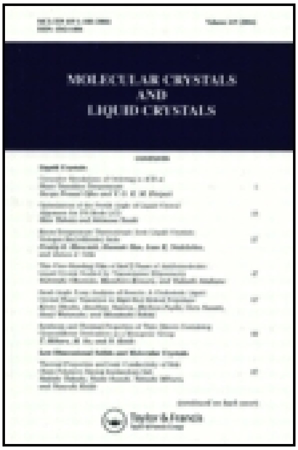

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Structure Enforced Assemblies of Porphyrin Based Metallomacrocycles. Control of Supramolecular Organization by Weak Interactions

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STRUCTURE ENFORCED ASSEMBLIES OF PORPHYRIN BASED METALLOMACROCYCLES. CONTROL OF SUPRAMOLECULAR ORGANIZATION BY WEAK INTERACTIONS

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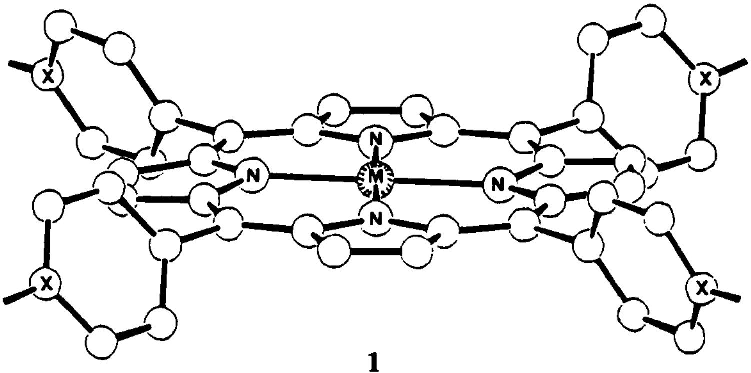
Abstract Control of supramolecular organization by weak noncovalent interactions is demonstrated in a series of crystalline materials based on functionalized porphyrin building blocks. The monomeric units associate *via* metal-ligand binding, hydrogen-bonding and halogen-halogen interactions into pseudo-rigid polymeric arrangements with porous architecture, giving rise to the formation of a large variety of hetero-molecular inclusion-type materials.

INTRODUCTION

Molecular crystals that incorporate open features such as extended channels and regular cavities are both technologically relevant and scientifically challenging. Such materials are now recognized as a reach source of potential solutions to problems of molecular separations, including enantiomer resolutions, lattice-controlled stereoselective reactions, photochemical and thermochemical processes, modifications of physical and chemical properties of solid materials, and design of molecular devices.[1,2] This potential of inclusion compounds has led to the development of several strategies for the designed construction of structure enforced supramolecular assemblies from suitable molecular building blocks.[3-8] Of specific interest within this context is the evaluation of weak intermolecular interactions, as metal-ligand binding, hydrogen bonding, dipolar and π-π interactions, as design elements in inclusion chemistry. Such knowledge and understanding of noncovalent intermolecular forces can be applied to syntheses of new and unconventional forms of functional solids based on organic and organometallic entities.[7,8] The versatility of the porphyrin compounds as crystalline hosts appears to be unequaled due to the large size, high symmetry, rigidity, and thermal stability of the molecular framework. It is also feasible to tailor their shape and functionality features by organic synthesis, and thus affect the microstructure of the resulting assembly.

Crystalline aggregation of unsubstituted tetraphenylmetalloporphyrins was found to be dominated primarily by the molecular shape and dispersion forces. It yields, in most cases, hollow interporphyrin architectures, which provide the driving force for the incorporation of a 'guest' component into the crystal lattice.[9-11] The structural systematics of such materials revealed conservation of the porphyrin host structure in over 200 lattice clathrates. In a series of more recent studies we have demonstrated that a suitable functionalization of the rigid metalloporphyrin molecular framework with polarized aryl groups (**1**) can be used to develop simple chemical models of self-assembly *via* weak intermolecular forces, and to affect the spontaneous built-up of the porphyrin lattice by molecular recognition properties of the respective sensor groups. This approach, employing readily available tetraarylporphyrins as modular building blocks, enables incorporation of the peripherally functionalized species into extended supramolecular arrays of a porouse nature. Representative examples of the unique architectures observed are discussed below.



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("X-" represents C-OH , C-COOH , C-Cl , C-Br or pyridyl N:)

COORDINATION POLYMERS

Self-assembly of polymeric aggregates from pyridyl-substituted metalloporphyrin monomers takes place in solution as well as in the solid state. The polymerization occurs through ligation of the porphyrin periphery on one molecule to the metal center of an adjacent porphyrin. Both triphenyl-pyridyl-porphyrin as well as tetrapyridyl-porphyrin form *one-dimensional* chains with a zigzag conformation, the inter-chain organization depending on the crystallization environment.[12,13] We have exploited further the coordination capacity of the tetrapyridyl-metalloporphyrin building blocks, by assembling a *three-dimensional* coordination polymer of this species. Formation of the extensively interlinked polymeric network involves a direct interporphyrin interaction, and is enhanced by the templating effect of the porphyrin metal center.[12] In the case of Zn(II)-derivatives the bridging metal-to-N(pyridyl) distance is near 2.15 Å in the polymeric chains (square-pyramidal coordination around the central ion) and near 2.37 Å in the polymeric networks (octahedral coordination around the ion). The two structural types, shown in Figure 1, are characterized by triclinic and hexagonal symmetry, respectively. Self-assembly of multiporphyrin arrays, through an external metal ion bridge between the peripheral pyridyl sites, have also been reported.[14,15]

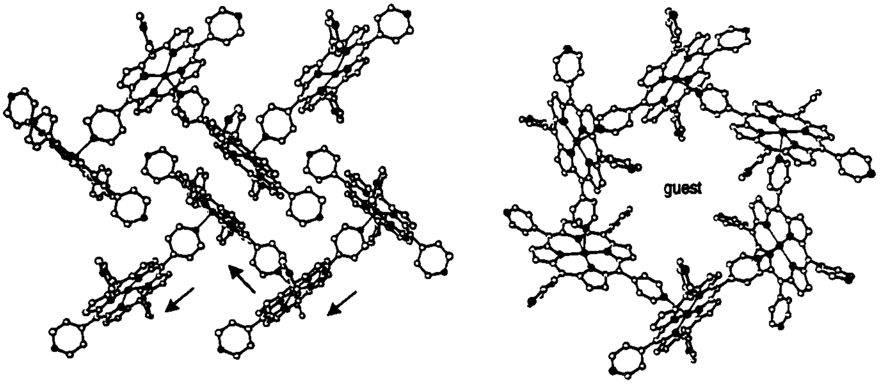

Figure 1. Sections of one-dimensional (left) and three-dimensional (right) coordination polymers of Zn(II)-tetra-(4-pyridyl)porphyrin. A double zigzag-shaped chain of the one-dimensional assembly is shown. Site for guest occlusion in the three-dimensional polymer is indicated; all of the metal centers are further coordinated from their other side to adjacent multiporphyrin aggregates.

HYDROGEN-BONDING CRYSTALLINE POLYMERS

Building blocks with -OH sensor groups.

The supramolecular organization of tetra(4-hydroxyphenyl)metalloporphyrins is dominated by interporphyrin directional hydrogen bonding interactions. It consists of continuous networks of coordinated monomeric entities with varying degrees of cross-linking and rigidity. Figure 2 illustrates representative examples of one-dimensional, two-dimensional and three-dimensional polymeric patterns observed in our study.[16] The nature of the crystallization environment has a significant effect on the polymer type which forms as well as on the stacking mode of the metalloporphyrin arrays in the crystal. In nonpolar solvents, an extensive interporphyrin hydrogen bonding becomes feasible, while in protic media competing solvent-porphyrin association may also occur. Moreover, in solvents with strong nucleophilic sites capable of forming coordinative bonds to the metal center a non-overlapping organization of the two-dimensional arrays will be favoured. On the other hand, flat aromatic constituents are better fit to induce a face-to-face stacking geometry, as they can be involved in charge-transfer interactions with the metalloporphyrin ring.

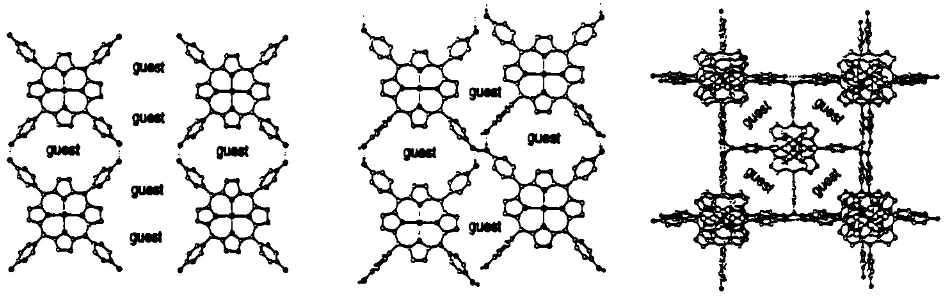

Figure 2. One-dimensional (left), two-dimensional (center) and three-dimensional (right) polymeric aggregation modes in crystals of the M-tetra(4-hydroxyphenyl)-porphyrin building blocks. The former two arrangements are coplanar. The inter-porphyrin guest sites in these patterns are indicated.

Building blocks with -COOH sensor groups.

Another variant of hydrogen-bond coordinated crystalline polymers of the metalloporphyrin species is based on the tetra(4-carboxyphenyl) derivative.[17] The tetra-acid molecules form pairwise hydrogen bonds between the carboxy groups of adjacent units, yielding flat polymeric networks with large interporphyrin voids. The nearly square-shaped central hole is considerably larger than the interporphyrin cavities in the hydroxy compounds. Attempts to incorporate sufficiently large guest entities into these arrays and enforce their layered arrangement have not been successful as yet, mostly due to severe solubility problems. Instead, in the available materials the two-dimensional network of the H-bonded molecules is doubly catenated by two other networks which extend roughly in a perpendicular direction (Figure 3). Molecules of the solvent occupy the axial coordination sites of the metalloporphyrin. Similarly interlaced architectures have been previously observed in the solids of other polycarboxylic compounds.[18-20]

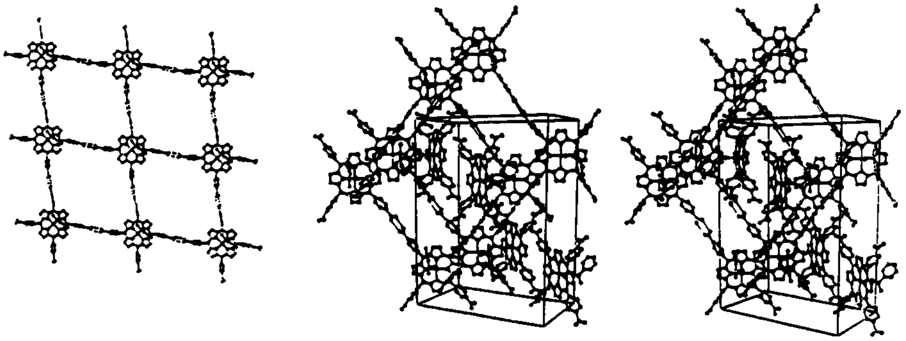

Figure 3. Structural features of the Zn(II)-tetra(4-carboxyphenyl)porphyrin crystalline polymer. (Left) The layered polymeric pattern of the porphyrin units. (Right) Stereoview of the crystal structure of the phenethylalcohol complex (monoclinic, a = 14.420, b = 24.678, c = 33.688 Å, β = 90.03°, space group $I2/a$), showing the self-catenation and crystal-packing mode of the hydrogen-bonded aggregates.

AGGREGATES OF HALOGEN SUBSTITUTED PORPHYRINS

Dipolar forces, halogen-halogen interactions and apparent C-H...halogen weak hydrogen bonds add to dispersion effects in directing the supramolecular organization of the halogen-substituted porphyrin species.[16,21] The most common motif of intermolecular architecture in metallated tetra(4-chlorophenyl)porphyrins and tetra(4-bromophenyl)-porphyrins[17] is a layered arrangement in which the neighboring entities interact through the *cis*-related chlorophenyl or bromophenyl residues (Figure 4). It resembles the structural modes observed in the crystals of the hydroxy derivatives (see above), in which assembly of the porphyrin building blocks is directed by H-bonding associations. The layered arrangement is further stabilized by electrostatic interactions between opposing C-X (X=Cl, Br) dipoles, as well as by weak hydrogen-bonding-type attractions between the periphery of the pyrrole rings and the halogen sites of adjacent molecules. The halogen-halogen and C-H...halogen contacts in these arrangements vary within: Cl...Cl 3.63-4.00 Å, Br...Br 3.84-4.00 Å, CH...Cl 2.7-2.8 Å, and CH...Br 2.8-2.9 Å. In most cases the observed distances are either equal to, or shorter than, the corresponding sums of van der Waals radii, and are indicative of specific interaction. The dominant appearance of the geometric patterns depicted in Figure 4 reflects on the importance of these interactions in the halogen-substituted porphyrin materials. The crystal structures consist of densely stacked porphyrin layers. In four-coordinate materials these layers overlap to a large extent, forming channel-type cavities propagating perpendicularly to the layered zones. In five-coordinate and six-coordinate compounds the axial ligands of one layer are accommodated within the localized interporphyrin cavities of an adjacent layer, yielding a tight key-to-lock type fit between them.

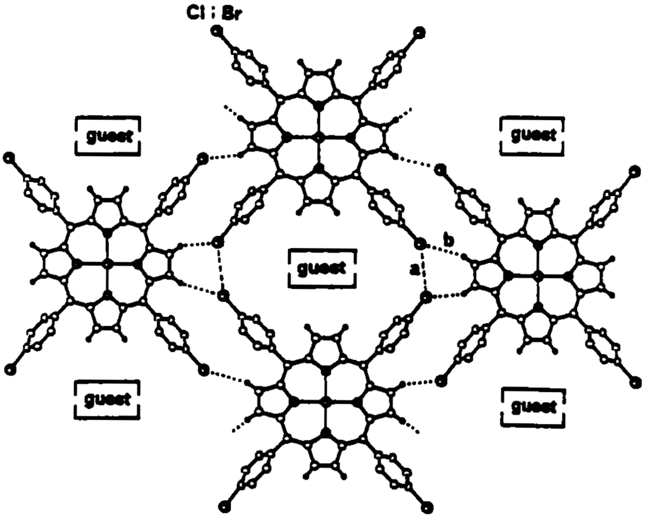

Figure 4. The most common pattern of interporphyrin interaction and guest occlusion observed in crystalline assemblies of the metallated tetra(4-chlorophenyl)porphyrin and tetra(4-bromophenyl)porphyrin species. Dotted lines denote specific halogen-halogen (**a**) and hydrogen bonding (**b**) contacts ranging from 3.63 to 4.00 Å and from 2.7 to 3.1 Å, respectively.

BRIDGING LIGANDS AND CROSS-LINKING FEATURES

Metalloporphyrin polymers where the polymer linkage is formed by a bridging ligand (e.g., pyrazine) are known.[22] Cofacial assembly of metalloporphyrin, and the related metallophthalocyanine, frameworks through axially positioned hydroxy ligands (via condensation) in the form of crystalline or liquid-crystalline polymers have also been reported.[23-25] Some of these materials demonstrated interesting electron-conductivity features, with the electrons flowing along the [-metal-ligand-metal-] polymeric backbone. The significant role that the porphyrin metal center can play in affecting the nature of the intermolecular association is illustrated by water ligated tetra(4-methoxyphenyl)porphyrin systems (Figure 5). The methoxy substituent is a weak functional group of low polarity, which can not be utilized in directional interporphyrin linkage.

However, introduction of a suitable ligand into the lattice may provide the bridging element. This is the case with water molecules which can simultaneously be bound to the metal of one porphyrin species and to a peripheral substituent of an adjacent porphyrin molecule, thus incorporating cross-links and rigidity into the layered arrangement of the porphyrin moieties.[16]

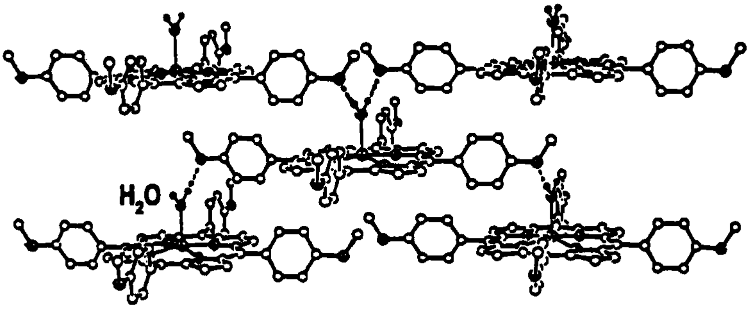

Figure 5. Typical cross-linked organization observed in the crystals of water-ligated tetra(4-methoxyphenyl)metalloporphyrins.

POTENTIAL APPLICATIONS

All the solids described above have a characteristic porous architecture, and a strong tendency to absorb small organic molecules in stoichiometric amounts. The pore structure consists of interporphyrin cavities and canals, the size and shape properties of which are determined by the directional intermolecular interactions involving the chosen sensor groups. In this respect, the structural properties of the functionalized-porphyrin materials, and their inclusion behaviour, resemble to some extent characteristic features of inorganic microporous solids widely utilized in storage and transport of molecules and ions. The porphyrin solids can also be used for a variety of applications such as isolation, separation and slow release of molecular moieties. Controlled release formulations are particularly attractive, being used in an enormous variety of medical, agricultural and consumer products.

ACKNOWLEDGMENT

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