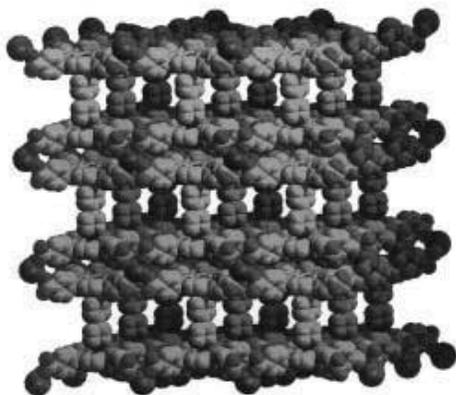


**[s9.m3.o1] Crystal Engineering of Metalloporphyrin Molecular Sieves and Zeolite Analogues.** I. Goldberg, *School of Chemistry, Sackler Faculty of Exact Sciences, Tel Aviv University, Ramat Aviv, 69978 Tel Aviv, Israel.*  
 Keywords: molecular interactions, supramolecular assemblies.

The design of molecular solids with structural and functional similarity to the inorganic zeolites is an exciting challenge in materials science. We attempted in this study to crystal-engineer cross-linked open networks and stable nanoporous solids, utilizing the concepts of supramolecular self-assembly. The rigid and thermally stable metalloporphyrin building blocks, readily available in diverse functional forms, have played a major role to this aim.

A variety of new materials have been rationally designed with the aid of appropriate molecular recognition algorithms. This includes formulations of extended two-dimensional hydrogen bonded polymers with hollow architectures,<sup>1</sup> network structures of homogeneous as well as heterogeneous coordination polymers,<sup>2</sup> polymeric patterns sustained by external metal centers, and molecular sieves (see Figure) with different channel widths (within the range of 0.5-1.5 nm) and dimensionality.<sup>3-5</sup> Construction of multiporphyrin networks with even larger pores (>2.2 nm) can be also realized.<sup>6</sup> Representative examples will be discussed in more detail.

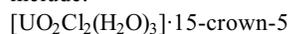


**Figure.** An open supramolecular array with 8x10 and 8x12.5 Å channels resembling a zeolite architecture.

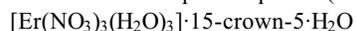
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**[s9.m3.o2] Crystal Engineering Low Symmetry Structures.** P.D. Prince, G. S. McGrady and J.W. Steed, *Department of Chemistry, King's College London, Strand, London WC2R 2LS. E-mail jon.steed@kcl.ac.uk* Peter C. Junk *James Cook University, Townsville, Qld., Australia.*  
 Keywords: molecular interactions, supramolecular assemblies.

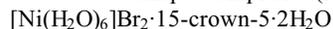
Work on an interesting series of hydrogen bonded polymers base on the unsymmetrical hydrogen bond acceptor 15-crown-5 is presented. These compounds are interesting because they all share the feature of having a large number of unique molecules in the crystallographic asymmetric unit. That is to say that there are a large number of supramolecular interactions between the molecular components that do not follow the usual "rules" of crystal packing. Particularly interesting examples include:



16 unique complexes ( $P3_2, Z = 48, Z' = 16$ )

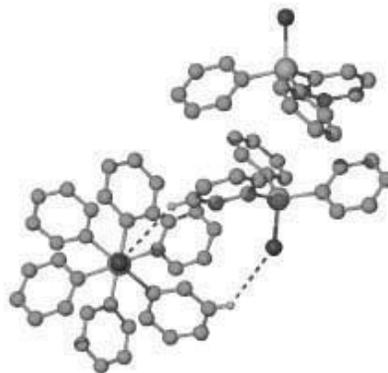


4 unique complexes ( $P1, Z = 8, Z' = 4$ )



4 unique half and two unique whole nickel complexes ( $P1, Z = 8, Z' = 4$ )

There is a remarkable number of other interesting low symmetry structures that may be still distinguished from glasses and in our own laboratory we have prepared two further entirely independent series of such compounds. In one case strongly hydrogen bonded amine complexes of mineral acids show a great deal of 'unsymmetry' arising from frustration between the conflicting driving forces towards close packing and maximisation of intermolecular interactions. One example based on diprotonated *o*-phenylenediamine contains eight unique cations and ten unique anions,  $[\{(\text{NH}_3)_2\text{C}_6\text{H}_4\}_8](\text{HSO}_4)_4(\text{SO}_4)_6 \cdot 8\text{H}_2\text{O}$ . In a completely unrelated series  $\text{GePh}_3\text{Cl}$  exhibits four independent molecules in space group  $P2_1/c$  arising from the occurrence of two 'sixfold embrace' motifs of the triphenyl moieties that interact *via* weak  $\text{CH} \cdots \text{Cl}$  hydrogen bonds (see figure). Different motifs with two independent molecules are observed for the analogous bromide and hydride compounds, all dependent on weak hydrogen bonds.



In this poster a range of such low symmetry structures will be discussed and their relevance to the control of crystalline architecture explored. Come along and browse and offer your opinions!

H. Hassaballa, J. W. Steed, P. C. Junk and M. R. J. Elsegood, *Inorg. Chem.*, 1998, 37, 4666-4671.