MS34-P18 Coordination Frameworks of Tetrakis[*meso*-(3,5-biscarboxyphenyl)]-Metalloprphyr with Polynuclear Metallic Nodes

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Metal organic frameworks deserve increasing attention as an emerging class of porous functional materials in recent years. The most successful design strategy for constructing these crystalline frameworks is to take advantage of the versatile geometry of organic building units (linkers) and metal centers (uni- and multinuclear connecting nodes), which greatly influence the resulting architectures of the formed framework. Tetrapyrrole macrocycles or porphyrin building blocks are quintessential for forming quadrangular open frameworks, owing to their bulkiness and D_{4h} symmetry. Multiple functionality of the organic linkers is important for promoting expansion of the formed framework in three dimensions.

Prior to this study formulation and characterization of octacarboxy porphyrin-based metal organic frameworks have enjoyed a rather slow progress in view of the synthetic difficulty in obtaining sizeable crystalline samples, as polycrystalline or amorphous solids are most frequently the outcome of common preparative procedures. On rare occasions, when small crystallites became available, their structural characterizations by X-ray diffraction technique required access to synchrotron radiation sources due to the weak diffraction power of such crystals and high content of the disordered solvent trapped in the channel-perforated lattice.

This work provides an insight into an improved synthetic methodology of crystalline framework solids with the fast-reacting octa-topic tetrakis(3,5-dicarboxyphenyl) metalloporphyrin linker and a variety of metallic nodes, using NaOH as a modulator to enhance crystal growth. During the supramolecular reaction the hydroxyl ions supplied by the NaOH compete with the carboxylate anions for coordinating to the metal (or metal cluster), slowing the reaction rate between the metal ions and the porphyrin, and thus enhancing crystal growth of the solid polymeric product. Here we describe crystalline framework materials of the octa-carboxy porphyrin ligand obtained with a series of metal centers, including lanthanoid and transition metal ions, as Pr, Eu, Gd, Tb, Mn, Fe, In and Ga, as well as Na centers. The structural diversity of the framework architectures and of the interaction synthons will be discussed.

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Keywords: metal-organic-frameworks

MS35 Simulation of dynamics in molecular compounds

Chairs: Anders Østergaard Madsen, Markus Meuwly

MS35-P1 Martensitic solid-to-solid transitions in amino acid crystals: what insight can simulations bring to the table?

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Many molecular compounds exhibit polymorphism: the ability to crystallize in different crystal structures. The polymorphic forms determine crystal properties such as the solubility rate, which is key in dose determination in a pharmaceutical context. Understanding of solid-to-solid transitions between different polymorphic forms is the first step in controlling the polymorphic stability of a compound.

Polymorphic transitions are driven by a free energy difference. If the relative stability of different polymorphic forms changes reversibly as a function of temperature, one speaks of enantiotropically related polymorphic forms. In the case of transformations in which the parent and daughter phase have similar structures, there is an ongoing debate whether the transformation mechanism is martensitic or occurs through nucleation and growth. I will present advanced Molecular Dynamics (MD) simulations of two enantiotropically related polymorphic forms of DL-norleucine: α (room temperature) and β (low temperature), which are thought to transform through a martensitic mechansism by sliding along two cell axes. I will show that the mechanism of the transition occurs through a cooperative movement of bilayers via an intermediate state [1,2]. Although the layers move in a concerted fashion, the results further indicate that local fluctuations in the conformations of the aliphatic chains play a crucial role in keeping the cooperative mechanism sustainable at large length scales (see figure). The results suggest a mechanism where formation of a nucleus of the new phase occurs through cooperative motion, which then grows through propagation in a wave-like manner through the crystal [3]. At the length scale of theinitial size of the cluster, classical nucleation theory and the cooperative mechanism could naturally come together.

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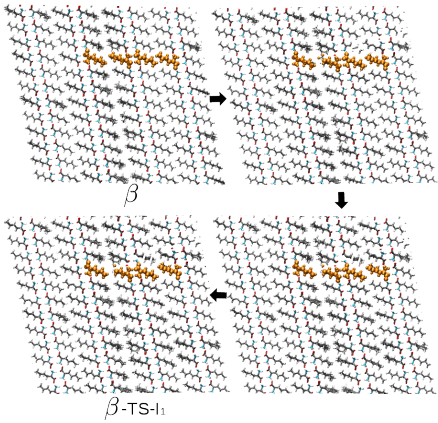

Figure 1. The initial stages of the β to α transition through intermediate state I1 towards the first transition state as obtained by Nudged Elastic Band calculations. A large simulations cell is used to assess the deviations from perfect cooperative motion.

Keywords: phase transitions, molecular dynamics simulations, DL-norleucine, martensitic

MS35-P2 Single Crystal Structures and Spectroscopic Analysis in Metal Complex Dynamics

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Since many dynamic processes (still) occur at the molecular level and at metal cores, fundamental understanding of structural behavior, and the associated influence on (kinetic) properties are of continued and prime importance. In this presentation we emphasize this in conjunction with an *integrated mechanistic approach* to evaluate bonding and reactivity, utilizing small molecule crystal structure data, spectroscopic techniques and reaction kinetics, to counteract trivialized conclusions often based on thermodynamic observations alone [1].

As example, we focus on dynamics in small coordination compounds ustilised as model radiopharmaceuticals, in particular incorporating the ^{99m}Tc, ^{188}Re, ^{186}Re isotopes [2,3]. We discuss some basic characteristics, and the dynamics of the versatile synthon *fac*-$[M^{I}(CO)_3]^+$ and complexes thereof, which include its low-valent, low-spin, kinetically 'inert' organometallic core and the high potential for *in vivo* stability. This starting material and its characteristics must be well understood both in terms of structure and the dynamics therein, before utilization is possible. It coordinates many types of ligands and allows bifunctional chelator ligand design which determines different properties and significantly influences the reactivity in these organometallic molecular materials [1, 3-4].

The above arguments also hold for the dynamics in other processes, in particular homogeneous catalysis [4].

This presentation will underline some of these aspects of small coordination compounds, and illustrate the importance of structure and kinetics and concurrent different processes/ factors which may significantly influence the course of the reaction and the dynamics therein [1, 3-4].

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Keywords: Small Molecules, Reaction Mechanism, Kinetics, Dynamics, Spectroscopy