New effective synthons for supramolecular self-assembly of *meso*-carboxyphenylporphyrins

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Tesselation of new supramolecular motifs of the tetra(4-carboxyphenyl)porphyrin building blocks by metal ion templates has been demonstrated in crystals, characterizing the square-planar $[Na^+ \cdot (-COOH)_4 \cdot X^-]$ and the tetrahedral $[Zn^{2+} \cdot (-COOH)_2 \cdot (-COO^-)_2]$ molecular recognition elements for effective multiporphyrin assembly.

The *meso*-tetra(4-carboxyphenyl)porphyrin (TCPP) framework turned out to be an extremely versatile building block for effective supramolecular self-assembly and fabrication of new materials.[1–4] We have reported previously the formation of interpenetrating as well as non-penetrating two-dimensional arrays of TCPP with large interporphyrin voids through cooperative hydrogen-bonding between the terminal carboxylic groups of adjacent porphyrin entities.[2,3] Noteworthy is a unique and remarkably stable molecular sieve structure with nanosized (15 Å wide) channels.[4] Here, we communicate the first formulations of extended TCPP networks sustained by metal ion templates through multiple coordination to the carboxylic substituents.[5] Such templates may provide higher enthalpic driving force for the self-assembly process than the soft hydrogen bonding interactions alone, by adding ion-pairing attractions between the assembling entities. They could be thus more helpful in efforts to tailor porous solids based on robust multiporphyrin architectures.

Mononuclear and binuclear metallo-carboxylic/carboxylate assemblies are quite abundant in crystallographic databases. Yet, these synthons have not been used thus far in the context of porphyrin supramolecular chemistry. The large and rigid TCPP is in fact an excellent building block to this aim containing four coordination sites, each one pointing in a different direction. Here, we describe two representative examples of TCPP networks tesselated by metal ion auxiliaries which provide the supramolecular organizing force by multiply coordinating to the carboxylic functions (compounds **1** and **2**).† The self-assembly process of the free-base TCPP in the presence of NaCl and benzoic acid leads to the formation of two-dimensional multiporphyrin arrays sustained by sodium ions. The resulting motif of the supramolecular organization, involving TCPP and sodium benzoate (associated with deprotonation of the benzoic acid and expulsion of HCl) is illustrated in Fig. 1. It charaterizes the $Na^+(-COOH)_4$ synthon (see also Fig. 3) in which every alkali metal cation is coordinated (at 2.318–2.360 Å) to the carboxylic groups of four surrounding porphyrin moieties. The O(=C) binding sites involved in these interactions form an approximate square planar arrangement around the central cation. The coordination sphere around each cation is supplemented on one side by a coordinating molecule of the ethyl benzoate solvent (at $Na^+ \cdots O$ 2.261 Å). The benzoate anion provides another enforcement to the layered porphyrin structure by approaching the sodium cation from the opposite side, its carboxylate oxygens acting as effective proton acceptors for the four carboxylic groups of the converging porphyrins (this forces all O–H proton donors to point in the same direction, inducing a chiral polar structure in space group $P2_1$). The corresponding $O \cdots (H)O$ distances of these hydrogen bonds are within 2.57–2.68 Å, reflecting on a relatively strong
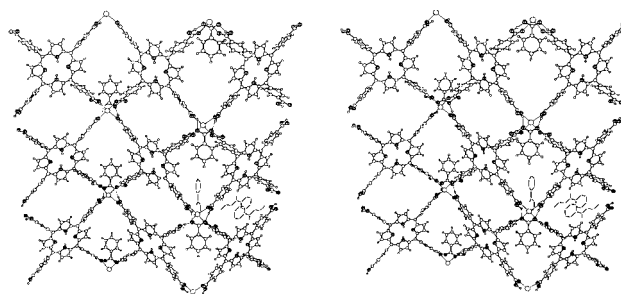

Fig. 1 Stereoview of the TCPP 'wavy' open networks formed in **1**, which are assembled by multiple coordination of the porphyrin units to the sodium benzoate template (*b* is horizontal and *a–c* is vertical). These layers stack tightly in the crystal along *a + c*. The interporphyrin channels thus formed are accommodated by molecules of the ethyl benzoate solvent (one of them coordinating to the sodium ion as well), as illustrated for clarity only in the lower right corner. The sodium ion is represented by a large uncrossed circle.

attraction. Every TCPP unit associates in this way with four different sodium benzoate entities (through four partly charged hydrogen bonds and four coordinative bonds to sodium), thus yielding a rather robust coordination polymer in two dimensions. Geometric optimization of these interactions results in the formation of corrugated ('wavy') porphyrin layers, adjacent units being related to each other either by pure lattice translation or by screw axis symmetry. van der Waals stacking of such layers one on top of the other in the normal direction (along *a + c*), at an average distance of *ca.* 4.21 Å between the corresponding porphyrin sections, composes the three-dimensional crystal structure. Additional molecules of the ethyl benzoate solvent fill effectively the channel voids which propagate in the lattice between the porphyrin columns of the stacked layers (Fig. 1).

The formation of the multiporphyrin networks in **2** is associated (in the absence of other acidic species in the crystallization environment) with double deprotonation of ZnTCPP to preserve neutrality. The observed assembly of the anionic porphyrin arrays templated by zinc ions is shown in Fig. 2. As commonly observed, the zinc ion residing within the porphyrin core is five-coordinated deviating outward from the porphyrin plane and attracting one molecule of the ethylene glycol solvent as an axial ligand. The external zinc cation is rather strongly coordinated (at 1.948–1.967 Å) to four different ZnTCPP units, maintaining an approximate tetrahedral geometry of coordination around it; it represents the $[Zn^{2+} \cdot (-COOH)_2 \cdot (-COO^-)_2]$ synthon (Fig. 3). This assembly mechanism *via* ion-pairing forces is assisted by additional intermolecular hydrogen bonding between the converging ZnTCPP units (involving the ethylene glycol axial ligand as well). Further coordination of any given ZnTCPP moiety to four different cations yields continuous diamondoid arrays consisting of chain-segments of nearly coplanar porphyrins which propagate in an alternating manner roughly in perpendicular directions. The resulting robust arrays thus extend in three dimensions, and the only way to pack them in a condensed
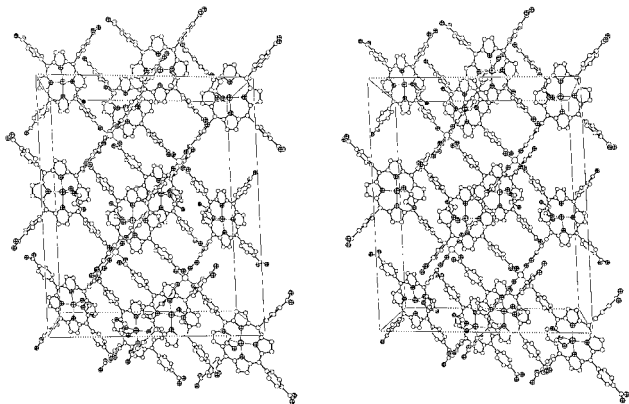
Fig. 2 Crystal structure of **2** (stereoview approximately down the *b*-axis; *a* is horizontal). It shows the diamondoid networks of ZnTCPP^{2-} units templated by external Zn^{2+} cations, and the way they interpenetrate into one another. Large channel voids (*ca.* 7.5 Å in vdW diameter) centered at ($\frac{1}{2}$, 0, *z*) and (0, $\frac{1}{2}$, *z*) extend in the crystal along the *c*-axis between the concave surfaces of the porphyrin bands, explaining the large solvent content of this lattice. The zinc-ion template is represented by a large uncrossed circle. Hydrogen atoms are omitted for clarity.

crystalline phase must involve interpenetration.[6] Fig. 2 illustrates this feature, confirming that this is indeed the case. In the observed interwoven structure overlapping porphyrin bands of adjacent networks lie parallel to each other (at 4.33 and 4.62 Å) in the commonly observed offset stacked manner. The glycol–ZnTCPP^{2-}–Zn^{2+} networks occupy only about 40% of the crystal volume, reflecting on the geometric rigidity of this structure. Hexagonally shaped channels, which extend between the interpenetrating arrays, account for most of the remaining space. These channels propagate along the *c*-axis of the crystal between the concave surfaces of the porphyrin moieties, are centered at ($\frac{1}{2}$, 0, *z*) and (0, $\frac{1}{2}$, *z*), and have an average van der Waals diameter of 7.5 Å. They are filled in a diffused manner with numerous molecules (about 100 per unit cell) of the glycol solvent, which preserves the crystallinity of this open lattice.

The high significance of the metal ion templates to the formulation of TCPP-based networks with high structural rigidity has been demonstrated most recently by a successful crystal engineering of a stable metalloporphyrin zeolite analogue.[7] The latter represents three-dimensionally structured open arrays of interlinked (ZnTCPP)$^{2-}$ and 4,4′-bipyridyl units sustained by binuclear [(Na^{+})$_2$·(–COOH)$_6$·(–COO^{-})$_2$] synthons (Fig. 3). It has been shown previously that cooperative hydrogen-bonding and coordination forces are sufficiently robust to direct concerted intermolecular organization and formation of stable nanostructures in solution as well.[5b,8]
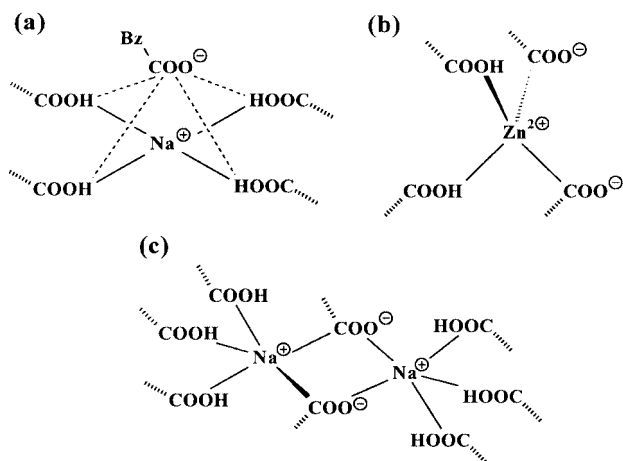

Fig. 3 The tesselation modes of TCPP supramolecular networks *via* metal ion templates in (a) **1**, (b) **2** and (c) the zeolite analogue reported in ref. 7. Every carboxylic or carboxylate group displayed here belongs to a different TCPP/ZnTCPP building block of the supramolecular aggregate.

Correspondingly, the above described molecular recognition algorithms can be also useful in the synthesis of *discrete* porphyrin-based supramolecular domains for the formulation of biomimetic photonic models and other molecular devices.[9]

Notes and references

† Crystals of **1** were obtained by dissolving TCPP in a mixture of methanol, ethyl benzoate and benzoic acid in the presence of NaCl; those of **2**, by dissolving ZnTCPP in a hot mixture of methanol and ethylene glycol in the presence of Zn(OAc)$_2$. Both crystals turned out to contain a considerable amount of solvent in interporphyrin channels (see below).

Crystal data: **1**, [(C$_{48}$H$_{30}$N$_4$O$_8$)·3(C$_9$H$_{10}$O$_2$)·(C$_7$H$_5$O$_2$)$^{-}$·Na^{+}]: M = 1385.4, monoclinic, space group $P2_1$, a = 9.854(1), b = 32.338(1), c = 11.358(1) Å, β = 110.52(1)°, V = 3389.6(2) Å^3, Z = 2, T = 110 K, D_c = 1.357 g cm^{-3}, μ(Mo-Kα) = 1.00 mm^{-1}, 10388 unique reflections ($2\theta_{max}$ = 51.5°). The final $R1$ = 0.065 for 7865 observations with F_o > 4σ(F_o), $R1$ = 0.095 ($wR2$ = 0.178) for all unique data, |$\Delta\rho$| $\leqslant$ 0.74 e Å^{-3}.

2, [(C$_{48}$H$_{26}$N$_4$O$_8$Zn)$^{2-}$· Zn^{2+}·(C$_2$H$_6$O$_2$)$_x$]: monoclinic, space group $C2/c$, a = 27.694(1), b = 19.510(1), c = 32.598(1) Å, β = 92.72(1)°, V = 17593.1(2) Å^3, Z = 8, T = 115 K, 13909 unique reflections ($2\theta_{max}$ = 50.0°). For x = 13 (see below) M = 1724.2, D_c = 1.302 g cm^{-3}, μ(Mo-Kα) = 0.63 mm^{-1}. This crystallographic refinement converged at $R1$ = 0.175 for 6785 reflections with F > 4σ(F), $R1$ = 0.30 and $wR2$ = 0.42 for all the data. One molecule of ethylene glycol is coordinated to the five-coordinate zinc ion residing in the porphyrin center. The remaining solvent molecules incorporated the interporphyrin voids of the crystal lattice were found to be heavily disordered, and their structure could not be modeled. The contribution of the diffused solvent was thus subtracted from the diffraction pattern by the 'Squeeze' method.[10] This refinement converged smoothly at final $R1$ = 0.076 for 5931 observations with F_o > 4σ(F_o), $R1$ = 0.150 ($wR2$ = 0.165) for all unique data, |$\Delta\rho$| $\leqslant$ 0.27 e Å^{-3}. The integrated total residual electron density accounted for the presence of at least twelve additional molecules of ethylene glycol, or a corresponding combination of ethylene glycol and methanol (which represents about 45% of the overall electron count), in the asymmetric unit of this structure. CCDC 182/1562. See http://www.rsc.org/suppdata/cc/b0/b001189o/ for crystallographic files in .cif format.

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10 P. Van der Sluis and A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, 194; A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, C34. The 'Squeeze' method referred therein is widely used in crystallographic analysis of compounds containing substantial amounts of disordered solvent which cannot be located precisely from diffraction data.

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