#### FA4-MS31-T01

### Large Metal Ion Assisted Supramolecular

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X-ray structure determination of large non-covalently bound supramolecular complexes and assemblies can be both difficult and essential in resolving the true nature of the interactions involved in the formation of the assembly and in the possible host-guest interactions. Metal ion assisted selfassembly can produce very large, up to the size of small proteins, nearly purely organic structures with fascinating properties and features. Over the last 15 years our research interest has been focused on the studies of weak non-covalent intermolecular, viz. supramolecular interactions as the driving force in self-assembly and molecular recognition, especially in the solid state by single crystal X-ray diffraction. The lecture will highlight the most recent examples of X-ray studies on large (MW = 3000 - 8500) metal ion assisted helicates [1a], rotaxanes [1b,d,f], porphyrin assembles [1e], grids [1b] and cages [1g,h]

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Keywords: cages, grids, helicates, rotaxanes

## FA4-MS31-T02

### **Rotor-Stator and Ordered Phases of Fullerene-**

**Cubane Cocrystals.** <u>Sándor Pekker</u><sup>a</sup>, Gábor Bortel<sup>a</sup>, É. Kováts<sup>a</sup>, I. Jalsovszky<sup>b</sup>. <sup>a</sup>*Research Institute for Solid State Physics and Optics, Budapest, Hungary.* <sup>b</sup>*Department of Organic Chemistry, Eötvös Loránd University, Budapest, Hungary.* E-mail: <u>pekker@szfki.hu</u>

Fullerene-cubane cocrystals represent a new family of mesomorphic systems in between the orientationally ordered and the plastic crystalline phases. The interactions of the separate sublattices of rotating fullerene and static cubane components give rise to unusual dynamics, the so called rotor-stator properties [1]. These properties can be attributed to a common structural feature: the match of the molecular surfaces of the convex fullerenes and concave cubanes. The almost perfect match of the surfaces of  $C_{60}$  and  $C_8H_8$  in the prototype structure is modified by the lower symmetry molecules in derivatives of higher fullerenes and/or 1,4-disubstituted cubanes, resulting in a series of materials with slightly variable structures and dynamics. Further importance of this family of materials is the formation of high-stability copolymers at elevated temperatures.

Earlier studies focussed on the development of the materials and on the properties of the rotor-stator structures. In the last few years 9 fullerene-cubane cocrystals were prepared with 10 rotor-stator type and 3 orientationally ordered phases, and polymerization were observed in 4 cases. Recently Bortel et al. [2] determined the crystal structure of the orientationally ordered phase of  $C_{60}$ . $C_8$ H<sub>8</sub>. With the knowledge of this orthorhombic structure, it was possible to work out intermolecular  $C_{60}$ - $C_{60}$  and  $C_{60}$ - $C_8$ H<sub>8</sub> potentials to model the interactions in these materials. The potentials are based on Lennard-Jones type and electrostatic interactions, and, describe not only the structures of the two phases of  $C_{60}$ . $C_8$ H<sub>8</sub>, but those of the parent  $C_{60}$  and  $C_8$ H<sub>8</sub> crystals.

The study of these supramolecular interactions helps a better understanding of the characteristics of the rotor-stator phases and their orientational orderings. The most important results will be outlined. The repulsive fullerene-cubane interactions of the nearest neighbors distinguish these rotor-stator materials from host-guest systems of similar structure, like  $C_{60}$ .CH<sub>4</sub>. The attractive fullerene-fullerene interactions are less sensitive to the orientations, explaining the unusually low temperature of ordering and the effect of molecular bearing suggested previously [1]. The smooth intermolecular potentials allow some jump rotation of fullerenes even in the oriented phase, similarly to the case of pure  $C_{60}$ .

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# Keywords: fullerenes, cocrystals, supramolecular interactions

#### FA4-MS31-T03

Coordination and Hydrogen Bonding Networks of Tetrapyridylporphyrins with Lanthanoid Metal Ions. Sophia Lipstman, <u>Israel Goldberg</u>. School of Chemistry, Tel Aviv University, Israel. E-mail: <u>goldberg@post.tau.ac.il</u>

Crystalline engineering of porphyrin-based framework solids received tremendous attention in recent years due to their potential utility in a wide range of applications, including e.g. gas storage, molecular sensing and heterogeneous catalysis. The tetrapyridylporphyrin (TPyP) has played a significant role in the construction of diverse polymeric architectures. It is characterized by rigid square-planar geometry, bears peripheral pyridyl molecular recognition sites for metal coordination as well as H-bonding, and consequently reveals an extraordinarily rich supramolecular chemistry. Of particular interest is the coordination polymerization of this scaffold through exocyclic metal ion connectors, which often results in the formation of robust porous architectures with remarkable sorption and de-sorption features. The use of lanthanoid ions to this end is rather rare. Only recently have hybrid organicinorganic networks composed of tetra(carboxyphenyl)porphyrins and various lanthanoid metals been reported by our group [1]. Prior to our studies, the H-bonding capacity of the TPyP scaffold in the formulation of supra-molecular networks has not been explored. Construction of assemblies sustained by hydrogen bonds requires reaction of the TPyP Lewis base with complementary linkers, such as organic acids, or metal complexes with proton-donating ligands in their coordination