

**FA4-MS31-T01**

**Large Metal Ion Assisted Supramolecular Assemblies.** Kari Rissanen. *Department of Chemistry, Nanoscience Center, University of Jyväskylä, Finland.*  
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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 self-assembly 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 assemblies [1e], grids [1b] and cages [1g,h]

[1] a) D. Funeriu, K. Rissanen and J.-M. Lehn, (2001), *Proc. Natl. Acad. Sci. USA* (2001), 10546. b) P. Baxter, H. Sleiman, J.-M. Lehn and K. Rissanen, *Angew. Chem., Int. Ed. Eng.* (1997), 1295. c) E. Breuning, M. Ruben, J.-M. Lehn, F. Renz, Y. Garcia, V. Ksenofontov, P. Gutlich, E. Wegelius and K. Rissanen, *Angew. Chem., Int. Ed. Eng.* (2000), 2504. d) J. Frey, C. Tock, J.-P. Collin, V. Heitz, J.-P. Sauvage and K. Rissanen, *J. Am. Chem. Soc.* **130** (2008), 11013. e) M. Beyler, V. Heitz, J.-P. Sauvage, B. Ventura, L. Flamigni and K. Rissanen, *Inorg. Chem.* **48** (2009), 8263. f) J.-P. Collin, F. Durolo, J. Frey, V. Heitz, F. Reviriego, J.-P. Sauvage, Y. Trolez and K. Rissanen, *J. Am. Chem. Soc.* (2010), in press g) P. Mal, D. Schultz, K. Beyeh, K. Rissanen and J.R. Nitschke, *Angew. Chem.* **47** (2008), 8297. h) P. Mal, B. Breiner, K. Rissanen and J. R. Nitschke, *Science* **324** (2009), 1697.

**Keywords:** cages, grids, helicates, rotaxanes

**FA4-MS31-T02**

**Rotor-Stator and Ordered Phases of Fullerene-Cubane Cocrystals.** Sándor Pekker<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.*

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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  $C_{60}\cdot C_8H_8$ . With the knowledge of this orthorhombic structure, it was possible to work out intermolecular  $C_{60}\cdot C_{60}$  and  $C_{60}\cdot C_8H_8$  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  $C_{60}\cdot C_8H_8$ , but those of the parent  $C_{60}$  and  $C_8H_8$  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  $C_{60}\cdot CH_4$ . 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

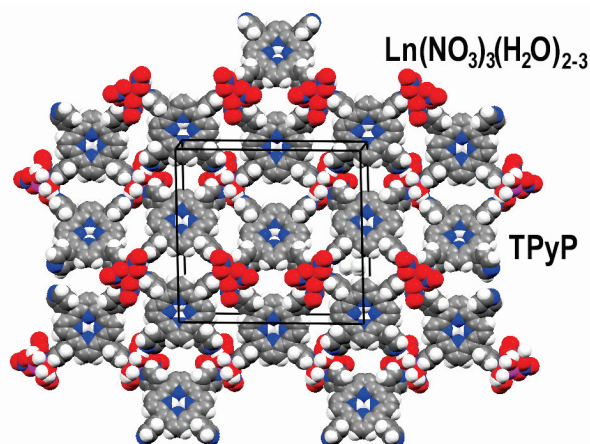
**FA4-MS31-T03**

**Coordination and Hydrogen Bonding Networks of Tetrapyrrolylporphyrins with Lanthanoid Metal Ions.** Sophia Lipstman, Israel Goldberg. *School of Chemistry, Tel Aviv University, Israel.*

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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 tetrapyrrolylporphyrin (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 organic-inorganic 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

sphere. In addition, partial protonation of the pyridyl substituents of TPyP may also induce self-complementary hydrogen bonding between the pyridinium and pyridyl functions of the porphyrin scaffolds. In this work we explore the networking capacity of TPyP with aqua nitrates of various lanthanide ions, while taking advantage of coordination as well as hydrogen bonding features of the porphyrin entity [2]. Details of the supramolecular assembly modes of these materials will be presented.



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**Keywords:** crystal engineering, porphyrin networks, supramolecular structures

#### FA4-MS31-T04

**Fantastic Voyage: Molecular Recognition Viewed Through Macroscopic Properties.** Alessia Bacchi, Giulia Cantoni, Davide Cremona, Paolo Pelagatti. *Dipartimento di Chimica GIAF, Parma University, Italy.*

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One of the most appealing skills of the chemist is being able to tinker with invisible molecules and evanescent forces in order to create sizable objects. Crystal engineering deals with elaboration of concepts at the molecular scale in order to act on macroscopic properties. Here we explore the fascination of the reverse approach: we analyze and measure macroscopic morphologies obtained by crystallizing from different solvents an organometallic molecule  $\text{Ru}(\text{p-cym})\text{Cl}_2(\text{LOH})$  that contains functions potentially able to give many supramolecular synthons, and derive from these measures a ranking of the intermolecular forces responsible for molecular self recognition. We also test and quantify how different functional groups interact with different solvents. The model of Periodic Bond Chains (PBC) is generally used to predict the growth morphology of minerals or of organic compounds by estimating the most relevant interaction energies [1]. By reversing the approach, here we identify the supramolecular synthons active in the packing through the analysis of the growth morphology, by using the argument that the most developed faces must contain two non parallel PBCs. This allows to single out the supramolecular pairs linked by the

main PBCs and stabilized by the principal supramolecular synthons. In addition, the comparison of the the growth rates along the different PBCs depending on the solvent allows to estimate the degree of interaction between the solvent and the different functional groups exposed on the faces.

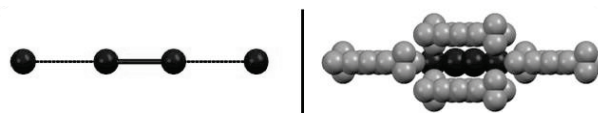
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**Keywords:** Crystal Engineering, Molecular Recognition, Periodic Bond Chains

#### FA4-MS31-T05

**Size Matching of Interacting Moieties: A Design Principle in Crystal Engineering.** Giuseppe Resnati<sup>a,b,c</sup>, Antonio Abate<sup>a</sup>, Manu Lahtinen<sup>d</sup>, Pierangelo Metrangolo<sup>a,b</sup>, Tullio Pilati<sup>c</sup>, Kari Rissanen<sup>d</sup>, Giancarlo Terraneo<sup>a,b</sup>. <sup>a</sup>NFMLab - D.C.M.I.C. "Giulio Natta", Politecnico di Milano, Via L. Mancinelli 7, 20131 Milan, Italy. <sup>b</sup>CNST - IIT@POLIMI, Politecnico di Milano, Via G. Pascoli 70/3, 20133 Milan, Italy. <sup>c</sup>C.N.R. - I.S.T.M., University of Milan, Via C. Golgi 19, 20133 Milan, Italy. <sup>d</sup>Department of Chemistry, Nanoscience Center, University of Jyväskylä, Post Office Box 35, Jyväskylä FI-40014, Finland. E-mail: [giuseppe.resnati@polimi.it](mailto:giuseppe.resnati@polimi.it)

Theoretical investigations proved that the linear  $\text{I}_4^{2-}$  ion is unstable. A search in the Cambridge Structure Database (CSD), in fact, reveals that there are only eight crystal structures containing the symmetric polyiodide  $\text{I}_4^{2-}$  as a discrete unit. The symmetric  $\text{I}_4^{2-}$  species may be described as an  $\text{I}_2$  molecule bound at both ends each to one  $\Gamma$  ion through linear halogen bonding, that is the intermolecular interaction involving halogen atoms as electrophilic species [1]. We reasoned that matching the symmetric  $\text{I}_4^{2-}$  polyiodide species with a dication wherein the space separation of the two positive charges is similar to the size of the  $\text{I}_4^{2-}$  dianion, should increase the strength of electrostatic interactions in the ionic lattice, thus driving forcefully the selective formation of the target polyiodide species. In this communication, we show that bis(trimethylammonium)hexane diiodide encapsulates iodine from solution and through a gas/solid reaction yielding in a predictable and controllable manner the selective formation of the rare polyiodide species  $\Gamma \cdots \text{I} \cdots \text{I} \cdots \Gamma$ , which matches in length the chosen dication [2]. The size matching method is general and can be extended to the predictable obtainment of other uncommon polyhalide species. This has the potential for significantly augmenting our knowledge of polyhalide species, as well as providing a novel approach to the field of their design and synthesis.



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