

pharmaceutical targets [1] to multiple metal binding stoichiometries [2], from the assessment of relative interdomain motions in multidomain proteins [3] to the elucidation of the structure of a protein-protein complex where one partner is largely unstructured [4].

[1] Bertini I., Calderone V., Fragai M., Lee Y.-M., Luchinat C., Mangani S., Turano, *Proc. Natl. Acad. Sci.*, in press. [2] Calderone V., Dolderer B., Hartmann H.J., Echner H., Luchinat C., Del Bianco C., Mangani S., Weser U., *Proc. Natl. Acad. Sci.*, 2005, **102**, 51. [3] Bertini I., Del Bianco C., Gelis I., Katsaros N., Luchinat C., Parigi G., Peana M., Provenzani A., Zoroddu M.A., *Proc. Natl. Acad. Sci.*, 2004, **101**, 6841. [4] Bertini I., Del Bianco C., Gupta Y., Luchinat C., Parigi G., Peana M., Zoroddu M.A., in preparation.

Keywords: NMR, protein structures, dynamics

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The Organization of the Organic Structural Framework in the Enamel Biominerization Processes

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The growth of crystals within a preformed organic structural framework (the organic matrix) is a basic mode of skeletal formation adopted by many different organisms. Protein self-assembly into ordered structures is a critical step towards the control of mineral deposition in biomining systems such as bone, teeth and mollusc shells.^[1]

Mammalian tooth enamel is the hardest tissue in the vertebrate body and is a secretory product of cells of epithelial origin called ameloblasts. Enamel mineralization is a dynamic process that includes protein secretion, matrix assembly and initiation and growth of the crystals within an amelogenin-rich matrix. The assembly of the mineralized enamel matrix continues through the transition stage during which ameloblast activity is drastically reduced and the bulk of the protein matrix is eventually processed during the maturation stage, concomitant with the rapid growth and maturation of the mineral. Supra-molecular self-assembly of the dental enamel protein amelogenin into nanospheres has been recognized to be a key factor in controlling the oriented and elongated growth of carbonated apatite crystals during dental enamel biomining. We report the formation of birefringent micro-ribbon structures that were generated through the supramolecular assembly of amelogenin nanospheres. These micro-ribbons have diffraction patterns that clearly indicate a periodic structure of crystalline units along the long axis. Linear arrays of nanospheres were observed as intermediate states prior to the micro-ribbon formation. The induction and c-axial orientated organization of apatite crystals parallel to the long axes of the micro ribbons were observed.^[2]

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Keywords: biomining, enamel, fiber diffraction

MS52 INORGANIC-ORGANIC FRAMEWORK MATERIALS

Chairpersons: Christoph Janiak, Stuart R. Batten

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High Connectivity Framework Polymers: A New Co-ordination Chemistry

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The concept of a co-ordination number and its relationship to specific co-ordination geometries describing the number and relative dispositions of ligands bound to a metal cation within a metal complex is very well established. In contrast, understanding which specific topology is associated with a particular connectivity of a metal ion within a framework polymer is less well developed, particularly for highly-connected nets. For example, 2-connected systems are

commonly associated with linear or zig-zag chains, 3-connected with ladder, brick-wall or herringbone motifs, 4-connected with (4,4) square or adamantoid cages, and 6-connected with cubic or alpha-polonium nets. Higher order frameworks of 5-, 7- and 8-connectivity are exceedingly rare, and we have developed, for the first time, a general route to such systems via the use of lanthanide nodes and N-oxide bridging ligands [1]. The use of N-oxide ligands as linkers in such systems is based upon the complementarity of hard lanthanide ions, showing relatively high co-ordination numbers, with hard O-donors. Furthermore, N-oxides do not impose severe steric constraints on binding up to eight such ligands to a lanthanide centre.

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Keywords: coordination chemistry, lanthanide, topology

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Crystals and Nanostructures: a Unique Class of Tunable Inorganic-Organic Frameworks

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An exciting and promising area of materials research that concerns chemistry and physics of inorganic-organic hybrid materials is rapidly emerging. Hybrid materials that combine the superior electronic, magnetic, optical properties and thermal stability of inorganic frameworks with the structural diversity, flexibility, high processability, and light-weight of organic molecules may reveal new phenomena and new properties, and enhance/strengthen the existing functionality and performance. Thus, they are of both fundamental and technological importance. We have recently developed a unique class of crystalline hybrid nanostructured materials with systematically tunable structures and multifunctional properties. The framework structures of these materials are composed of, at our choice, II-VI semiconductor nanometer sized motifs (inorganic component) and suitable organic spacers (organic component). They possess numerous improved properties over conventional II-VI semiconductor bulk materials, including broad band-gap tunability, high absorption coefficients, and large carrier diffusion lengths, all highly desirable for optoelectronic applications such as photovoltaics and solid state lighting. More significantly, they exhibit extremely strong quantum size effect and their nano properties can be systematically tuned by changing the structure and dimensionality of the inorganic motifs.

Keywords: inorganic-organic hybrid material, II-VI semiconductor, nanostructure

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New Molecular Architectures of Copper Imidazoles and Triazolates

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We recently exploited simple exo-bidentate and exo-tridentate ligands such as imidazoles and triazolates to generate a number of copper coordination polymers. Copper(I) cations can be conveniently generated from the hydrothermal treatments of copper(II) salts with organic ligands. A metal valence tuning approach with pH and temperature control has been utilized to generate a series of new mixed-valence Cu^I/Cu^{II} imidazolate polymers exhibiting different Cu^I/Cu^{II} ratios and topologic structures. More interestingly, using appropriate organic templates, we could also isolate a series of molecular polygons, namely octagons [Cu₈(mim)₈] and decagons [Cu₁₀(mim)₁₀]. We also found that 1,2,4-triazolates can also be prepared by hydrothermal treatments of organonitriles and ammonia in the presence of copper(II) salts. Two new 3-connected 3D networks Cu(mtz) and Cu(ptz) exhibit novel 4.8.16 and 4.12² nets. A pre-designed metal-organic building block Cu(2-pytz) offers unusual supramolecular isomers upon variations of the reaction condition.

[1] Zhang J.-P., Zheng S.-L., Huang X.-C., Chen X.-M., *Angew. Chem. Int. Ed.*, 2004, **43**, 206. [2] Zhang J.-P., Lin Y.-Y., Huang X.-C., Chen X.-M., *Chem. Commun.*, 2005, *in press*. [3] Huang X.-C., Zhang J.-P., Chen X.-M., *J. Am. Chem. Soc.*, 2004, **126**, 13218. [4] Huang X.-C., Zhang J.-P., Lin Y.-Y., Yu X.-L., Chen X.-M., *Chem. Commun.*, 2004, 1100.

Keywords: copper complex, topology, hydrothermal synthesis

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Influence of the Substituent in the Crystal Packing of Copper(II)-malonates

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The design of new molecular materials with interesting magnetic properties can be achieved following different approaches. The introduction of a secondary ligand, the combination of metal centres or the modification of the primary ligand can be some of these strategies. In the context of our magneto-structural research with malonato-bridged copper(II) complexes and in order to obtain novel coordination modes that could enhance the magnetic exchange coupling we have studied the influence of the substituted malonate ligand in copper(II) complexes.

Complexes of the form $[\text{Cu}(\text{L}^{\text{I}})(\text{H}_2\text{O})_n]$ and $[\text{Cu}(\text{L}^{\text{II}})_2(\text{H}_2\text{O})_n]$ $[\text{Cu}(\text{H}_2\text{O})_n]$ with L^{I} = malonate, ethylmalonate, methylmalonate and L^{II} = malonate, phenylmalonate, are synthesized. Crystal structures vary from the discrete units of copper(II) malonate compounds [1] to the different conformations of two-dimensional structures of ethylmalonate and methylmalonate. Overall ferromagnetic exchange coupling is found in all of these compounds.

Subtle changes in the nature of the substituent can modify the crystal packing and hence the magnetic properties present in these compounds.

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Keywords: copper coordination compounds, crystal packing, magnetic properties

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Hydrogen Storage in Metal-Organic Frameworks

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Reticular synthesis (logical construction of networks from molecular building blocks) has yielded a new class of crystalline porous materials commonly referred to as metal-organic frameworks (MOFs) in which metal ions and clusters are linked by organic units. The ability to prepare MOFs in high yield and with adjustable pore size, shape and functionality has led to their study as gas sorption materials. We have demonstrated that systematic variation of the organic component in isoreticular metal-organic frameworks (IRMOFs) has a marked effect on their capacities for methane. More recently, we discovered that IRMOFs are also capable of storing significant amounts of H_2 , and inelastic neutron scattering studies of molecular hydrogen adsorbed in IRMOF-1 pointed to the organic unit as one of the important adsorption sites. Thus, there is an acute need to collect and analyze more hydrogen uptake measurements on such materials in order to establish the favorable factors for its storage. Hydrogen adsorption isotherms measured at 77 K show a distinct dependence of uptake on the nature of the link for a set of five MOF materials containing the $\text{Zn}_4\text{O}(\text{CO}_2)_6$ cluster. At 1 atm, the materials sorb between 4.2 and 9.3 molecules of H_2 per formula unit. The results imply a trend in hydrogen capacity with the number of rings in the organic moiety. Additionally, the significant influence of the inorganic unit, namely when open metal sites are present, on hydrogen uptake will be presented.

[1] Gummow R.J., Liles D.C., *Mat. Res. Bull.*, 1993, **28**, 1293. [2] Grittane A., Pastor A., Galindo A., Ienco A., Mealli C., *Chem. Commun.*, 2003, 512.

Keywords: hydrogen storage, metal-organic frameworks, adsorption

MS53 MATERIALS FOR ENERGY CONVERSION AND STORAGE

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Electrochemical Materials – Structure in Action

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There are a number of different examples of how *in situ* X-ray diffraction have been used to study lithium insertion/extraction mechanisms of electrode materials in Li-ion batteries [1,2]. In general, the structural changes during a continuous discharge or charge of the battery are followed, giving information about phase transformations in the material. Few, however, have utilized *in situ* X-ray diffraction during potential steps to get time resolved information of the material's response to, for instance, pulsed charges. With the use of synchrotron radiation with high beam intensity and therefore fast exposure times, new results will be presented for some important cathode materials in Li-ion batteries, for example $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, vanadium-oxide nanotubes and Mo_6S_8 . For this purpose, different instrument geometries and detector systems for transmission mode have been explored in combination with special built sample holders. All the experiments have been carried out at MAXlab, the Swedish synchrotron radiation source but the quality of the result will be discussed in the light of earlier obtained results using "in-house" *in situ* X-ray diffraction.

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Keywords: battery materials, time-resolved scattering studies, synchrotron X-ray diffraction

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PDF and NMR Study of Ordering in the Positive Electrode Material $\text{Li}(\text{NiMn})_{0.5}\text{O}_2$

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The local environments and short-range ordering of $\text{Li}(\text{NiMn})_{0.5}\text{O}_2$, a potential Li-ion battery positive electrode material^{1,2}, were investigated by using a combination of X-ray and neutron diffraction and isotopic substitution, Li MAS NMR spectroscopy and, for the first time, X-ray and neutron Pair Distribution Function (PDF) analysis, associated with Reverse Monte Carlo (RMC) calculations. $\text{Li}(\text{NiMn})_{0.5}\text{O}_2$ adopts the LiCoO_2 structure and comprises separate Li layers, transition metal (Ni,Mn) layers and O layers.

NMR experiments and Rietveld refinements showed that there is 10% of Li/Ni site exchange. Neutron PDF analysis revealed considerable local distortions in the layers that are not captured in the LiCoO_2 model. Large clusters were built to investigate cation ordering, by performing RMC calculations. Both NMR and RMC were consistent with a non-random distribution of Ni, Mn and Li cations in the transition metal layers. Constraints from both methods showed the presence of short-range order in the transition metal layers comprising LiMn_6 and LiMn_5Ni clusters combined with Ni and Mn contacts that are consistent with those found in some of the proposed structures based on Li_2MnO_3 -like ordering of the cations.

[1] Ohzuku T., Makimura Y., *Chem. Lett.*, 2001, 744. [2] Lu Z., MacNeil D. D., Dahn J.R., *Electrochem. Solid-State Lett.*, 2001, **4**, A191.

Keywords: lithium batteries, pair distribution function, NMR