Crystal engineering with tetraarylporphyrins, an exceptionally versatile building block for the design of multidimensional supramolecular structures

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Zinc *meso*-tetra(4-amidophenyl)porphyrin assembles into open two-dimensional arrays parallel to the porphyrin plane by self-complementary hydrogen bonding between the –$CONH_2$ recognition sites of adjacent molecules; manganese *meso*-tetraphenylporphyrin perchlorate and the bidentate 4,4′-bipyridyl ligand afford one-dimensional coordination polymers, which propagate in a direction perpendicular to the porphyrin plane; simultaneous application of these two modules of supramolecular design may lead to porous porphyrin-based materials with enhanced structural integrity.

The design of multiporphyrin architectures has drawn considerable attention in recent years, as such materials have diverse potential for scientific and technological applications as biomimetic models of photosynthetic systems or as functional molecular devices.[1,2] Tetraarylporphyrin molecules have a number of features that make them attractive building blocks for crystal engineering. These molecules are quite rigid, highly symmetric, and easily synthesized, and they exhibit a high degree of thermal and oxidative stability. The porphyrins can be easily 'programmed' by addition of various substituents and recognition sites to either the pyrrole or aryl groups, as well as by varying the nature of the metal atom inserted into the porphyrin core. Several successful attempts to assemble supramolecular porphyrin aggregates, in solution as well as in the solid state, have been reported recently.[3] In this context we have previously described formation of one-, two- and three-dimensional coordination polymers of zinc tetra(4-pyridyl)porphyrin and of zinc tetra(4-cyanophenyl)porphyrin.[4] We have also demonstrated, along with others, the utilization of hydrogen-bonding as an effective means of structural control in the design of homogeneous multiporphyrin architectures.[5,6] As part of this ongoing investigation we now report the structures of new materials based on controlled multiporphyrin aggregation which demonstrate two of the most plausible modes of supramolecular design, utilizing effective synthons for hydrogen-bonding and coordination polymerization.

Zinc *meso*-tetra(4-amidophenyl)porphyrin **1a** is representative of building blocks containing self-complementary recognition sites at the peripheral 4-position of the phenyl rings. The square-shaped tetraamide functionality and its hydrogen bonding capacity can dictate the formation of planar and rigid hollow networks sustained by hydrogen bonds.[7] On the other hand, the use of manganese *meso*-tetraphenylporphyrin **1b** should facilitate the construction of coordination polymers with suitable multidentate ligands, as Mn^{III} reveals high affinity for a six-coordinate environment. In view of the paramagnetic properties of the latter, these materials may also have significant potential as molecular magnets.[8a] Literature survey shows, however, that only a very small number of coordination polymers with metalloporphyrin frameworks have been successfully prepared thus far,[8] while the occurrence of monomeric Mn^{III} complexes is considerably more common. Compounds **1a** and **1b** were prepared by standard procedures of porphyrin synthesis. Single crystals of zinc tetra(4-amidophenyl)porphyrin·$4Me_2SO\cdot H_2O$ **2** suitable for X-ray diffraction analysis were grown by very slow cooling of the solution of **1a** in Me_2SO. Similarly, single crystals of the 1 : 1 complex of MnTPP·ClO_4 with neutral 4,4′-bipyridyl (**3**; crystallizing as a nitrobenzene solvate) were grown from a slowly cooled stoichiometric mixture of these two components in nitrobenzene. The structure and composition of these crystals were determined unequivocally by X-ray diffraction analysis.‡

Fig. 1 illustrates the interporphyrin arrangement in the crystal structure of **2**. As anticipated, the self-assembly process utilizes cooperatively the hydrogen-bonding potential of the amide functions,[7] affording open two-dimensional networks with no inter-penetration between them. Each porphyrin unit is involved in eight hydrogen-bonding interactions at NH···OC distances within 2.984–3.068 Å. The interporphyrin cavities in each layer are *ca.* 5.9–6.8 Å wide and *ca.* 10 Å long (estimated distances between the van der Waals surfaces of the surrounding environment). They are accommodated by two guest molecules of Me_2SO at each of the two crystallographically independent sites. One of the four species axially ligates to the metal center of a porphyrin unit in an adjacent layer at a Zn···O=S coordination distance of 2.151(7) Å. The five-coordinate Zn ion deviates by 0.28 Å from its porphyrin plane towards the axial ligand. The two-dimensional networks relate to each other by crystallographic inversion. They stack in the crystal in an offset manner with a characteristic average spacing of 4.6 Å[4a] to optimize van der Waals stabilization and the fit of the axial ligands from one layer into the interporphyrin cavities of the next layer. As shown earlier, the cavity size characteristics in such layered multiporphyrin motifs depend directly on the functional substituents attached to the porphyrin framework, which allows one to control to a considerable extent the porosity

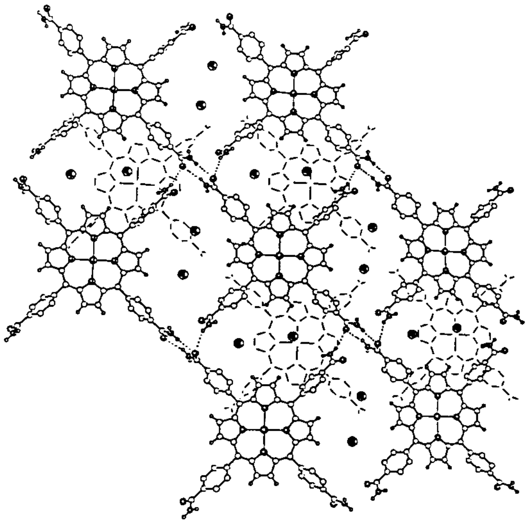

Fig. 1 Assembly of zinc tetra(4-amidophenyl)porphyrin building blocks in the form of two-dimensional open networks sustained by N–H···O=C hydrogen bonds. Each of the oval shaped interporphyrin cavities is occupied by two molecules of Me_2SO. For clarity, the positions of the latter are indicated by large darkened circles. The stick-only frameworks illustrate porphyrin molecules in a neighboring network and indicate the layered nature of the crystal structure.

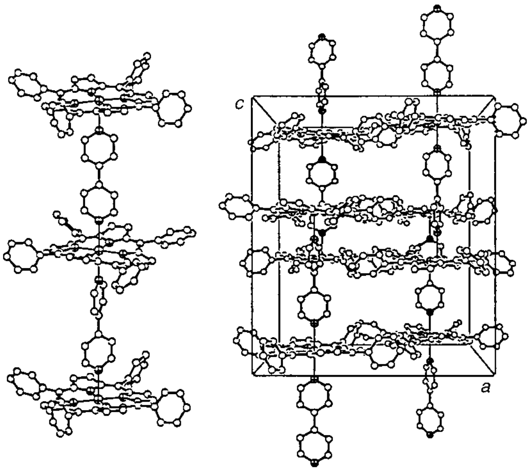

Fig. 2 (Left) Molecular structure of the coordination polymer composed of Mn^{III}–TPP and 4,4′-bipyridyl components. (Right) Perspective view of the crystal structure of this compound down the *b*-axis, showing the 'hollow' lattice of the crystal-packed polymers. The cavities are occupied by the perchlorate counter ions and by disordered solvent (not shown for clarity).

of the porphyrin layers thus formed. In relation to the present observation, the interporphyrin cavity dimensions found in homogeneous layered networks composed of tetra(4-hydroxyphenyl)porphyrin and of tetra(4-carboxyphenyl)porphyrin are 3.5 × 9.5 and 16 × 21 Å, respectively.[5]

The molecular structure of the coordination polymer units which compose **3** is displayed in Fig. 2(left). The linear polymeric strands consist of alternating metalloporphyrin and bipyridyl building blocks linked to each other from both ends by metal–ligand coordination, at $Mn\cdots N_{py}$ distances ranging from 2.321(7) Å to 2.409(7) Å. Along the chains the $Mn\cdots Mn$ separation is 11.79 Å, while between the chains the shortest $Mn\cdots Mn$ distance is 11.05 Å. The polymers are located on axes of twofold rotation at $(\frac{1}{4}, 0, z)$, and extend along the *c*-axis [Fig. 2(right)]. Their side packing in the *ab* plane is stabilized by dispersive interactions between the TPP frameworks (deformed from planarity to adopt a saddle conformation) as well as by coulombic forces through the anions located in between. The parallel alignment of the polymeric chains in the crystal leads to a nanoporous architecture of the three-dimensional assembly, with tubular shaped voids between the thinner bipyridyl sections of the polymers along the *a* and *b* crystal axes (directions parallel to the porphyrin planes), that are occupied by molecules of the nitrobenzene solvent (near 0.2, $\frac{1}{4}$, $\frac{1}{4}$ and 0.8, $\frac{1}{4}$, $\frac{1}{4}$) and the perchlorate counter ions (centered at 0.50, 0.08, 0.24). The smallest cross-section distance between the van der Waals surfaces of the channel walls is *ca.* 5 Å.

The structural integrity of the multiporphyrin architectures in **2** and **3** can be in principle increased by combination of the coordination polymerization and the lateral hydrogen-bonding features in the same material. Thus, cooperative hydrogen bonding between neighboring polymeric entities in **3** (which in that structure are displaced along the *a* and *b* crystal axes) can be introduced by substituting the TPP building block with suitable recognition groups on the porphyrin periphery (*e.g.* as observed in **2**). The structure of such a designed lattice can be fine-tuned by changing the size and shape of the bridging ligand as well as of the hydrogen-bonding sites on the porphyrin periphery. We are currently exploiting this promising methodology in an effort to construct a new series of structurally robust porous organic crystals and evaluate the potential applications of such molecular-sieve materials in molecular separation, transport and controlled release.

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Notes and References

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‡ *Crystal data*: **2**: $C_{48}H_{32}N_8O_4Zn\cdot 4C_2H_6SO\cdot H_2O$, M_r = 1180.7, triclinic, space group $P\bar{1}$, *a* = 11.653(1), *b* = 13.901(1), *c* = 17.708(1) Å, α = 78.38(1), β = 88.83(1), γ = 83.47(1)°, U = 2791.5 Å^3, Z = 2, D_c = 1.405 g cm^{-3}, $F(000)$ = 1232, μ(Mo-Kα) = 6.53 cm^{-1}, crystal size ≈ 0.20 × 0.10 × 0.10 mm, $2\theta_{max}$ = 46.6°, 6188 unique reflections, final $R1$ = 0.086 for 3461 reflections with $F > 4\sigma(F)$, $R1$ = 0.145, $wR2$ = 0.279 and GOF = 1.026 for all 6188 data. Two out of the four Me_2SO molecules in the asymmetric unit were found disordered; for one of them a twofold orientational disorder could be recognized and modeled accordingly.

3: $C_{44}H_{28}ClMnN_4O_4\cdot C_{10}H_8N_2\cdot C_6H_5NO_2$, M_r = 1046.4, orthorhombic, space group *Pnna*, *a* = 20.489(1), *b* = 20.611(1), *c* = 23.653(1) Å, U = 9988.6 Å^3, Z = 8, D_c = 1.392 g cm^{-3}, $F(000)$ = 4320, μ(Mo-Kα) = 3.80 cm^{-1}, crystal size ≈ 0.30 × 0.25 × 0.10 mm, $2\theta_{max}$ = 52.7°, 9896 unique reflections, final $R1$ = 0.099 for 4823 reflections with $F > 4\sigma(F)$, $R1$ = 0.175, $wR2$ = 0.40 and GOF = 0.961 for all 9896 data. The nitrobenzene solvent molecule was found translationally as well as orientationally disordered, and could not be modeled precisely. When its contribution to the structure factors was substracted by the 'Bypass' procedure,[9] $R1$ = 0.084 for 4754 reflections with $F > 4\sigma(F)$, $R1$ = 0.144 and $wR2$ = 0.315 for all 9896 data. The large atomic displacement parameters of the perchlorate oxygens are also indicative of wide-amplitude rotational motion of this ion. The diffraction data of the poorly diffracting crystals were collected at 293(2) K on a KappaCCD diffractometer system, using Mo-Kα (λ = 0.7107 Å) radiation and 0.6° ϕ scans. CCDC 182/886.

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