FA4-MS04-O1

Metal-Organic Materials: Strategies toward Functional Porous Materials. <u>Mohamed Eddaoudi</u>.

Department of Chemistry, The University of South Florida, 4202 E. Fowler Avenue, CHE205, Tampa, Florida, 33620, USA.
E-mail: eddaoudi@cas.usf.edu

The quest for functional materials targeted for specific applications is ever increasing as societal needs and demands mount with advancing technology. One class of inorganic-organic hybrid materials, metal-organic materials (MOMs), has burgeoned in recent years due, in part, to effective design strategies (i.e. reticular chemistry) for their synthesis and their inherent [and readily interchangeable] hybrid, highly functional character. The molecular building block (MBB) approach introduces the ability to generate rigid and directional building blocks, mostly *in situ*, for the construction of MOMs having specific underlying networks and/or targeted functions/properties. Here we will discuss three basic strategies based on the MBB approach. Three classes of MBBs can be targeted and utilized in the assembly of functional MOMs: 1) single-metal-ion-based MBBs, which promote the rational construction, by forcing rigidity and directionality through control of the metal coordination sphere and judicious selection of suitable hetero-functional (N-, O- coordination) organic ligands, of porous MOMs with extra-large cavities, including zeolite-*like* metal-organic frameworks (ZMOFs);[1] 2) multi-nuclear metal cluster-based MBBs, where, for example, simple metal-carboxylate clusters possess multiple metal-oxygen coordination bonds that result in the generation of rigid nodes with fixed geometry that, when combined with organic ligands of specific geometry, lead to the construction of desired MOMs (e.g. *soc*-MOFs);[2] and 3) supermolecular building blocks (SBBs), which involve enhanced built-in directional and structural information (e.g. high degree of symmetry and connectivity) compared to simple MBBs and allow the construction of high-connectivity nets (e.g. *rht*-MOFs).[3] The MBB approach and associated strategies, as well as physical properties of some corresponding MOMs (i.e. porosity, hydrogen sorption, catalysis, inclusion and sensing) will be discussed.
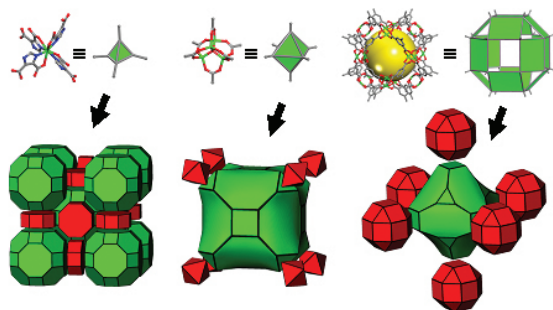
[1]. (a) Liu, Y.; Kravtsov, V. Ch.; Larsen, R. W.; Eddaoudi M. *Chem. Commun.* 1488-1490, **2006**; (b) Liu, Y.; Kravtsov, V. Ch.; Eddaoudi, M. *Angew. Chem. Int. Ed.* 47, 8446-8449, **2008**; (c) Alkordi, M. H.; Liu, Y.; Larsen, R. W.; Eubank, J. F.; Eddaoudi, M. *J. Am. Chem. Soc.* 130, 12639-12641, **2008**. [2]. Liu, Y.; Eubank, J. F.; Cairns, A. J.; Eckert, J.; Kravtsov, V. Ch.; Luebke, R.; Eddaoudi, M. *Angew. Chem. Int. Ed.* 46, 3278-3283, **2007**. [3] Nouar, F.; Eubank, J. F.; Bousquet, T.; Wojtas, L.; Zaworotko, M. J.; Eddaoudi, M. *J. Am. Chem. Soc.,* 130, 1833-1835, **2008**.

FA4-MS04-O2

Interpreting Competition Experiments in Host-Guest Chemistry. <u>Luigi R. Nassimbeni</u>. *Department of Chemistry, University of Cape Town, South Africa.*

E-mail: luigi.nassimbeni@uct.ac.za

In order to study the various parameters which determine the affinity between a host and a guest compound in the solid state, we have carried out a series of guest-competition experiments. We have thus exposed a given host to a series of liquid guest mixtures of known composition, varying the mole fractions systematically from 0 to 1. When considering a host H and two guests A and B, with the mole fraction of A, X_A in the liquid, we then determine the mole fraction of this guest in the ensuing crystals, Z_A. A selectivity curve of Z_A vs X_A can then be drawn and a selectivity coefficient $K_{A:B} = Z_A / Z_B * X_B / X_A$ may be calculated at all points along this curve. The value of $K_{A:B}$ is a function of the relative affinities of the host H for the guests A and B.

For a given temperature of crystallization, the questions that arise are:

(i) what are the structures of the solids along the selectivity curve?

(ii) is the selectivity constant dependent on the electronic properties of the guest molecule?

(iii) what is the importance of shape and size of the guest molecule with respect to the packing of the host-guest compound?

Various examples of host-guest selectivity will be presented in order to answer these questions.

**Keywords: molecular recognition; competition experiments; selectivity**

FA4-MS04-O3

Designer Porphyrin Assemblies. <u>Israel Goldberg</u>[a], Sophia Lipstman[a], Sankar Muniappan[a]. *[a]School of Chemistry, Sackler Faculty of Exact Sciences, Tel Aviv University, Israel.*

Email: goldberg@post.tau.ac.il

This presentation addresses the scientific challenge of predictably self-organizing porphyrin molecules into materials with complex topologies, with an emphasis on rational construction of molecular networks and systems exhibiting supramolecular chirality. In order to achieve these goals, the porphyrin scaffold is deliberately functionalised with different molecular recognition groups prone to engage in robust supramolecular synthons. This allows to reasonably control the self-assembly process and to alter systematically the composition and topology of the supramolecular arrays that form. The crystal-engineering approach represents an attractive "bottom-up" strategy to tailoring ordered lattice materials and network architectures

[1].

In the above context, we focus here on porphyrins bearing carboxyphenyl, pyridyl and iodophenyl molecular recognition functions, along with their core-metalated derivatives. This work evaluates the supramolecular reactivity of representative scaffolds, utilizing metal-ligand coordination as well as hydrogen and halogen bond synthons in the construction of polymeric as well as oligomeric structures. It demonstrates also the induction of supramolecular chirality (chiral arrangement of achiral molecular components in a non-covalent assembly), which has been achieved with asymmetrically substituted porphyrin building blocks, using either hydrogen or halogen bonds as directors of the intermolecular organization [2]. Protocols for the rational design of the different modes of supramolecular porphyrin ensembles will be discussed, in relation to the substitution pattern of the recognition sites on the porphyrin moiety.
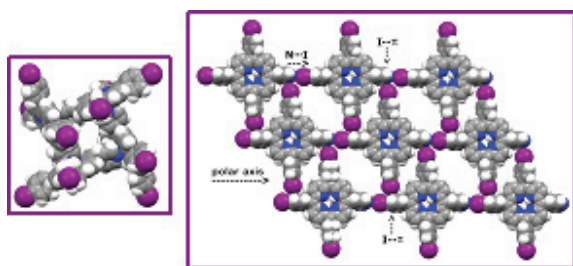
[1] I. Goldberg, *Chem. Comm.* **2005**, p. 1243; I. Goldberg, *CrystEngComm* **2008**, *10*, 637. [2] S. Muniappan, S. Lipstman, I Goldberg, *Chem. Commun.* **2008**, p. 1777; S. Lipstman, S. Muniappan, I. Goldberg, *Cryst. Growth Des.* **2008**, *8*, 1682.

**Keywords: crystal engineering; supramolecular chirality; porphyrin solids**

FA4-MS04-O4

Self-Assembly of Amphiphilic Calixarenes: Crystal Structure of an Inverted Micelle. <u>Kinga Suwinska</u>[a], Barbara Lesniewska[a], Said Jebors[b], Anthony W. Coleman[b]. *[a]Institute of Physical Chemistry, Polish Academy of Sciences, Warszawa, Poland. [b]IBCP, CNRS UMR 5086, Lyon, France.*
E-mail: <u>kinga@ichf.edu.pl</u>

Amphiphilic calixarenes are well know to self-assemble in layers (mono- and bilayers) and/or micelles or inverted micelles. Both, layers and spherical species are of great interest for pharmaceutical and bio-medical applications.

For the first time we were able to observe crystallization of spherical species in the form of inverted micelles and to solve crystal structure of such an assemblies.
12 Calixarene molecules are arranged in cuboctahedron (one of the Archimedean solids) with hydrophobic exterior and hydrophilic internal cavity of 141 Å^3.
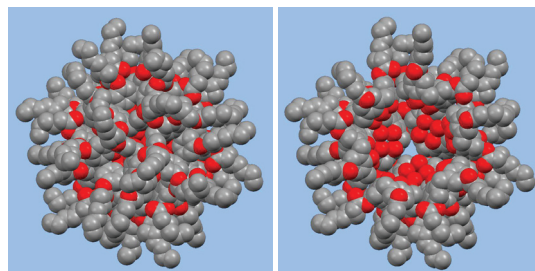
Inverted micelle: hydrophobic exterior (left) and hydrophilic interior of the inverted micelle. Hydrogen atoms are not shown.
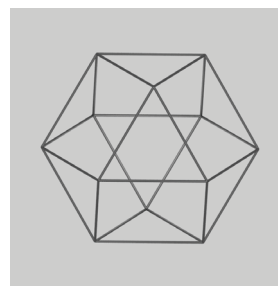
cuboctahedron

Keywords: amphiphilic calixarene; inverted micelle; structure

FA4-MS04-O5

Head-to-tail Hydrogen-bonded Chains in the Crystal Structures of Dipeptides-A Comprehensive Survey. <u>Carl Henrik Görbitz</u>. *Department of Chemistry, University of Oslo, Norway.*
E-mail: <u>c.h.gorbitz@kjemi.uio.no</u>

At the time when Suresh & Vijayan [1] wrote their classic paper describing head-to-tail sequences as the main mode of interaction between peptide molecules in the solid state, only a limited number of experimental structures were available. The present work provides a comprehensive updated investigation of head-to-tail hydrogen-bonded interactions in the crystal structures of dipeptides, focusing on patterns in which two concomitant chains generate a two-dimensional sheet. It is shown that the presence of such sheets is more abundant than one may initially realize, and furthermore that the vast majority of the observed sheets fall into four well-defined classes, two where molecules in a chain are related only by translation (a), and two where a two-fold screw operation is involved (b). Relating the observed hydrogen bonding patterns to the amino acid composition of the dipeptide, it is clear that the selection between classes is not random; the side chains and even the occasional presence of cocrystallized solvent molecules dictate the outcome of dipeptide crystallization with a high degree of likelihood.