

From porphyrin sponges to porphyrin sieves: a unique crystalline lattice of aquazinc tetra(4-carboxyphenyl)porphyrin with nanosized channels

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A unique supramolecular solid assembly with very wide channels has been formulated with aquazinc tetra(4-carboxyphenyl)porphyrin building blocks; the open porphyrin lattice is sustained by characteristic stacking interactions and multiple hydrogen bonding, it comprises only about 39% of the crystal volume, and preserves its crystallinity up to about 360 K.

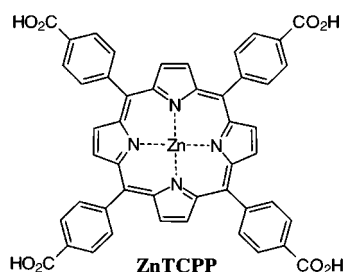
A remarkable effort has been directed in recent years towards the design, by noncovalent *supramolecular* synthesis, of new molecular solids with structural and functional similarity to the inorganic zeolites.^{1,2} We have also launched an extensive research program in this area, utilizing porphyrin metallo-macrocycles as building blocks. The latter readily form expansible clathrates with guest components of versatile size and shape, in which the architecture of the porphyrin lattice is, however, strongly conserved.³ Indeed, the vast majority of these structures consist of offset-stacked porphyrin layers with an average interlayer distance of 4.5 Å, the layered arrangement of the roughly flat porphyrin species representing a fundamental property of the porphyrin–porphyrin interaction.^{3–5} We anticipated that the transformation from materials with variable interporphyrin voids ('sponges') to materials with fixed-size tubular cavities ('sieves') can be achieved by incorporation of a suitable molecular recognition algorithm in the porphyrin building blocks.⁴ Here we report on a novel porphyrin-sieve type structure with rather large channels, the crystal lattice of which consists of a single component, aquazinc tetra(4-carboxyphenyl)porphyrin (aqua-ZnTCPP), and occupies only 39% of the crystal volume. The architecture of this structure is determined entirely by interporphyrin hydrogen bonding and stacking interactions, without resorting to external auxiliaries. The only other known example of a porphyrin-based lattice with wide open channels consists of heterogeneous assemblies of porphyrins *via* transition metal bridges.² The interiors of the channels in both crystals are partly filled with a small number of disordered molecules of nitrobenzene, which acts as a template.

We have shown previously that molecules of ZnTCPP may self-assemble through self-complementary hydrogen bonding in different ways to yield hollow network architectures.^{4d,e} This includes formation of two-dimensional arrays with large interporphyrin voids (16 × 21 Å)[†] through (CO₂H)₂ hydrogen bonding between the terminal carboxylic functions of adjacent porphyrins.^{4d} However, the latter were found to mutually interlock into one another to fill the interporphyrin voids, as

commonly observed for other systems with large intermolecular spacing.⁶ More recently, two-dimensional patterns with considerably smaller cavities (8.5 × 11.0 Å)[†] have also been constructed, by utilizing potassium or sodium 18-crown-6 as template.^{4e} These networks do not interpenetrate as the interporphyrin voids are conveniently accommodated by the macrocyclic template.

From the above observations it has become clear that in order to prevent interpenetration in the former case and to yield network structures with larger pores, it is essential to use sizeable solubilizing and templating agents with a low tendency to interact with the ZnTCPP lattice. After numerous trials, the following experimental procedure based on slow diffusion gave successful results. First, tetra(4-aminophenyl)porphyrin was dissolved in nitrobenzene, and this solution was placed at the bottom of a glass tube. This porphyrin derivative bears four amino groups which on one hand represent non-complementary binding sites for self-assembly, and on the other hand are weaker proton donors than the carboxylic function (and therefore have little chance to interact with the ZnTCPP). A second layer of ethylene glycol was placed above this solution. Then, a third layer of ZnTCPP dissolved in MeOH was placed on top. In such a manner, the ZnTCPP was allowed to diffuse slowly from the MeOH phase into the bottom layer. At saturation after several days, a phase separation occurred at the bottom solution yielding tiny needle-shaped crystals of ZnTCPP and an amorphous solid containing the tetraaminoporphyrin. The presence of the tetraaminoporphyrin in the bottom solution is essential in order to drive the ZnTCPP into the nitrobenzene layer (ZnTCPP is otherwise insoluble in nitrobenzene) and thus facilitate its self-organization *via* (CO₂H)₂ hydrogen bonding [Fig. 1(a)] around the nitrobenzene template (see below).

Fig. 1 illustrates the fascinating porphyrin sieve structure which characterizes the emerged crystals.[‡] It consists of open very efficiently hydrogen-bonded networks of aqua-ZnTCPP, which stack in an offset manner along the normal direction. Four porphyrin units and eight hydrogen bonds [at OH...O distances of 2.611(4) Å] encircle any given pore within the network. The perpendicular distance between adjacent layers is 4.68 Å. The porphyrin core is slightly inclined (by 18°) with respect to plane of the network, as a result of which the van der Waals width of the open channel propagating through the crystal at its narrowest point is reduced from 16 Å^{4d,e} to about 15 Å. In spite of the fact that the aqua-ZnTCPP lattice occupies only about 39% (after accounting for the van der Waals radii of all the atoms including hydrogens) of the crystal volume,⁷ the presence of neither tetraaminoporphyrin nor of other species in the interporphyrin channels could be identified from the diffraction data. NMR experiments do indicate however that the crystals contain nitrobenzene solvent with an approximate 1:4 porphyrin : solvent ratio (which slowly reduces with time).[§] The randomly distributed residual electron density peaks found in the channels did not exceed 0.85 e Å⁻³, suggesting only partial occupancy of the channels (the very loose crystal packing is reflected also in relatively large atomic thermal displacement parameters) and a significant disorder of the solvent molecules even at 115 K. Nevertheless, the structure refinement based on



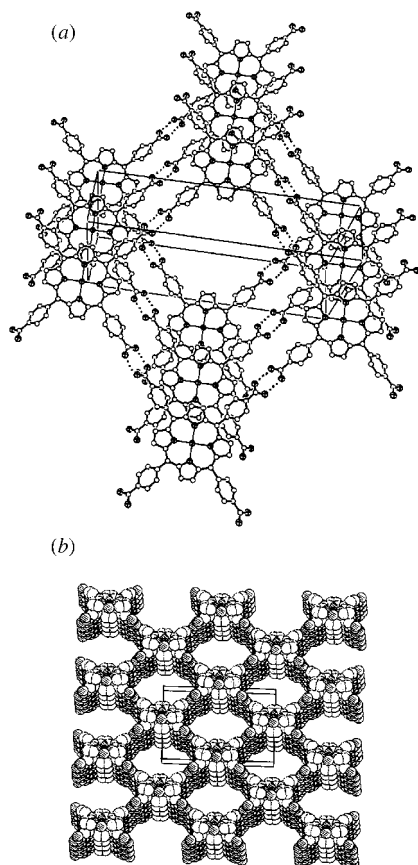


Fig. 1 (a) Ortep illustration of the crystal lattice, projected approximately on the plane of the porphyrin layers, showing their offset-stacked organization (the axial water bound to zinc is omitted for clarity). (b) Space-filling (CPK) representation of the open structure, viewed approximately down the channels which propagate along the *c*-axis of the crystal lattice. It shows best the space proportions between porphyrin lattice and the 1.5 nm wide open channels (the latter being partly occupied by disordered nitrobenzene solvent).

the ZnTCPP lattice alone converged at a relatively low (for such 'hollow' systems) *R*₁ value of 13.9%. These surprising observations led us to conduct independent full-set measurements on three different crystals, but all provided identical results. Crystals of this material do deteriorate slowly when left in an open air, but are quite stable when covered with a very thin layer of light oil. Their structure and morphology does not change upon heating or cooling (apart from natural thermal expansion or contraction) within the temperature range of 115–360 K, as indicated by repeated measurements of the crystal data on the same crystal at various temperatures in this range. Despite the solvent disorder, the experimental data monitored by a CCD detector were sensitive enough to allow at this stage the location of all the hydrogen atoms on the porphyrin framework in difference Fourier maps. As the contribution of the disordered solvent to the diffraction pattern could not be rigorously included in the crystallographic calculations, it was subtracted in the next stage by the Squeeze/Bypass procedure.⁸ The resulting refinement of the aqua-ZnTCPP lattice converged with reasonable precision at a considerably lower *R*₁ value of 7.1%, without affecting to any significant extent the porphyrin structure. The combination of the above findings confirm with a high degree of certainty the correctness of this unique structure.

This study demonstrates that hydrogen bonding interactions combined with dominant molecular shape features (van Waals forces) can be very effective in formulations of nanoporous materials from porphyrin building blocks which recognize each other through multiple molecular recognition sites, in the presence of a suitable template. The enthalpies of such interactions when considered alone are relatively small, 20–33

kJ mol^{-1} for hydrogen bonds in the carboxylic acid dimers,⁹ and $\leq 46 \text{ kJ mol}^{-1}$ for π - π stacking between two partially overlapping zinc porphyrin moieties.⁵ However, their cooperative effect (each ZnTCPP is involved in eight hydrogen bonds and is sandwiched between two adjacent porphyrins) approaches the strength of a covalent bond, and appears to be adequate to stabilize the observed molecular sieve structure even with only partial occupation of the 1.5 nm wide channels by solvent. Thus, although the porphyrin lattice occupies only 39% of the crystal volume, it forms an ordered and relatively stable solid. The preset study, along with the previous observations,^{4,d,e} also shows the ability of the ZnTCPP system to self-assemble into different supramolecular architectures (pseudo-polymorphism), and emphasizes the significance of the templating agent in inducing the preferred organization.

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Notes and references

† Dimensions of interporphyrin voids refer throughout this paper to distances between van der Waals surfaces of the porphyrin framework.

‡ *Crystal data* for aqua-ZnTCPP: $\text{C}_{48}\text{H}_{28}\text{N}_4\text{O}_8\text{Zn}\cdot\text{H}_2\text{O}\cdot 4(\text{C}_6\text{H}_5\text{NO}_2)$, § *M_r* = 1364.6, monoclinic, space group *C2/m*, *a* = 19.622(1), *b* = 29.649(1), *c* = 7.513(1) Å, β = 99.24(1)°, *V* = 4314.2(6) Å³, *Z* = 2, ρ_c = 1.050 g cm^{-3} , $\mu(\text{MoK}\alpha)$ = 0.34 mm^{-1} , *T* = 115 K, 6103 measured reflections (one hemisphere), 3629 unique reflections, *R_{int}* = 0.039. The diffraction data of the poorly diffracting crystals were collected on a KappaCCD diffractometer system, using Mo-K α (λ = 0.7107 Å) radiation and 0.5° ϕ and ω scans. Final *R*₁ = 0.139 for 2329 reflections with *F* > 4 σ (*F*), *R*₁ = 0.194, *wR*₂ = 0.381 and *GoF* = 1.379 for all 3629 data. All hydrogen atoms of the porphyrin framework were located on difference Fourier maps; their positions were slightly adjusted to conform to standard bond lengths and angles. The porphyrin complex (with five-coordinate zinc ion) is located on, and disordered about, the inversion center. Only very diffused residual electron density was observed in the channel voids. It corresponds to a highly disordered nitrobenzene solvent, the structure of which could not be modeled. After subtraction of the disordered and diffused solvent contribution to the diffraction pattern (see text) (ref. 7, 8), final *R*₁ = 0.071 for 2096 reflections with *F* > 4 σ (*F*), *R*₁ = 0.112, *wR*₂ = 0.198 and *GoF* = 0.985 for all 3629 data. CCDC 182/1391. See <http://www.rsc.org/suppdata/cc/1999/1961/> for crystallographic data in .cif format.

§ Content of the disordered solvent species in the analysed crystals was assessed by ¹H NMR (DMSO, 500MHz): δ 8.80 (8H, s, β -pyrrole of ZnTCPP), 8.25 (8H, d, nitrophenol), 7.85 (4H, t, nitrophenol), 7.70 (8H, t, nitrophenol).

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