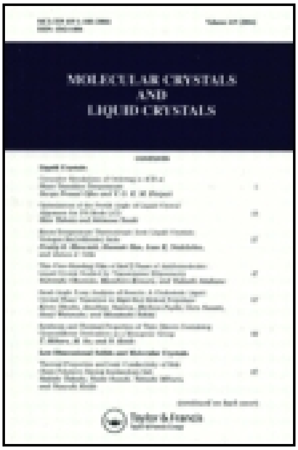

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Self-Assembly of Functionalized Metalloporphyrins into Microporous Polymeric Networks

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Self-Assembly of Functionalized Metalloporphyrins into Microporous Polymeric Networks

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This study deals with the preparation and structural characterization of crystalline assemblies based on the tetra(4-cyanophenyl), tetra(4-nitrophenyl) and tetra(4-amidophenyl) derivatives of metallated porphyrin as building blocks, toward the design of novel coordination polymers and microporous organic solids. The cyanophenyl derivative forms under selected conditions two-dimensional coordination polymers through direct ligation of the -CN functions to the metal centers of neighboring porphyrins. In most other cases it self-assembles into layered multiporphyrin arrays which consist of uniquely structured supramolecular chains and networks with large cavities. Similar intermolecular architectures were observed in solids based on the nitrophenyl and amidophenyl porphyrin entities. The layered organization in these materials is dominated to a large extent by molecular shape and aromaticity of the porphyrin frameworks, while its porous nature is sustained and controlled by non-covalent interactions between the amidophenyl, cyanophenyl or nitrophenyl sensor groups of adjacent metallomacrocyclic units.

Keywords: crystal engineering; supramolecular interactions; metalloporphyrin self-assembly

INTRODUCTION

Supramolecular aggregation of molecular building blocks into network structures has drawn considerable attention in recent years in an effort to tailor crystalline solids with specific and practical applications.[1] The versatility of the porphyrin-based metallomacrocycles, as molecular building blocks for

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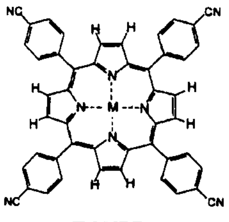
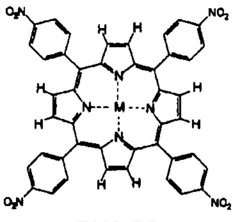
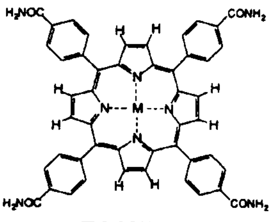
self-assembly purposes, appears to be unparalleled owing to the large size, high symmetry, rigidity and thermal stability of the molecular framework.[2] Moreover, these macrocycles offer a range of sites wherein the chemical modifications can imparted in such a way as to induce intermolecular recognition, and thus control the manner in which these molecules aggregate in the solid state. Functionalization of the porphyrin periphery with polar sensor groups has been successfully employed in this laboratory to evaluate the potential of directing and controlling molecular recognition, organization and cohesion in these materials by means of weak interactions.[3] Our efforts focused on the design of hollow supramolecular patterns in which the metallomacrocyclic units are interlinked into multi-dimensional polymeric architectures *via* metal-ligand coordination, hydrogen bonding and dipolar association. Over the last few years various metalloporphyrin macrocycles functionalized with potential hydrogen bond formers (-PhCOOH and -PhOH), metal coordinating ligands (pyridyl) and polar groups capable of engaging in other charge interactions (-PhF, -PhCl, and -PhBr) have been successfully assembled into porous crystalline solids.[3] Our latest findings in this series of investigations relate to the use of metallated tetra(4-cyano-phenyl)porphyrin [TCNPP], tetra(4-nitrophenyl)porphyrin [TNO_2PP] and tetra(4-amidophenyl)porphyrin [$TCONH_2PP$] derivatives as building blocks.



TCNPP



TNO_2PP



$TCONH_2PP$

The driving force for using the linear -CN sensor lies in its highly versatile functionality. This group is strongly polar, it may readily coordinate to transition metal ions, and its N: site may also act as proton acceptor in hydrogen bonds. Moreover, the dimeric aggregate of CN-substituted aromatic fragment is a very robust supramolecular synthon in crystals of organic entities.[4] Similar considerations apply to the polar -NO_2 substituent which also has multiple coordination capacity to transition metals and to proton donating functions. The -$CONH_2$ functional group contains proton donor as well as proton acceptor sites which can be self-complementary in intermolecular association. Correspondingly, it is an excellent sensor for inducing structurally well defined either dimeric or polymeric aggregation through hydrogen bonding.[5] The unique coordination properties of these three sensor groups provide a strong motivation for their application, as molecular recognition sites, in the design of supramolecular architectures of molecular-based solids. This report surveys the characteristic structural patterns and supramolecular interaction schemes in a series of newly prepared microporous solids based on the TCNPP, TNO_2PP and $TCONH_2PP$ frameworks.

RESULTS AND DISCUSSION

Coordination Polymers of TCNPP[6]

Crystallizations of the zinc-metallated TCNPP from pure chloroform, as well as from most solvent mixtures containing chloroform, led to the self-assembly of two-dimensional coordination polymers of the porphyrin moieties. The interporphyrin polymeric architecture in the corresponding solids is propagated by metal-ligand interaction, each monomeric unit being linked to four neighboring porphyrin molecules. It utilizes two *trans*-related cyano substituents to ligate with the metal center of two adjacent porphyrins along one axis, while the metal ion at the center of each TCNPP binds two -CN functions of other monomeric units approaching from both sides of the molecular framework as axial ligands. This layered polymeric pattern is illustrated in Figure 1. The typical translational symmetry within these layers is characterized by a 8.8-9.1 Å displacement of the porphyrin building blocks in one direction, and 22.1-22.4 Å displacement along the other direction. The coordination distances and approach angles of the ligating linear -CN groups to the porphyrin metal center are within 2.7-2.8 Å and 123-129°, respectively. The corrugated surface of the polymeric layer, lined with those cyanophenyl arms of the porphyrin constituents which do not ligate to the metal ions of adjacent units, prevents dense packing and leads to the intercalation the solvate/guest species (e.g., chloroform, nitrobenzene) between these layers (Figure1). The above observations related to the formation of two-dimensional polymeric architectures with TCNPP, add to our earlier results on multi-dimensional coordination polymerization based on zinc-tetrapyridylporphyrin building blocks.[3g]

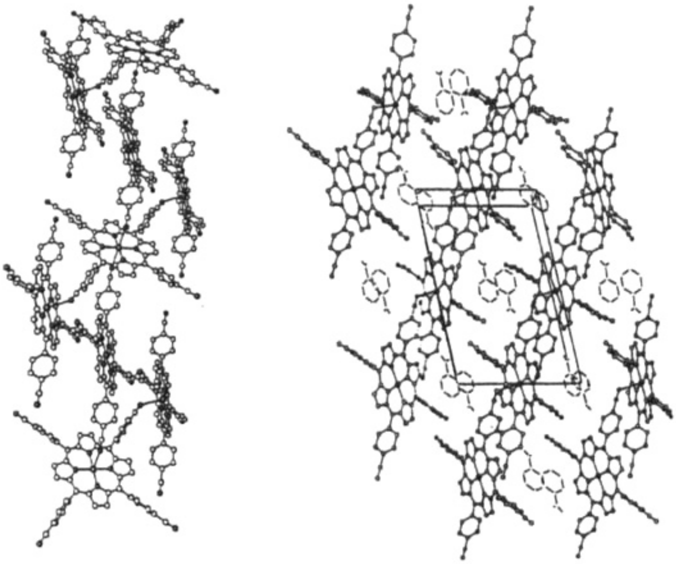


FIGURE 1. (Left) Structure of the coordination polymer of TCNPP. (Right) Intercalation of nitrobenzene between the TCNPP polymeric layers.

Layered Networks of the Porphyrin Materials

Presence of competing axial ligands or strongly solvating species in the crystallization environment, or placement of metal ions with four-coordination preference within the core framework, may prevent self-coordination of the porphyrin building blocks through metal-ligand interaction. In such cases the molecular shape features of the porphyrin materials dictate dominantly the formation of *layered* structures consisting of flat and hollow multiporphyrin assemblies. In the TCNPP solids, the porphyrin units within these layers are interlinked by dipolar forces assisted by C-H...N hydrogen bonding either in one or two dimensions. The interporphyrin voids are conveniently accommodated by guest molecular species of suitable size.

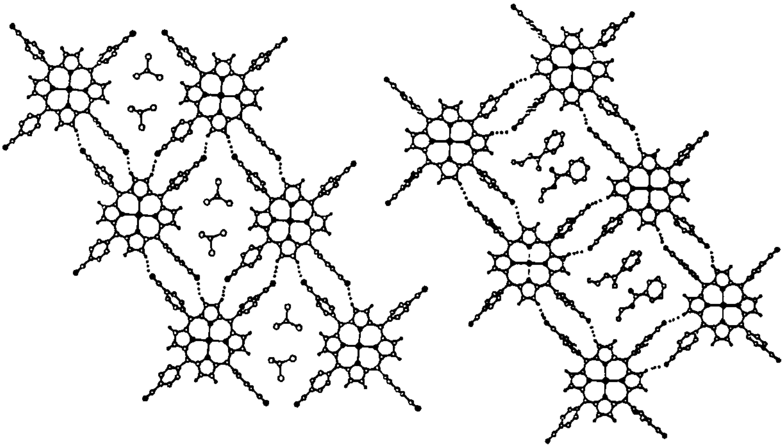


FIGURE 2. Condensed two-dimensional open networks of TCNPP. The smaller oval-shaped interporphyrin cavities (left) can be occupied by two molecules of chloroform. The larger square-shaped cavities (right) are suitable to accommodate two entities of ethylbenzoate.

The layers are stacked in the crystal one on top of the other in an offset manner. The interlayer separation is typically maintained within the 3.8-4.4 Å range, irrespective of the degree of coordination around the metal centers, as the axial ligands (if present) of one layer are effectively inserted into the interporphyrin pores of adjacent layers. The dominant structural motif in these crystals consists of linear chains of the porphyrin species characterized by an anti-parallel arrangement at close proximity of the cyanophenyl fragments of adjacent units. Such dimeric aggregation at each interaction site is characterized by a perpendicular distance of about 3.9 Å between the Ar-CN axes and by relatively short and nearly linear C-H...N≡C- contacts along the chain. Thus, it appears to be stabilized by effective dipolar van der Waals interactions assisted by weak hydrogen bonding. In view of the square-planar symmetry of the porphyrin building blocks this aggregation mode may extend in structures composed of either four-coordinate or five-coordinate metalloporphyrin entities in two dimensions, yielding an open porphyrin network (Figure 2). Two differently structured arrangements are possible with pores of either elliptical or nearly square shape. The approximate dimensions of these pores within the porphyrin assemblies available for guest inclusion (after substracting the van der Waals radii of atoms which line the walls of the cavity) are: 6.4x11 Å and 10x10 Å, respectively.[6]

In materials containing six-coordinate TCNPP metalloporphyrin units, the dipolarly stabilized interporphyrin association prevails only in one direction, and it is disrupted along the other axis (Figure 3). This is particularly so with aromatic axial ligands which lie nearly parallel to the porphyrin core.

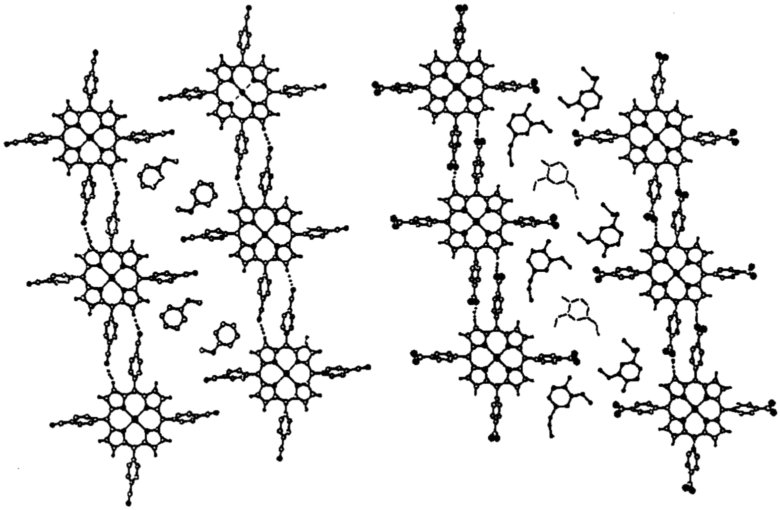


FIGURE 3. Expanded layers in materials composed of six-coordinate building blocks. The ligands accommodated between the porphyrin chains in one layer coordinate axially to the porphyrin cores of adjacent layers. (left) TCNPP with anisole. (right) TNO_2PP with eugenol.

Interpenetration of the ligands of one layer into the open interporphyrin voids of adjacent layers located above and below, in order to optimize the interlayer stacking (see above), requires relatively large space. This prevents a close approach between the porphyrin chains and formation of compact two-dimensional networks as in the previous examples. In such case, additional molecules of the solvent may be incorporated into the lattice to fill the remaining empty space between adjacent porphyrin-chain motifs. Figure 3 describes such layered patterns in solids of six-coordinate zinc-TCNPP and of similarly structured six-coordinate zinc-TNO_2PP.[6] The layered arrays in these structures consist of parallel chain motifs of strongly interlinked porphyrin units through hydrogen-bonding and dipolar interactions. The porphyrin chains are interspaced by guest ligand molecules coordinated to the metal centers of neighboring porphyrin sheets. A third noncoordinating solvent species is also included between these chains. In the latter case, presence of the nitro-substituents on the tetraphenylporphyrin, and their nearly perpendicular alignement with respect to the core framework, allows for hydrogen bonding interactions between the stacked layeres as well, thus rigidifying the multi-porphyrin assembly.

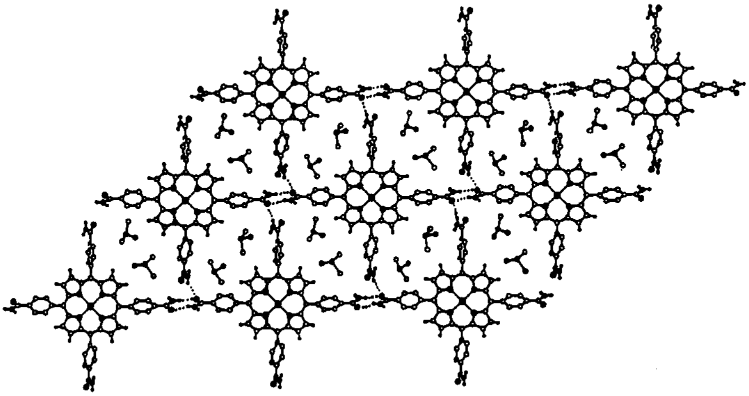


FIGURE 4. Open layered architecture of hydrogen-bonding polymers of $TCONH_2PP$ in its 1:4 crystalline adduct with DMSO. The inter-porphyrin voids are filled in the crystal by two units of the guest molecule [triclinic, a = 11.678(4), b = 13.732(3), c = 17.818(5) Å, α = 78.03(2), β = 88.64(3), γ = 83.43(3)°, space group P1bar (No. 2)].

In the crystals of $TCONH_2PP$ the porphyrin building blocks are interlinked by pairwise hydrogen bonds between the terminal amide functions as shown in Figure 4. Each molecule is bound to two neighboring species approaching from two opposite directions, thus forming linear hydrogen-bonding polymers. The multiple hydrogen-bonding capacity of the amide function leads to strong association of the linear polymers into layered open two-dimensional networks through additional H-bonding (Figure 4). In the crystal, these networks stack one on top of the other with an average 4.6 Å spacing. The two types of interporphyrin cavities formed within the layered motifs have a slightly different van der Waals widths of about 5.9 and 6.8 Å, accommodating two DMSO entities at each site.

CONCLUDING REMARKS

The present series of studies on the self-assembly of functionalized metalloporphyrins demonstrates the feasibility of a controlled formulation of supramolecular multiporphyrin arrays by rational modification of the porphyrin building blocks. Construction of novel coordination polymers[7] is particularly attractive in the wider context of modelling electron transfer processes. On the other hand, the conservation of the open porphyrin chain or network motifs and of the interporphyrin offset stacking geometry in the layered structures allows one to control to a considerable extent the porosity of the molecular layers by changing the type of the sensor groups attached to the porphyrin framework (Figure 5). It has been demonstrated previously that the cavity size characteristics in layered multiporphyrin motifs are significantly different in structures based on the PhOH, PhF, PhCl or PhBr porphyrin derivatives.[3b] The corresponding van der Waals width of the open space within the multiporphyrin chains ranges from 3.5 Å in the PhOH material (suitable to accommodate an aromatic moiety edge-on) to 5.5 Å in the PhBr material (which can be occupied either by a flattened aryl moiety or by two molecules of a smaller guest). The interporphyrin pore size in the layered condensed networks based on the $TCONH_2PP$ and TCNPP frameworks are even larger (5.9-6.8 Å in the former and 6.4-10 Å in the latter), allowing convenient inclusion within these open networks of two molecular entities.

Even larger voids of a rhombal shape (16 x 21 Å) can be obtained in lattices based on the tetra(carboxyphenyl)porphyrin (Figure 5).[3b]

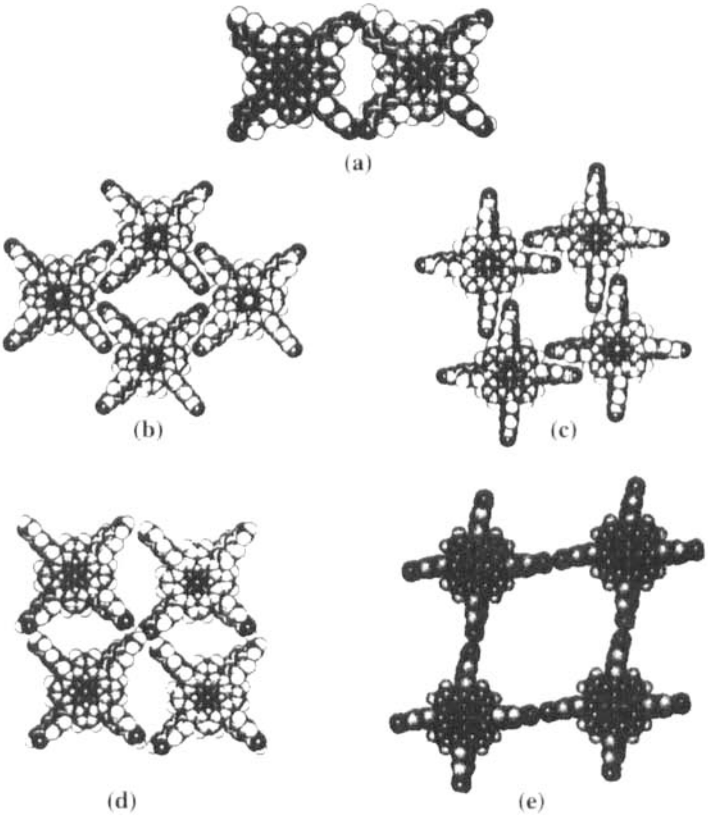


FIGURE 5. Space-filling representation of the different porphyrin-based supramolecular motifs, illustrating the interporphyrin pore variation in crystalline materials based on the tetrahydroxy (a), tetracyano (b) and (c), tetraamido (d), and tetracarboxy (e) derivatives.

Acknowledgment

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