination of the amide nitrogen to give $[VOLH_{-1}]^+$ and $[VOLH_{-2}]$ species. The structures of the complexes and their EPR

parameters are predicted through DFT

methods.



# **Vanadium Coordination Chemistry**

L. Pisano, D. Kiss, K. Várnagy, D. Sanna, G. Micera,\* E. Garribba\* ..... 2362-2374

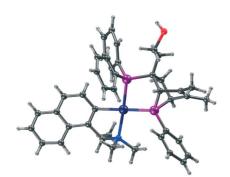
Potentiometric, Spectroscopic and DFT Study of the V<sup>IV</sup>O Complexes Formed by Di(pyridin-2-yl) Ligands



**Keywords:** Vanadium / Bioinorganic chemistry / EPR spectroscopy / Density functional calculations

# **Metal Template Synthesis**

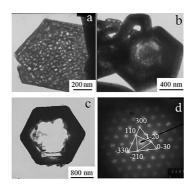
An organoplatinum complex was employed as a promoter and chiral auxiliary in the asymmetric Diels—Alder reaction of phosphane-functionalized terminal alkenols with the diene 3,4-dimethyl-1-phenylphosphole. The cycloaddition reactions proceeded smoothly at room temperature, leading to the generation of alcohol-functionalized diphosphane ligands in high yields and excellent stereoselectivities.



Enantioselective, High-Yielding Synthesis of Alcohol-Functionalized Diphosphanes Utilizing Asymmetric Control with a Chiral Auxiliary

**Keywords:** Asymmetric synthesis / Platinum / Chiral auxiliaries / Cycloaddition / P ligands

# Single-crystal LaF<sub>3</sub> with a ring-like structure is prepared by a simple molten salt route without the need for a template. The intrinsic crystallography of the sample is studied by XRD and HRTEM, and a formation mechanism involving central-etching of nanoplates is proposed on the basis of experiments performed with varying reaction times. The fluorescent properties of this compound are characterized by doping with Eu<sup>3+</sup> cation.



#### **Lanthanum Halide Nanostructures**

Synthesis and Characterization of Single-Crystalline Lanthanum Fluoride with a Ring-Like Nanostructure



**Keywords:** Molten salt synthesis / Nanostructures / Crystal growth / Lanthanum / Halides

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# **CONTENTS**

#### **Hierarchical Nanostructures**

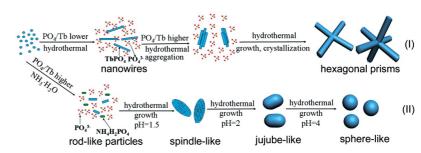
J. Bao, R. Yu,\* J. Zhang, X. Yang,

D. Wang, J. Deng, J. Chen,

X. Xing\* ...... 2388-2392

Controlled Synthesis of Terbium Orthophosphate Spindle-Like Hierarchical Nanostructures with Improved Photoluminescence

**Keywords:** Self-assembly / Hydrothermal synthesis / Luminescence / Nanostructures



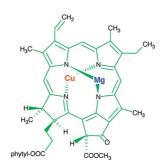
Spindle-like TbPO<sub>4</sub>·H<sub>2</sub>O hierarchical nanostructures with improved photoluminescence were prepared through a con-

trolled synthesis by using a facile templatefree hydrothermal route. The formation mechanism of the products was proposed.

#### **Metallochlorophylls Formation**

Mechanistic Information on Cu<sup>II</sup> Metalation and Transmetalation of Chlorophylls

**Keywords:** Chlorophylls / Copper / Metalation / Transmetalation / Kinetics and mechanisms

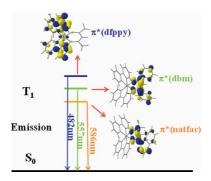


Kinetic studies on the reactions of chlorophyll a and pheophytin a with  $CuAc_2$  showed that the rates and mechanisms of these reactions depend strongly on the properties of the solvent. As a consequence, the transmetallation in MeOH leads to the formation of a stable bimetallic intermediate, whereas in MeCN it terminates at the very initial stage of the reaction.

#### **Color Tuning of Ir Complexes**

Tuning the Emission Color of Iridium(III) Complexes with Ancillary Ligands: A Combined Experimental and Theoretical Study

**Keywords:** Iridium / Ligand effects / Dyes/ Pigments / Density functional calculations / Charge transfer



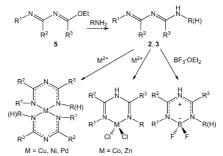
Color tuning of iridium(III) complexes is achieved by attaching electron-donating or electron-withdrawing substituents to the ancillary ligand L^X. The calculated results show that the low-lying excitations have MLCT and ILCT character. For the emission process, the main transition of FIr(acac) is [d(Ir) +  $\pi$ (C^N)  $\rightarrow \pi$ \*(C^N)] and those of FIr(dbm) and FIr(natfac) are [d(Ir) +  $\pi$ (L^X)  $\rightarrow \pi$ \*(L^X)].

#### N-Rich Bidentate Ligands

I. Häger, R. Fröhlich, E.-U. Würthwein\* ...... 2415–2428

Synthesis of Secondary, Tertiary and Quaternary 1,3,5-Triazapenta-1,3-dienes and Their Co<sup>II</sup>, Zn<sup>II</sup>, Pd<sup>II</sup>, Cu<sup>II</sup> and BF<sub>2</sub> Coordination Compounds

**Keywords:** *N*-Imidoylimidoates / Triazapentadienes / N ligands / Hydrogen bonds



The secondary and tertiary 1,3,5-triaza-penta-1,3-dienes  $\mathbf{2}$  and  $\mathbf{3}$  were prepared either from amidines and imidoyl chlorides or from N-imidoylimidoates  $\mathbf{5}$  and primary amines. Treatment with  $\mathbf{M^{II}}$  salts or  $\mathbf{BF_3}$  led to novel 1:1 and 2:1 coordination compounds with six-membered anionic or neutral triazapentadienyl chelate ligands.

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

If not otherwise indicated in the article, papers in issue 15 were published online on May 12, 2009

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