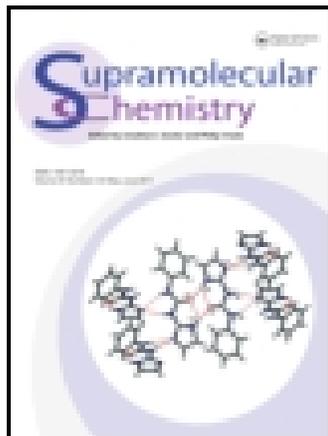


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Supramolecular Networks of Octahydroxy Porphyrins

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Multifunctionalized octahydroxy porphyrins, 5,10,15,20-tetrakis(2',6'-dihydroxyphenyl)-porphyrin, $H_2T(2',6'-DHP)P$, and 5,10,15,20-tetrakis-(3',5'-dihydroxyphenyl)porphyrin, $H_2T(3',5'-DHP)P$, have been developed as solid state building blocks for the self-assembly of hydrogen bonded supramolecular networks. A series of solid state X-ray structures of these porphyrins with various solvates show strong inter-porphyrin interactions through their peripheral hydroxyl substituents by means of directional hydrogen bonding. The position of the hydroxyl groups and the nature of the lattice guest (i.e., solvate) have dramatic influences on the molecular packing and the porosity of the structures. In particular, with ethyl acetate as solvate, the crystal structure of $H_2T(3',5'-DHP)P$ exhibits a one dimensional columnar network, whereas $H_2T(2',6'-DHP)P$ shows essentially a two dimensional, hydrogen-bonded, layered structure. With benzonitrile as solvate, the structure of $H_2T(3',5'-DHP)P$ changes substantially to a two dimensional corrugated structure in order to accommodate a larger pore size. The pore volumes filled by solvate in these structures are exceptionally large: 56%, 61%, and 67% of the unit cell volume, respectively. Crystal structure data for $H_2T(3',5'-DHP)P \bullet 5 EtOAc$: $C_{64}H_{70}N_4O_{18}$, $M = 1183.24$, triclinic, $P\bar{1}$, $a = 7.245$ (2) Å, $b = 14.727$ (3) Å, $c = 14.835$ (4) Å, $\alpha = 90.18$ (2)°, $\beta = 92.90$ (2)° and $\gamma = 90.02$ (2)°, $V = 1580.8(7)$ Å³, $Z = 1$; $R1 = 0.113$, $wR2 = 0.280$ (on 2588, $I > 2\sigma(I)$ observed data). For $H_2T(2',6'-DHP)P \bullet 4 EtOAc$: $C_{60}H_{62}N_4O_{16}$, $M = 1095.14$, triclinic, $P\bar{1}$, $a = 13.736$ (3) Å, $b = 14.032$

(3) Å, $c = 17.029$ (3) Å, $\alpha = 93.77$ (3)°, $\beta = 110.92$ (3)° and $\gamma = 111.81$ (3)°, $V = 2770.9$ (10) Å³, $Z = 2$; $R1 = 0.045$, $wR2 = 0.112$ (on 6260, $I > 2\sigma(I)$ observed data). For $H_2T(3',5'-DHP)P \bullet 7 C_7H_5N$: $C_{93}H_{65}N_{11}O_8$, $M = 1464.56$, monoclinic, $P2_1/m$, $a = 11.105$ (4) Å, $b = 25.744$ (7) Å, $c = 14.022$ (3) Å, $\beta = 108.09$ (2)°, $V = 3811(2)$ Å³, $Z = 2$; $R1 = 0.062$, $wR2 = 0.130$ (on 2588, $I > 2\sigma(I)$ observed data).

Keywords: Porphyrins, hydrogen bonding, network solids, clathrate

In order to develop nanoporous materials with desired properties, a wide range of organic molecules have been employed as molecular building blocks [1]. Porphyrins and metalloporphyrins provide an important, but relatively unexplored, class of such building blocks because of their large size, ease of synthesis, excellent thermal stability, and diverse coordination and catalytic chemistry. Furthermore, porphyrins provide an extremely versatile platform on which to build desired peripheral functionality with designed orientations. Such functionality can provide the intermolecular

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interactions that control self-assembly both in solution and in the solid state. There have been a few recent reports on the supramolecular architectures of porphyrin solids with metal-organic coordination [2] and hydrogen bonded [3] networks. In addition, the extensive structural work that exists for porphyrins and metalloporphyrins [4] provide a database for the systematic examination of intermolecular interactions in the solid state. Notably, Strouse and coworkers [5] have reported a wide range of clathrate-like host/guest solid state structures of H_2TPP and its metal derivatives. *Meso*-tetraphenylporphyrins are the most widely used systems due to their ease of synthesis and facile functionalization.

In order to more rationally control the structure of porphyrinic solids, we have examined a pair of symmetric octahydroxy substituted porphyrins, wherein the three dimensional structure is determined by the directional hydrogen bonding of hydroxyl groups. We report here the use of octahydroxy porphyrins, [6] $H_2T(2',6'$ -DHP)P and $H_2T(3',5'$ -DHP)P (Fig. 1) as building blocks for the synthesis of network crystalline solids, together with three X-ray structures derived from these porphyrins.

To delineate the effect of substituent position on the crystal packing and porosity of the structure, diffraction quality crystals of $H_2T(3',5'$ -DHP)P and $H_2T(2',6'$ -DHP)P porphyrin crystals were obtained with the same lattice guest, ethyl acetate [7–9]. A one-dimensional

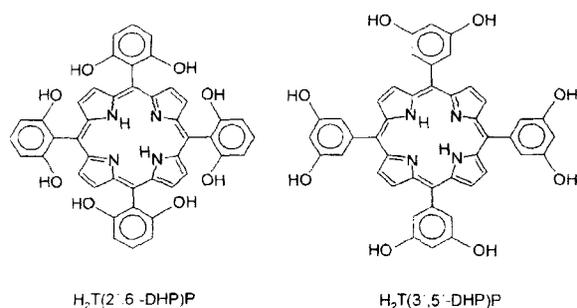


FIGURE 1 Chemical structures of octahydroxy porphyrins 5,10,15,20-tetrakis(2',6'-dihydroxy-phenyl)porphyrin ($H_2T(2',6'$ -DHP)P) and 5,10,15,20-tetrakis-(3',5'-dihydroxyphenyl)porphyrin ($H_2T(3',5'$ -DHP)P).

columnar packing is observed for $H_2T(3',5'$ -DHP)P•5 EtOAc (Fig. 2). The structure is controlled by the presence of strong, directional hydrogen bonding between the *meso*-phenyl hydroxyl groups. The porphyrin rings are almost planar and are nearly eclipsed with respect to one another in the columns. There is hydrogen bonding [10] only between each porphyrin and its nearest neighbor above and below with an inter-porphyrin separation of 7 Å. As a result, there is minimal π - π interaction between the porphyrins. There is no hydrogen bonding between columns. Two solvate-filled channels

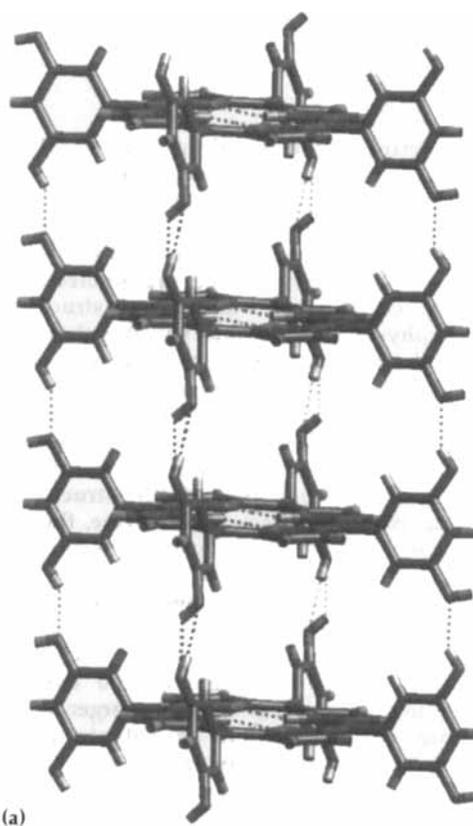


FIGURE 2 Molecular packing diagram of $H_2T(3',5'$ -DHP)P•5 EtOAc complex; (a) the one-dimensional columnar structure; (b) perpendicular view of packing diagram (van der Waals spheres shown at 0.7 of atomic radii), showing solvate-filled channels of 6.5 by 6.5 Å between the columns. Solvate molecules are not shown for clarity. Distances shown for the channels exclude van der Waals radii.

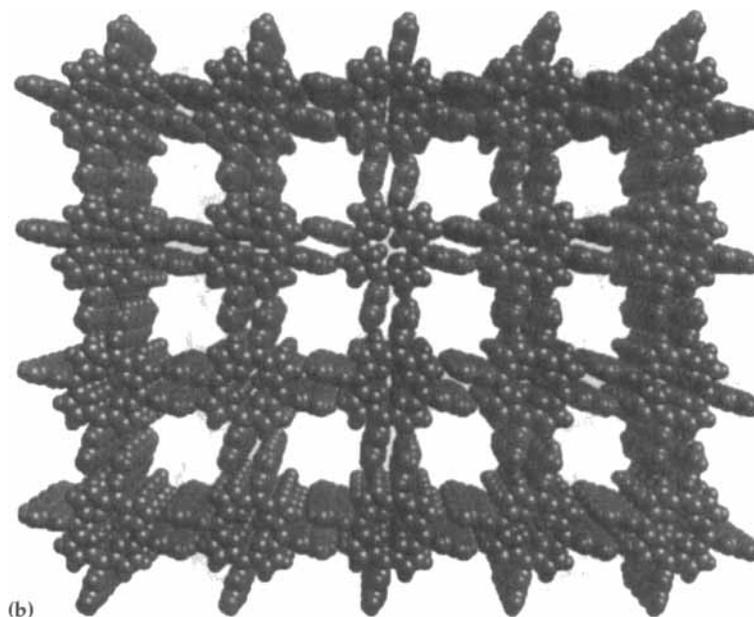


FIGURE 2 (Continued).

3.4 by 3.4 Å (van der Waals surface to van der Waals surface) are observed between the porphyrin planes, normal to one another and normal to the porphyrin columns. Four such columns form a network resulting in a bigger channel size of 6.5 by 6.5 Å (Fig. 2b). For a given channel all four porphyrins lie in the same plane. The phenyl rings of porphyrins in adjacent columns interleave and are 4.5 Å apart, indicating limited π - π interaction.

Upon changing the position of the hydroxy substituents from the *meta*- to the *ortho*- positions of the phenyl rings, a substantial change in the structure occurs: $\text{H}_2\text{T}(2',6'\text{-DHP})\text{P} \bullet 4 \text{ EtOAc}$ has a two-dimensional layered structure, as shown in the molecular packing diagram of Figure 3. The porphyrin rings are slightly ruffled and show strong directional hydrogen bonding induced by the peripheral hydroxyl groups [10]. Each porphyrin has four hydrogen bonded nearest neighbors in an offset orientation. In a given layer, the vertical distance between the offset porphyrins is 7.0 Å. The center-to-center distance between the adjacent layers is 11.8 Å. A

large channel of about 3.0 by 3.6 Å runs parallel to the layers and the porphyrin planes and is filled with ethyl acetate molecules; no hydrogen bonding occurs between the porphyrinic layers. Ethyl acetate molecules in the lattice are hydrogen-bonded through their carbonyl groups to the hydroxyl groups of the porphyrins.

To examine the effect of the solvate on the molecular packing in these systems, crystals of $\text{H}_2\text{T}(3',5'\text{-DHP})\text{P}$ were grown from benzonitrile, a much larger solvate molecule [11]. The solid-state structure is dramatically altered by the benzonitrile (Fig. 4). The structure has changed from a one dimensional columnar (for ethyl acetate) to a two dimensional corrugated structure, with a pore structure matched to the benzonitrile. Each porphyrin is hydrogen bonded to three closest neighbors. There is some loss of hydrogen bonding between the hydroxyl groups of the porphyrins, which is replaced by hydrogen bonding to nitrile groups of the benzonitrile. The molecular packing models show varying solvate-filled channels in different directions along the unit cell axes. The center-to-

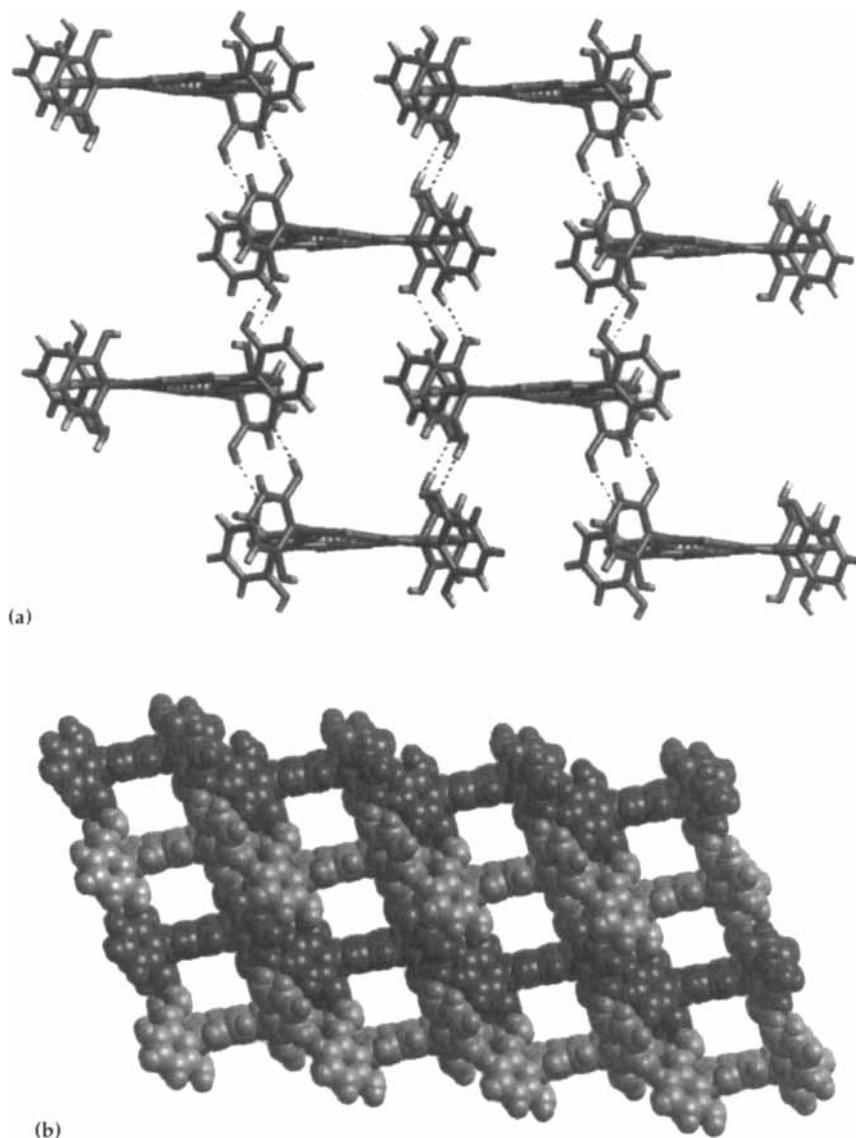


FIGURE 3 Molecular packing diagram of $H_2T(2',6'-DHP)P \bullet 4 EtOAc$ complex; (a) two dimensional layered structure. (b) perpendicular view of van der Waals (0.7 of atomic radii) packing diagram showing 3.4 by 3.4 Å wide solvate-filled channels along the layers. Solvate molecules are not shown for clarity. Distances shown for the channels exclude van der Waals radii. Porphyrins in light and dark shades indicate that they are closer and further away, respectively.

center distance between the adjacent layers is about 12.6 Å and the vertical distance between nearest hydrogen-bonded porphyrins is 7.40 Å.

The porosity filled by solvate in these structures is striking: while most free-base porphyrin structures have less than three solvates per

porphyrin [2, 5] (triclinic H_2TPP , for example, has *no* solvate [12]), our porphyrins have as many as seven. As a quantitative measure, the total void volume (i.e., unit cell volume minus the porphyrins' van der Waals volume [13]) in our structures is 56%, 61%, and 67% of the unit

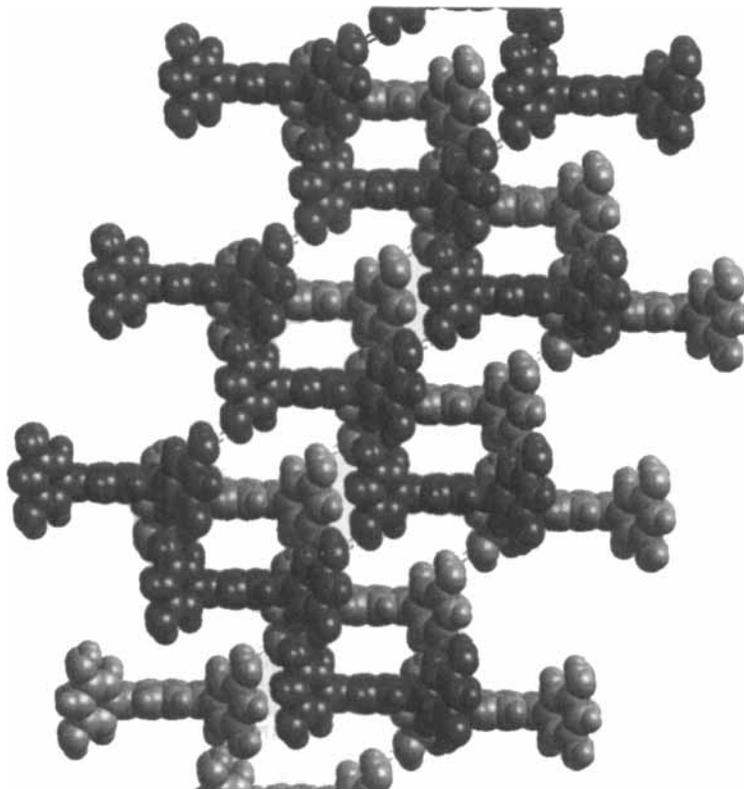


FIGURE 4 van der Waals (0.7 of their atomic radii) packing diagram of $\text{H}_2\text{T}(3',5'\text{-DHP})\text{P} \cdot 7 \text{C}_6\text{H}_5\text{CN}$ complex showing 3.0 by 4.0 Å wide solvate-filled channel; normal to this view there is a second channel, 6.5 by 5.5 Å. The porphyrins shown light and dark shades indicate that they are in front and back directions, respectively. Solvate molecules are not shown for clarity. Distances shown for the channels exclude van der Waals radii.

cell volume for $\text{H}_2\text{T}(2',6'\text{-DHP})\text{P} \cdot 4 \text{EtOAc}$, $\text{H}_2\text{T}(3',5'\text{-DHP})\text{P} \cdot 5 \text{EtOAc}$, and $\text{H}_2\text{T}(3',5'\text{-DHP})\text{P} \cdot 7 \text{C}_6\text{H}_5\text{CN}$, respectively. For comparison, the structure of H_2TPP has a void volume of only 26% [12,13]. The three dimensional self-assembly of these porphyrins is strongly influenced by directional hydrogen bonding and is largely independent of π - π interactions. The present study demonstrates the effect of the directionality of the porphyrin substituents and size of the solvate on the supramolecular architectures of these molecules. We are now expanding these supramolecular architectures to metal-substituted porphyrins and find similar solid-state structures; further work is underway to use the established reactivity of metallopor-

phyrins to create heterogeneous catalysts for shape selective oxidations [14].

Acknowledgements

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Supporting Information Available

Tables of crystallographic data including atomic positional and thermal parameters, for $\text{H}_2\text{T}(3',5'\text{-DHP})\text{P} \cdot 5 \text{EtOAc}$ (7 pages), $\text{H}_2\text{T}(2',6'\text{-DHP})\text{P} \cdot 4 \text{EtOAc}$ (8 pages), and $\text{H}_2\text{T}(3',5'\text{-DHP})\text{P} \cdot 7 \text{C}_6\text{H}_5\text{CN}$

(7 pages) are available from the corresponding author.

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- [7] Crystals were grown by diffusion of *n*-heptane to a saturated H₂T(3',5'-DHP)P solution in ethyl acetate over a period of two days. Crystal structure data for H₂T(3',5'-DHP)P•5 EtOAc: red prismatic crystals were mounted to a thin glass fiber under oil (paratone-N, Exxon) and cooled immediately to 198 K. C₆₄H₇₀N₄O₁₈, M = 1183.24, triclinic, P $\bar{1}$, *a* = 7.245 (2) Å, *b* = 14.727 (3) Å, *c* = 14.835 (4) Å, α = 90.18 (2)°, β = 92.90 (2)° and γ = 90.02 (2)°, *V* = 1580.8(7) Å³, *Z* = 1. The structure was refined using full-matrix least-squares on F_o² (data/restraints/parameters: 4369/336/391), converging to R1 = 0.113, wR2 = 0.280 (on 2588, I > 2σ(I) observed data); R1 = 0.197, wR2 = 0.356 (all data). The solvate molecules were highly disordered.
- [8] Porphyrin crystals were obtained by direct diffusion of heptane to a saturated solution of porphyrin in ethyl acetate at room temperature over a period of four days. Crystal structure data for H₂T(2',6'-DHP)P•4 EtOAc: purple prismatic crystals were mounted as before. C₆₀H₆₂N₄O₁₆, M = 1095.14, triclinic, P $\bar{1}$, *a* = 13.736 (3) Å, *b* = 14.032 (3) Å, *c* = 17.029 (3) Å, α = 93.77 (3)°, β = 110.92 (3)° and γ = 111.81 (3)°, *V* = 2770.9 (10) Å³, *Z* = 2. Single crystal diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer at 198 K using Mo K α (λ = 0.71073 Å). The structure was refined using full-matrix least-squares on F_o² (data/restraints/parameters: 8624/64/846), converging to R1 = 0.045, wR2 = 0.112 (on 6260, I > 2σ(I) observed data); R1 = 0.087, wR2 = 0.151 (all data). Porphyrin crystals tend to loose crystallinity upon removal from the mother liquor at room temperature.
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- [10] In all the structures, the O—O distances (hydrogen bonded OH—OH groups) were 2.55–2.8 Å, which indicates strong, directional hydrogen bonding interactions.
- [11] The crystals of H₂T(3',5'-DHP)P•7 C₇H₅N complex were grown by diffusion of solvent *n*-heptane to the solution of porphyrin in benzonitrile over a period of two days. Crystal structure data for H₂T(3',5'-DHP)P•7 C₇H₅N: purple plate-like crystals were mounted as before. C₉₃H₆₅N₁₁O₈, M = 1464.56, monoclinic, P2₁/m, *a* = 11.105 (4) Å, *b* = 25.744 (7) Å, *c* = 14.022 (3) Å, β = 108.09 (2)°, *V* = 3811(2) Å³, *Z* = 2. The structure was refined using full-matrix least-squares on F_o² (data/restraints/parameters: 6106/0/548), converging to R1 = 0.062, wR2 = 0.130 (on 2588, I > 2σ(I) observed data); R1 = 0.184, wR2 = 0.175 (all data).
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