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Self-assembly patterns of porphyrins in crystals. Structures of hydrogen-bonding and coordination polymers of manganese tetra(carboxyphenyl)porphyrin

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Crystallizations of manganese-tetra(4-carboxyphenyl)porphyrin chloride from different reaction environments led to the formation of new extended polymeric architectures sustained either by cooperative hydrogen-bonding or by self-coordination of the porphyrin units. In one mode the manganese ion in the metalloporphyrin core coordinates axially from both sides to water molecules. The porphyrin species then associate to each other into open layered arrays by multiple hydrogen bonding between the carboxylic functions of adjacent units. The offset-stacked layers are tightly inter-linked (at an average spacing of 3.94 Å) by additional hydrogen bonding between the apical water ligands of one array and the carboxylic groups of neighboring assemblies. Thus resulting interporphyrin organization represents a single-framework *hydrogen-bonding* polymer. The interporphyrin voids within the layers are accommodated by guest solvent components. In another mode, an unprecedented two-dimensional *coordination* polymer is assembled from the tetra-acid building blocks by direct coordination of the metalloporphyrin cores and carboxylic groups to the corresponding topical sites of adjacent species. Stacking of the polymeric layered arrays in the condensed crystalline phase incorporates molecules of crystallization solvent within the inter-layer voids.

Supramolecular chemistry and crystal engineering offer an attractive strategy for the formulation of non-covalent polymeric architectures. These methods involve the generation of higher-order structures with controlled geometries from molecular building blocks ("tectons") by exploring the relatively weak and thermodynamically labile interaction motifs ("synthons") that can exist between molecules. The remarkable structural robustness and thermal stability of the metalloporphyrins, along with their unique chemical properties and readily accessible chemical modification, make them particularly attractive building blocks to this end. The coordination properties of the metal entity in the center of the porphyrin ring, along with tailored functionality of the molecular periphery by suitable substituents, provide diverse "programming" elements for the design of the desired structural motifs. We have introduced a few years ago the *meso*-tetra(carboxyphenyl)porphyrin (TCPP, or M-TCPP in its core-metalated form) moiety as a uniquely versatile tecton unit,[1] and demonstrated several different algorithms of its self-assembly.[2] These include mechanisms of interporphyrin hydrogen bonding, and intercoordination through either external metal ion templates (which may link to the peripheral carboxylic/carboxylate groups of several neighboring porphyrins), or organic bidentate ligands (by bridging axially between parallel metalloporphyrin cores).[3–5] In spite of the high coordination and hydrogen-bonding capacity of the Mn-TCPP tecton, both through the central manganese ions and the equatorial carboxylic functions, only a single Mn-TCPP-based structure has been reported thus far.[6] As part of our continuing investigation to develop effective design strategies for supramolecular porphyrin-based materials, we describe in this paper two different modes of directed self-assembly of this building block through hydrogen bonding (structure **1**) and metal–ligand coordination (structure **2**). The latter compound represents the first homogeneous coordination polymer formulated by *direct* binding between the acidic M-TCPP porphyrin units. All previously known (one-, two- and three-dimensional) coordination polymers of this type, *i.e.* without resorting to external bridging auxiliaries, were based on the basic tetra-aminoporphyrin derivatives.[7–9] The two crystalline materials are composed of the MnTCPP building block shown in Scheme 1, and contain solvent of crystallization. They are defined as:[MnTCPP·2(H_2O)]·DMSO·$PhNO_2$ (**1**), and [MnTCPP]·DMF·2.55(H_2O) (**2**).

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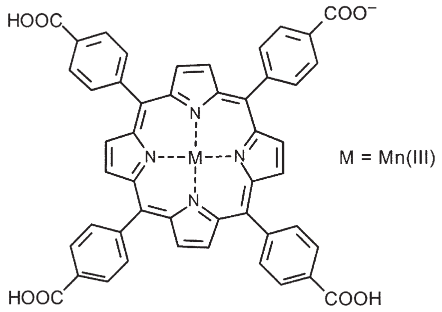
Experimental and crystal data

Synthesis

The Mn^{III}-tetra(4-carboxyphenyl)porphyrin chloride was procured commercially from Porphyrin Systems GbR. It was used without further purification. Compound **1** was obtained by dissolving 8.8 mg (~0.01 mmol) of the porphyrin complex and 6.1 mg (0.05 mmol) of *p*-carboxypyridine in 1 ml of dimethyl sulfoxide (DMSO) and a few drops of nitrobenzene, by heating in an oil bath for 24 hours. The resulting solution



Scheme 1

was then left in the open air for two months until sizeable dark-red crystals of **1** had appeared. The added *p*-carboxypyridine ligand was intended as an axial bridging ligand to the Mn-centers, but it was not incorporated in the crystals that formed. The second compound was obtained by dissolving 3.7 mg ($\sim$0.004 mmol) of the starting porphyrin material in 1 ml of hot dimethylformamide (DMF) in the presence of a few drops of KOH (to assist in deprotonation of the porphyrin tetra-acid), to which a DMF solution of 4,4′-bipyridyl ($\sim$5 mg) was added. Crystals of compound **2** that formed in this solution after standing for a few days only in open air did not incorporate the bipyridyl ligand. The same applies to the chloride anions, and the charge balance of the crystalline solids was achieved by deprotonation of the tetra-acid. The yields of the single-crystals products **1** and **2** (Table 1) were rather low, on a less than one-milligram scale in a single reaction run, which were inadequate for reliable elemental or thermo-gravimetric characterizations. The actual composition of the crystalline products was derived therefore from the X-ray diffraction analysis. The identity of the formed crystal lattices in a given crystallization batch was confirmed in each case by repeated measurements of the unit-cell dimensions from different single crystallites. Adequate amounts of X-ray quality crystalline material for other analyses (*e.g.*, TGA) are achievable by repeating the crystallization procedures in separate batches, yet in this case identical solvent content in the latter cannot be ensured.

Single crystals of the porphyrinoid materials are generally difficult to obtain. The major obstacles include severe solubility problems of the MTCPP compounds (which consist of a large lipophilic framework and several hydrophilic peripheral groups), a considerable rigidity of the bulky porphyrin moieties, their packing non-complementarity in three dimensions, and the topological requirements associated with optimal saturation of all the potential binding sites of intermolecular interaction. The topological constraints often lead to the formation of 'porous' multiporphyrin lattices perforated by cavities and channels, and incorporation of guest solvent components in the crystal to fill the void space and solvate the polar functions unused in the interporphyrin binding. The quality of the resulting crystals, and thus of the diffraction data they produce, can be severely reduced by inefficient crystal packing, and in particular by structural disorder of the incorporated solvent (see below).

Table 1 Hydrogen-bonding and coordination parameters

D–H	A (symmetry)	D–H (Å)	H–A (Å)	O···A (Å)	D–H···A (°)
Structure **1**					
OH(1)	O4′ (x − 1, y, z + 1)	0.94	1.69	2.600(4)	162
OH(5)	O4 (−x, −y, 1 − z)	0.89	1.74	2.627(4)	175
OH(7)	O3′ (2 − x, 1 − y, 1 − z)	0.97	1.67	2.554(4)	150
OH(1′)	O3′ (1 − x, 1 − y, 1 − z)	0.85	1.77	2.607(4)	169
OH(5′)	O3 (1 + x, y, z − 1)	1.04	1.53	2.558(4)	167
OH(7′)	O4 (−x − 1, −y, 1 − z)	0.98	1.56	2.513(3)	163
OH(9a)	O2′ (x, y, z)	0.84	1.91	2.751(4)	171
OH(9b)	O8 (x − 1, y, z)	0.86	1.91	2.762(4)	173
OH(10a)	O6′ (x, y, z + 1)	0.90	1.89	2.751(4)	162
OH(10b)	O7′ (−x, −y, 1 − z)	0.94	1.96	2.869(4)	162
OH(9′a)	O63 (x, y, z)	1.00	1.70	2.701(4)	177
OH(10′a)	O6 (x, y, z)	0.89	1.91	2.787(4)	168
OH(10′b)	O8′ (1 + x, y, z)	0.95	1.80	2.722(4)	162

Metal	Ligand (symmetry)	Bond distance (Å)
Structure **1**		
Mn1	O9 (x, y, z)	2.191(3)
Mn1	O10 (x, y, z)	2.251(3)
Mn1′	O9′ (x, y, z)	2.254(3)
Mn1′	O10′ (x, y, z)	2.207(3)
Structure **2**		
Mn1	O1 $(1 - x, y + \frac{1}{2}, \frac{1}{2} - z)$	2.228(3)
Mn1	O1 $(x, \frac{1}{2} - y, z - \frac{1}{2})$	2.228(3)

[a] In **1**, O1 through O8 and O1′ through O8′ represent the oxygen atoms of the carboxylic/carboxylate groups of the two crystallographically independent porphyrin species, respectively. O9–O10 and O9′–O10′ represent oxygens of the four water molecules bound to the manganese ions of the two porphyrins. O63 is part of the ordered DMSO solvent. In **2**, O1 is the Mn-coordinated site, while O2 and O3 and O4 represent the non-coordinated oxygens of the porphyrin carboxylic functions.

X-ray crystallography

The diffraction measurements were carried out on a Nonius KappaCCD diffractometer, using graphite monochromated MoKα radiation ($\lambda = 0.7107$ Å). The crystalline samples of the analyzed compounds were covered with a thin layer of light oil and freeze-cooled to *ca.* 110 K in order to minimize solvent escape, structural disorder and thermal motion effects, and increase the precision of the results. The crystal structures were solved by direct methods (SIR-97, SHELXS-86), and refined by full-matrix least-squares on F^2 (SHELXL-97).[10] All non-hydrogen atoms were refined anisotropically. The hydrogens of the porphyrin were located in idealized positions, and were refined using a riding model with fixed thermal parameters [$U_{ij} = 1.2\ U_{ij}$ (eq.) for the atom to which they are bonded]. Those bound to O-atoms in **1** were located in difference-Fourier maps. Crystals of **1** and **2** diffracted poorly and required extended X-ray exposure times, and they were found to contain severely disordered solvent. The asymmetric unit of **1**, which exhibits a pseudo-monoclinic symmetry (see below), consists of two molecules of the porphyrin complex, and two pairs of the DMSO and nitrobenzene solvent molecules (one of the pairs being severely disordered). In **2** the metalloporphyrin species are located on centers of inversion (the deprotonated carboxylate being thus disordered between two or more sites), and there are two partial molecules of water and one DMF in the asymmetric unit. Structural disorder was exhibited also by one of the carboxyphenyl residues in **2**. The atomic positions of the disordered solvent could be approximately located in electron-density maps, but not refined with satisfactory precision. The conventional refinements converged at relatively high *R*-values of $R_1 = 0.16$ (**1**) and $R_1 = 0.12$ (**2**) for intensity data above threshold measured to $2\theta_{max} = 50°$. Correspondingly, the contribution of the disordered solvent (one of the two pairs of DMSO and nitrobenzene molecules in **1**, and one molecule of DMF in the asymmetric unit of **2**) was subtracted from the corresponding diffraction patterns by the Squeeze/Bypass procedure[11] in order to improve the structural characterization of the ordered fragments. The latter is widely used in crystallographic analysis of compounds containing substantial amounts of disordered solvent. The calculated solvent-accessible volumes of about 1250 Å^3 per unit-cell in **1** and 570 Å^3 per unit-cell in **2**, along with the assessed residual electron densities in these voids,[11] match reasonably well the assumed solvent stoichiometries. Despite the solvent disorder, the experimental data were sensitive enough to allow reliable identification (by C–O bond distance distribution) of the deprotonated carboxylic group in **1**, and the location of all the O-bonded hydrogen atoms involved in the H-bonding interactions from difference-Fourier maps. Moreover, the crystallographic refinements of the two materials based on the reduced data converged reasonably well, and provided reliable models of the molecular structures and the porphyrin supramolecular organization. In **2** the carboxylic protons could not be located. The crystal and experimental data of the two compounds are as follows.

1, $[C_{48}H_{27}N_4O_8Mn{\cdot}2(H_2O)]{\cdot}C_2H_6SO{\cdot}C_6H_5NO_2$: formula weight 1079.95, triclinic, space group $P\bar{1}$, $a = 12.9340(4)$, $b = 16.7600(5)$, $c = 24.6090(9)$ Å, $\alpha = 89.859(1)$, $\beta = 89.597(2)$, $\gamma = 83.111(2)°$, $V = 5295.9(3)$ Å^3, $Z = 4$,

$\rho_{calcd.} = 1.354$ g·cm^{-3}, $\mu(\text{MoK}\alpha) = 0.36$ mm^{-1}, 33 356 collected reflections, 18 427 unique reflections ($R_{int} = 0.057$), after Squeeze[11] final $R1 = 0.069$ ($wR2 = 0.165$) for 9243 reflections with $F_o > 4\sigma(F_o)$, $R1 = 0.133$, $wR2 = 0.186$ for all unique data. This crystal structure is geometrically (as well as from the point of view of the interporphyrin organization) pseudo-monoclinic. However, the distribution of the non-coordinated solvent incorporated in the crystal, as indicated also by the distribution of the diffracted intensity data, is incommensurate with the monoclinic symmetry.

2, $[C_{48}H_{27}N_4O_8Mn]\cdot 2.55(H_2O)\cdot C_3H_7NO$: formula weight 961.71, monoclinic, space group $P2_1/c$, $a = 13.6910(5)$, $b = 8.7440(3)$, $c = 20.5930(6)$ Å, $\beta = 91.695(2)°$, $V = 2464.2(1)$ Å^3, $Z = 2$, $\rho_{calcd.} = 1.296$ g·cm^{-3}, $\mu(\text{MoK}\alpha) = 0.33$ mm^{-1}, 13 531 collected reflections, 4301 unique reflections ($R_{int} = 0.066$), after Squeeze[11] final $R1 = 0.062$ ($wR2 = 0.177$) for 3240 reflections with $F_o > 4\sigma(F_o)$, $R1 = 0.080$, $wR2 = 0.191$ for all unique data.

CCDC reference numbers 221 194 (**1**) and 221 195 (**2**). See http://www.rsc.org/suppdata/nj/b3/b312183f/ for crystallographic data in .cif or other electronic format.

Results and discussion

The structures reported in this paper represent two different modes of intermolecular organization, induced by the molecular recognition features characteristic of the Mn-TCPP building blocks. The topological points of designed interaction of this species include the four symmetrically disposed carboxylic sites suitable for both hydrogen as well as coordination bonding,[12,3] and the two axial sites of the trivalent manganese center which usually adopts a six-coordinate environment.[8c,13,14] For hydrogen bonding, the carboxylic recognition functions on the periphery of the Mn-TCPP porphyrin framework are self-complementary as they can act both as proton donors and proton acceptors at the same time. The cooperative intermolecular association through these functions may occur in directions parallel to the porphyrin core, involving either cyclic-dimeric $(COOH)_2$ or chain-polymeric aggregation modes of the carboxylic groups to yield open multiporphyrin networks.[12] The preferred organization is affected by the crystallization environment and the potential templates present in the reaction mixture.[2] The axial coordination sites of the manganese ions are readily accessible by a wide variety of ligands (mainly of the oxo-, cyano- or amine-type), to afford either monomeric or polymeric assemblies.[15] Attempts were made to enforce crystallization of the desired materials from mostly lipophilic environments, to make all the functional sites optimally expressed in the interporphyrin interaction. However, compounds **1** and **2** could crystallize only when the corresponding solutions were left to stand in the open air and absorb molecules of water. The very long exposure to moisture of the DMSO/nitrobenzene environment is most probably responsible for the incorporation of water as axial ligands to the manganese ions in **1**. On the other hand, water did not interfere in the formation of the multiporphyrin coordination polymers in **2**.

In structure **1** the axial ligation sites of the metalloporphyrin species are occupied by molecules of water, which coordinate from above and below to the manganese ion center. The structure can be best described as composed of layers consisting of multiply hydrogen-bonded $[Mn(H_2O)_2TCPP]$ entities (Fig. 1). Adjacent species along one direction link to each other by *cis*-related carboxyphenyl arms, forming zigzag-chain assemblies. The latter interconnect sideways by additional hydrogen bonds. The relatively short hydrogen-bonding $OH\cdots{}^{-}OOC$ distances within 2.51–2.63 Å (Table 1) reflect the strong interactions between the porphyrin units. All three carboxylic substituents of the porphyrin entities are aligned nearly perpendicular to the layers, utilizing their hydroxyl-OH and carbonyl-O sites for intra- and inter-layer (see below) binding, respectively. The deprotonated COO^- functions lie roughly parallel to the layers, acting as proton acceptors from neighboring porphyrin entities (Fig. 1).

In the crystal, adjacent parallel stacked layers (at *ca.* 3.94 Å) are offset about half of the grid size along one of the porphyrin molecular axes, in order to position the axial water ligands of one layer in a close proximity to the hydrogen-bonding sites of neighboring arrays. This facilitates formation of multiple inter-layer links from three of the axial water ligands to the exposed carbonyl-O sites located above or below, at $OH\cdots O(=C)$ distances of 2.72–2.87 Å (Table 1, Fig. 2a). One of the water species H-bonds also to the ordered DMSO solvent. The charge-assisted (within layers) as well as the neutral (between layers) hydrogen-bonding interactions referred to above reveal standard geometric features.[16] The stacked-layered assembly is characterized by parallel channel voids (of approximate van der Waals width of 4.5 Å), which propagate throughout the crystal perpendicular to the layered arrays (Fig. 2b). To fill the empty space, formation of this structure is associated with incorporation of the DMSO and nitrobenzene solvent from the

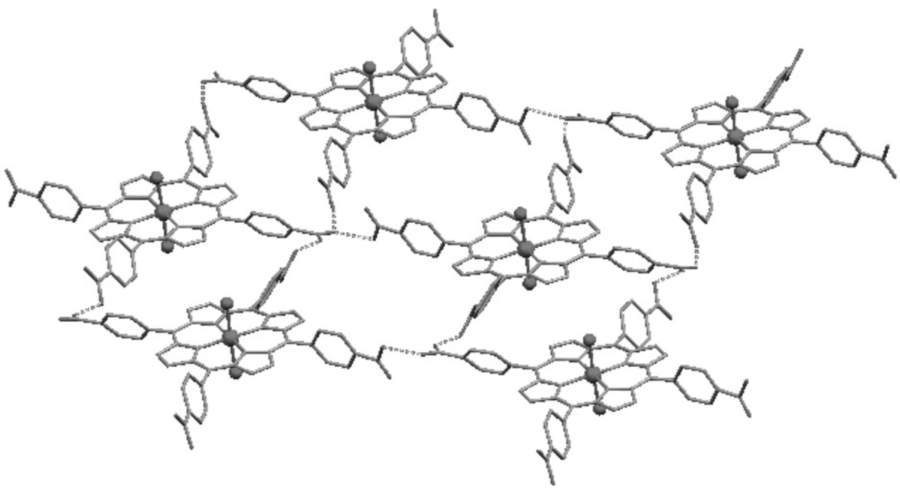


Fig. 1 Illustration of the hydrogen-bonded (dotted lines) layered organization of the $Mn(H_2O)_2$-TCPP moieties in **1**. The manganese ions and the water oxygen atoms are represented, respectively, by large and small spheres. In the crystal structure, the water axial ligands are further hydrogen bonded to the carboxylic oxygens of adjacent layers located above and below the depicted one. The mean spacing between the layers is 3.94 Å. The solvent species that protrude into the interporphyrin voids are not shown.

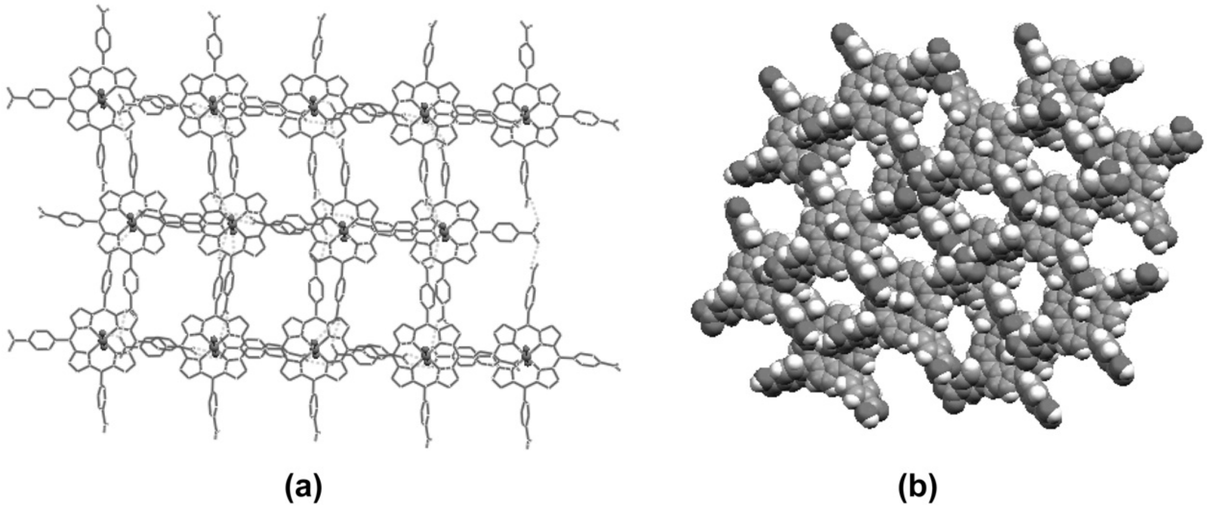


Fig. 2 Crystal structure of **1**. (a) Offset stacking of two neighboring porphyrin layers. Note that the axial water ligands of one layer protrude onto the hydrogen bonding sites of the next layer to facilitate inter-layer hydrogen bonding. (b) Space-filling illustration (including all H-atoms) of the structure viewed down the stacking axis. Note the ~4.5 Å wide channel voids which accommodate the DMSO and nitrobenzene solvent (not shown).

crystallization mixture into the channelled lattice, which is partly disordered.

Structure **2** represents a unique homogeneous coordination polymer of the Mn-TCPP moieties. It is sustained by direct coordination of their Mn-centers from above and below to the carboxylic/carboxylate groups of two adjacent species at Mn–O distance of 2.23 Å (Table 1). Correspondingly, each Mn-TCPP unit uses two *trans*-related carboxylic functions to coordinate (through a single oxygen site) to the metal centers of neighboring entities, thus making a four-point connection to the surrounding molecules. This yields an extended two-dimensional coordination polymer parallel to the *bc*-plane of the crystal (Fig. 3). The other pair of carboxyphenyl functions is not involved in the interporphyrin interaction. In the crystal structure they are partly disordered, pointing into void space above and below the multiporphyrin layers and exhibiting a flapping-type motion/disorder of the aryl groups. These carboxylic groups are thus solvated by water incorporated into the lattice. In the layered polymer the porphyrin cores of the directly interacting species are nearly perpendicular to each other, being related by the glide/screw symmetry. This type of polymerization is revealed here for the first time in the context of supramolecular chemistry of porphyrins, although the six-coordinate [$MnN_4(COOH/COO^-)_2$] coordination synthon could be found in a number of simple organometallic structures reported earlier as well.[15]

The polymeric layers have a corrugated surface due to the perpendicularly oriented MnTCPP building blocks, and in the crystalline phase they pack very inefficiently in the normal direction; *i.e.*, along the *a*-axis of the crystal (Fig. 4). Nevertheless this arrangement is stabilized by the aniparallel alignment of the non-coordinated carboxylic functions, which stick out fom the layers surface on both sides. This leads to the formation of an intercalate pattern, wherein the interface between adjacent layers is filled by solvate molecules of water and, in a diffused manner, of dimethylformamide.

In summary, our efforts to formulate porphyrin-based network materials which resemble molecular-sieve structures and zeolite analogues, by utilizing diverse synthetic (in the crystal-engineering sense) strategies, have led us to investigate

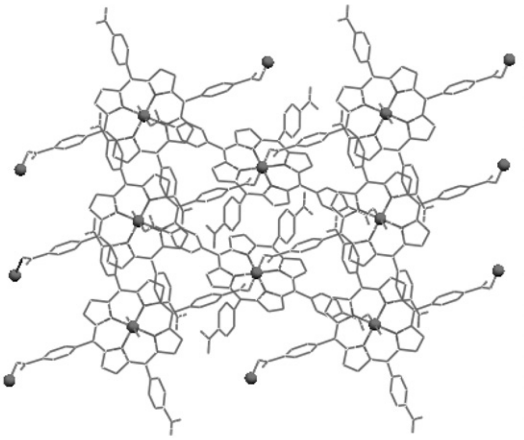


Fig. 3 Illustrations of the two-dimensional coordination polymer array in **2**, which extends parallel to the *bc* plane of the crystal (the *a*-axis is normal to the arrays shown). Two of the carboxylic groups of every porphyrin unit are coordinated to the metal ion centers of adjacent entities, through one of the oxygen atoms . The three remaining O-sites are solvated by water molecules incorporated into the lattice (not shown).

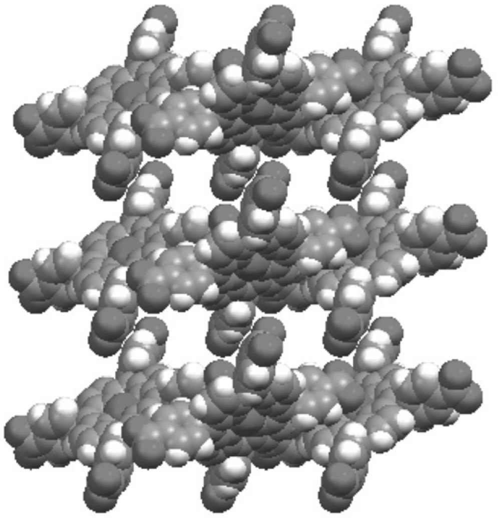


Fig. 4 Side view of three adjacent layers of the coordination polymer in **2** down the *b*-axis of the crystal (space-filling representation; *a* is vertical). Note the inefficient stacking, which creates voids between the layers. The DMF (severely disordered) and water solvent species included in these voids, as well as the carboxylic protons that could not be located reliably, are not shown.

typical aggregation modes of the Mn-TCPP moiety which is characterized by six topical binding sites. This work revealed two types of supramolecular multiporphyrin assemblies uniquely tailored by either cooperative hydrogen-bonding[6] or coordination polymerization, depending on the crystallization environment. The structural parameters of these interactions are given in Table 1. The corresponding crystal structures represent channel-clathrate and intercalate organizations, respectively. The two-dimensional coordination polymer described herein is the first report of the previously unknown direct intercoordination of a tetracarboxyphenyl metalloporphyrin species, which follows our earlier discovery of the three-dimensional polymer of the tetrapyridylporphyrin analogue.[8a]

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