

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., Fragni 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

#### MS51.27.5

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#### The Organization of the Organic Structural Framework in the Enamel Biomineralization 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 biomineralizing systems such as bone, teeth and mollusc shells.<sup>[1]</sup>

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 biomineralization. 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.<sup>[2]</sup>

[1] Falini G., Fermani S., Roveri N., *Current Topics in Crystal Growth Research*, 2005, in press. [2] Du C., Falini G., Fermani S., Abbott C., Moradian-Oldak J., *Science*, 2005, in press.

**Keywords:** biomineralization, enamel, fiber diffraction

#### MS52 INORGANIC-ORGANIC FRAMEWORK MATERIALS

**Chairpersons:** Christoph Janiak, Stuart R. Batten

#### MS52.27.1

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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.

[1] Hill R.J., Long D.-L., Champness N.R., Hubberstey P., Schröder M., *Acc. Chem. Res.*, 2005, in press and references therein.

**Keywords:** coordination chemistry, lanthanide, topology

#### MS52.27.2

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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 Imidazolates and Triazolates

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We recently exploited simple exo-bidentate and exo-tridentate ligands such as imidazolates 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<sup>I</sup>/Cu<sup>II</sup> imidazolate polymers exhibiting different Cu<sup>I</sup>/Cu<sup>II</sup> ratios and topologic structures. More interestingly, using appropriate organic templates, we could also isolate a series of molecular polygons, namely octagons [Cu<sub>8</sub>(mim)<sub>8</sub>] and decagons [Cu<sub>10</sub>(mim)<sub>10</sub>]. 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 4.12<sup>2</sup> nets. A pre-designed metal-organic building block Cu(2-pytz) offers unusual supramolecular isomers upon variations of the reaction condition.