Crystal Engineering of 2-D and 3-D Multiporphyrin Architectures − The Versatile Topologies of Tetracarboxyphenylporphyrin-Based Materials

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This study explores diverse crystal engineering concepts in the formulation of a series of new porphyrin-based supramolecular arrays, utilizing tetrakis(4-carboxyphenyl)porphyrin as an effective building block. Different modes of the supramolecular assembly are demonstrated. They include: (a) self-assembly of the porphyrin units into extended networks through multiple hydrogen bonding, (b) intermolecular coordination assisted by external sodium ion auxiliaries which link between the carboxylic/carboxylate groups of several units, (c) formation of coordination polymers with the aid of bidentate ligands as bridges between the metal centers of the porphyrin molecules, and (d) various combination motifs of concerted hydrogen bonding and coordination features. The resulting multiporphyrin architectures obtained in this study illustrate the expression of several motifs (synthons) of noncovalent interaction in the construction of network solids, which can be potentially useful in the design of new porphyrin-based materials with attractive properties.

Introduction

Supramolecular chemistry provides effective means for the formulation of a large variety of extended multiporphyrin architectures in solution as well as in the solid state by noncovalent forces.[1−3] The significance of such systems lies in their potential use as molecular sensing and delivery systems, charge and energy transport devices, and redox catalysts.[1] In recent years there has been a widespread interest in the design of complex porphyrin-based arrays in order to model light-harvesting systems or to construct novel solid-state receptors and microporous materials (zeolite mimics). In the latter context, we have introduced the tetrakis(carboxyphenyl)porphyrin moiety (TCPP, Scheme 1) as a uniquely versatile building block (tecton) in our efforts to crystal-engineer network solids.[4] This was followed by a demonstration that these building blocks can also be utilized effectively in the construction of molecular sieves and organic zeolite analogues.[5] The square-shaped TCPP is a robust tecton unit that can be assembled into rigid high-order structures in different ways through diverse interaction motifs (synthons). In the equatorial directions, the peripheral carboxylic functions (oriented roughly perpendicular to the porphyrin plane) provide self-complementary binding sites for a simultaneous association of every TCPP building block to several neighboring species.[4b][5b] The array of multiple hydrogen bonds that may form in such cases provides sufficient enthalpic driving force to overcome solvation and negative entropy effects and stabilize open network arrangements. The formation of other kinds of multiporphyrin arrays can be facilitated by the use of metal ion auxiliaries that prefer high coordination environments and may readily coordinate several carboxylic moieties at the same time.[4a] The preferred coordination geometries of these auxiliaries have a dominant influence on the topology of the formed supramolecular assembly (e.g., layered vs. diamondoid, and interpenetrating or grid-type networks). The additional positive charge introduced to the structure by the metal ions can be easily balanced by a single or multiple deprotonation of TCPP, without the need to incorporate additional anions (which is often the case in hybrid inorganic/organic coordination polymers).[6] This is a particularly useful feature of the TCPP framework, as the presence of external anionic species may hamper the construction of open architectures. The insertion of metal ions with high affinities for five- or six-coordinate environments into the porphyrin core (e.g., Zn^{II} or Mn^{III}, as opposed to Cu^{II}, which is usually four coordinate and not effective in axial coordination) provides another programming element for effective supramolecular design.[5a,7] These metal ions may allow additional coordination to other species in the axial direction (i.e., perpendicular to the porphyrin plane). A concerted expression of suitable molecular recognition algorithms along the lateral and axial directions in the same material represents the most desirable approach to the construction of multiporphyrin architectures with a high structural integrity.[8] The square-planar geometry of the porphyrin macrocycle, the directionality of *meso*-substituted carboxylic recognition groups of TCPP, and the coordination properties of the metal ions involved should provide effective means for inducing extended noncovalent connectivity in the design of supramolecular multiporphyrin arrays. This diversity of the TCPP building block is demonstrated by the preparation and structural characterization of four new MTCPP-based ($M = Mn^{III}, Zn^{II}$) materials (Scheme 1) which provide representative examples of characteristic 2-D and 3-D supramolecular assembly modes of the metalated porphyrin moiety. The considerable complexity associated with steering

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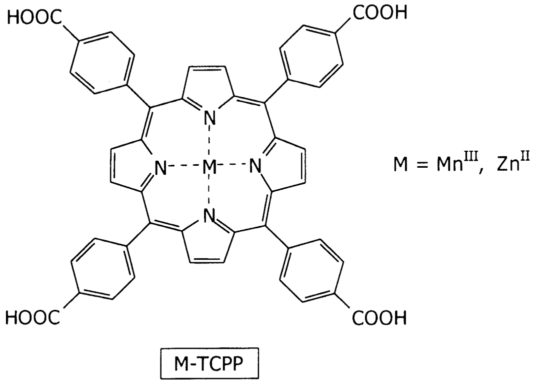


Scheme 1. The TCPP building block

the construction of stable high-order network structures of large organic species (such as the porphyrins in question) by noncovalent forces makes the current effort quite a challenging one.

Results and Discussion

Organic carboxylic acids tend to form supramolecular arrays in crystalline solids by interconnecting through hydrogen bonds into a wide variety of extended networks. These interaction motifs may consist either of the cyclic dimeric $(COOH)_2$ synthons, or of linear polymeric aggregates.[9] Although the hydrogen bonding interactions when considered alone are relatively weak (ca. 10−15 kJ/mol for a single dicarboxylic H bond involving uncharged species),[10] their cooperative effect appears to be sufficient to stabilize low-density supramolecular arrangements even in organic solids.[11] We have applied this concept to porphyrin supramolecular chemistry and demonstrated several formulations of interpenetrating as well as nonpenetrating hollow network architectures through self-complementary hydrogen bonding, without the use of external auxiliaries.[4b][4c] This includes the formation of two-dimensional arrays with either large interporphyrin voids (16 × 21 Å) or considerably smaller cavities (8.5 × 11 Å), depending on the size and nature of the template used. In the present study we describe a series of new MTCPP-based (Scheme 1) structures **1−4** of diverse architectures (their detailed composition is given in the Exp. Sect.). The following discussion focuses primarily on the unique features of the *supramolecular* assembly in these compounds; selected coordination and hydrogen bond lengths are summarized in Table 1.

Compound **1** (the ethyl benzoate solvate of the $Mn^{III}TCPP{\cdot}MeOH{\cdot}H_2O$ six-coordinate complex) provides a characteristic example in which multiple hydrogen bonds between the carboxylic functions positioned on the periphery of the square-shaped $Mn^{III}TCPP$ framework provide the main supramolecular organizing force of the observed assembly. Figure 1a illustrates the structure of the 2-D porphyrin β-networks formed in this case. It is directed by effective chain-polymeric-type hydrogen bonding between the carboxylic groups of adjacent molecules. These networks are anionic, as the extra positive charge of the trivalent manganese cation in the porphyrin core is balanced by the abstraction of one proton from the TCPP moiety. This is in line with the observed distribution of C−O distances in the carboxylic functions (1.22 and 1.31 Å for −COOH, and 1.24 and 1.28 Å for $-COO^-$, residues), as well as with the observed hydrogen bonding interactions ($OH{\cdots}O^-$ = 2.54−2.58 Å within the layer and OH···O = 2.72−2.78 Å between layers; see below). The networked supramolecular motif thus formed contains open spaces between the connecting units (Figure 1a). Only the larger voids are large enough (with van der Waals widths of about 7.0 Å) to host two molecules of the ethyl benzoate crystallization solvent oriented edge-on. The individual building blocks contain additional sites with hydrogen-bonding capacity, as the manganese cation has a high affinity for oxygen ligands and an octahedral coordination (the metalloporphyrin core is planar in such a case). Thus, under the applied conditions of crystallization the metal ion binds one water and one methanol molecule as axial ligands, which may then link further to other species. The porphyrin layers stack in the crystal in an offset manner, in which the porphyrin cores of one layer are positioned above the carboxylic sites of another layer (Figure 1b). This allows the axial water and methanol ligands (as proton donors) to approach the carboxylic groups to form interlayer hydrogen bonds. (Our efforts to cross-link between the overlapping H-bonded layers by a bidentate axial ligand that will coordinate on both sides to the Mn centers have not been successful as yet). In the observed arrangement, the ethyl benzoate molecules positioned within the inter-porphyrin voids of one layer perch on the smaller cavities (which are too small to fully accommodate a molecular species), thus yielding a rather

Table 1. Selected coordination and hydrogen bond lengths (related to diffraction measurements at 110 K)

Compound	**1**[a]	**2**[b]	**3**[b]	**4**[b]
M−N(pyrrole) bond length range [Å]	2.011−2.021	2.010−2.065	2.055−2.067	2.042−2.044
M's coordination number, and type of axial ligands	6, OH	4	5, OH	6, :N(pyr)
M's deviation from the N_4(corrole) plane [Å]	0.021	0.007	0.271	0.000
M−X(axial ligand) bond lengths [Å]	2.214, 2.246	−	2.141	2.694, 2.694
Sodium−porphyrin Na···O coordination distances [Å]	−	2.322−2.353	2.254−2.435	−
Porphyrin ligand/solvent COOH···X hydrogen bond length range [Å]	2.72−2.78[c]	2.56−2.68[d]	2.71−2.76[e]	2.68−2.79[f]
Interporphyrin hydrogen bond length range [Å]	2.54−2.58[g]	3.06[h]	2.51−2.58[g]	2.45[g]

[a] M = Mn^{III}. − [b] M = Zn^{II}. − [c] X = OH. − [d] X = COO^-. − [e] X = OH or :N. − [f] X = H_2O. − [g] $COOH{\cdots}{}^-OOC$. − [h] COOH···COOH.

tight crystal packing of the layered porphyrin−ethyl benzoate arrays. The formulation of closely related structures has been achieved by using anionic Zn^{II}TCPP building blocks and M$^+$−18-crown-6 (M = Na, K) templates.[4b]

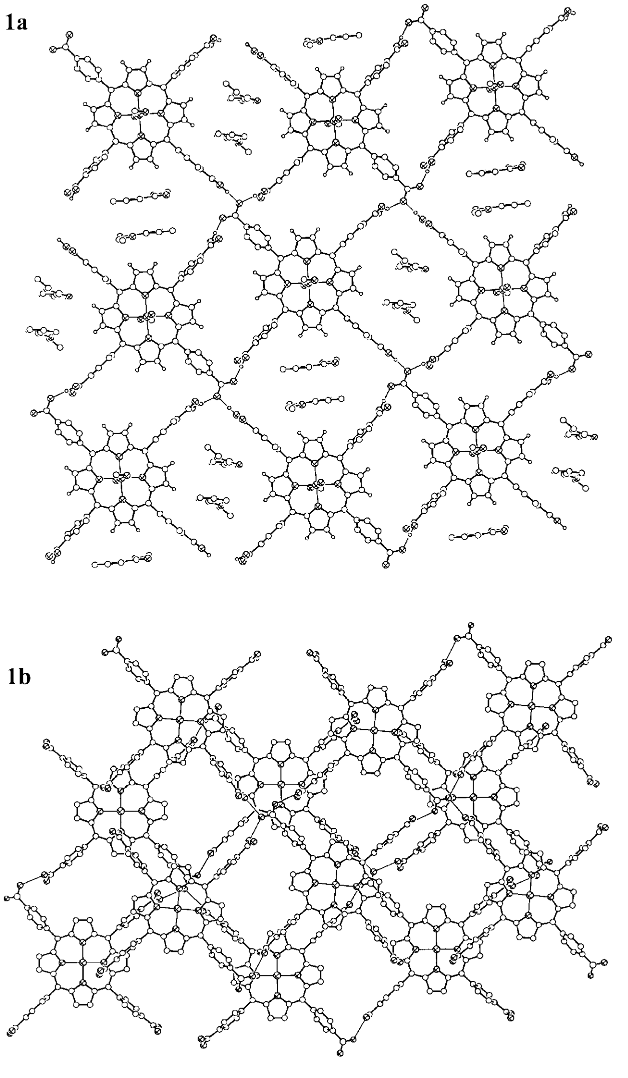


Figure 1. Intermolecular organization in **1**: (a) open layered arrays of the Mn^{III}TCPP building blocks, tessellated by chain-polymeric-type hydrogen bonding; the van der Waals width of the large inter-porphyrin enclosures that accommodate the solvent species is about 7.0 Å; (b) an offset stacking of two adjacent layers, approximately at 4.2 Å; the water and methanol axial ligands are omitted for clarity; the Mn, N and O atoms are denoted by crossed circles

Compound **2** (the ethyl benzoate solvate of the 1:1 Zn^{II}TCPP sodium benzoate complex) represents a supramolecular assembly process assisted by external sodium ion auxiliaries. As shown in Figure 2a, crystallization of Zn^{II}-TCPP in the presence of NaCl, ethyl benzoate and benzoic acid leads to the formation of 2-D multiporphyrin arrays sustained by the metal ions. In this arrangement every cation is coordinated (at 2.32−2.35 Å) to the carboxylic groups of four surrounding carboxylic moieties, forming a roughly square-planar mononuclear Na$^+$(COOH)$_4$ synthon (Scheme 2), and its positive charge is balanced by a neighboring molecule of deprotonated benzoic acid (Na$^+$···O$^-$ 2.24 Å). The latter also serves as an excellent proton acceptor in hydrogen bonding interactions with the carboxylic groups (O$^-$···HO 2.56−2.68 Å) of the four converging porphyrins. The resulting supramolecular arrangement has a wavy layer structure, which consists of two differently oriented porphyrin moieties related to each other by a monoclinic twofold axis, and represents a rather robust coordination polymer in two dimensions. The absence of axial ligands on the porphyrin core in this case allows for a close stacking of the porphyrin layers (with a small offset) in the normal direction (Figure 2b). It is characterized by an average interlayer distance of 4.3 Å between the overlapping segments, as commonly observed in layered tetraarylporphyrin structures.[12] The observed architecture contains small (approximately 5 Å wide) channels which propagate through the layers along the *a* axis of the crystal, and are accommodated by molecules of the ethyl benzoate solvent. The four-coordinate metal ion in the center of the porphyrin has no role in the organization mechanism of the observed pattern. It is not surprising, therefore, that isomorphously structured coordination polymers have been obtained recently from the free-base TCPP building blocks when subjected to similar preparative conditions.[4a]

The large size and the aromatic nature of the porphyrin framework reveals a high propensity for strong dispersive attractions between the roughly flat molecular surfaces of these units (i.e., when it is not obstructed by axially ligating species). This fundamental property of the porphyrin−porphyrin interaction is well reflected in the commonly observed layered organization of the porphyrin moieties at a narrow distance range of 4−5 Å.[12,13] Its dominating role in crystals suggests, however, yet another tool for fine-tuning the supramolecular arrangement. This involves the incorporation of rigid, flat, aromatic residues of appropriate size as effective “van der Waals spacers” between the porphyrin units. We have demonstrated previously the validity of this idea in 2-D and 3-D hydrogen-bonded networks based on the tetrakis(4-hydroxyphenyl)-porphyrin unit and spaced by aromatic intermediates.[14] A similar modification of the interlayer organization by the insertion of an aromatic spacer was obtained in compound **3** (the ethyl benzoate solvate of a 2:1 adduct of MeOH·Zn^{II}TCPP$^-$·Na$^+$ and 2,7-diazapyrene) by treating Zn^{II}TCPP with a large and rigid aromatic framework such as 2,7-diazapyrene (Scheme 3) in the presence of NaCl. The latter was also used to effect inter-porphyrin coordination in the lateral directions by the sodium ion auxiliaries.

The formation of **3** is associated with the deprotonation of one carboxylic substituent of the porphyrin molecule to balance the charge of the sodium cation. Moreover, the assembly of the anionic porphyrin arrays by sodium ions in this case is via a binuclear [(Na$^+$)$_2$(−COO$^-$)$_2$(−COOH)$_4$] synthon (centered on inversion), with two carboxylic groups bridging between the two cations (Scheme 2). The Na···O coordination distances lie within the range 2.25−2.44 Å, while the distance between the two sodium nuclei is 3.42 Å. The Zn^{II}TCPP units are now five-coordinate, revealing a

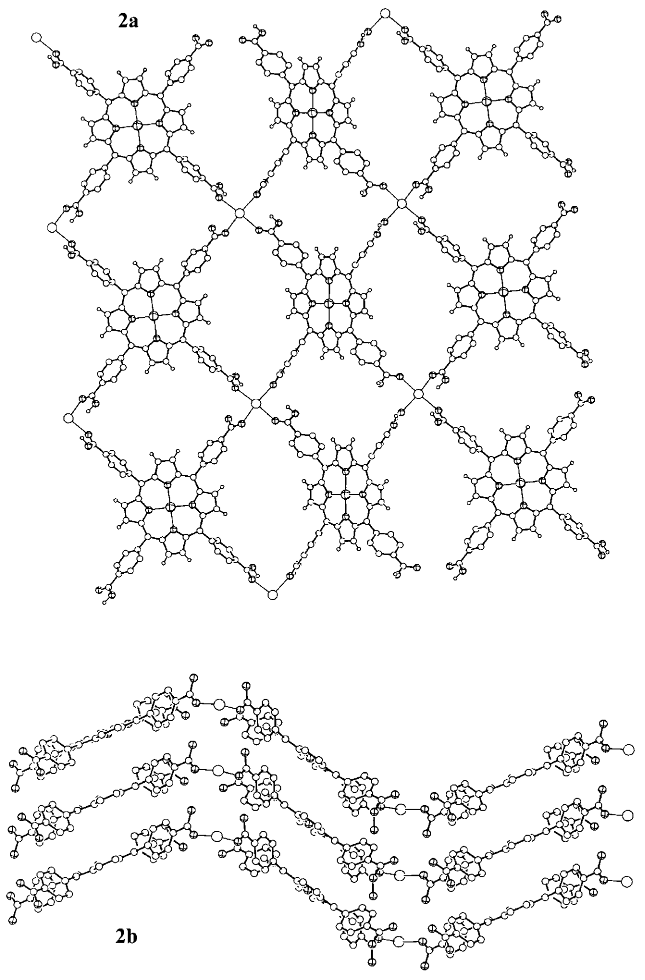
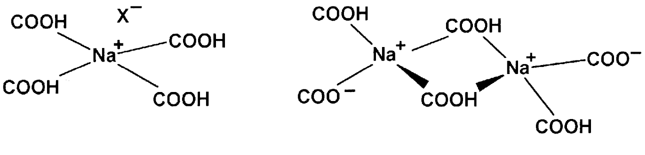
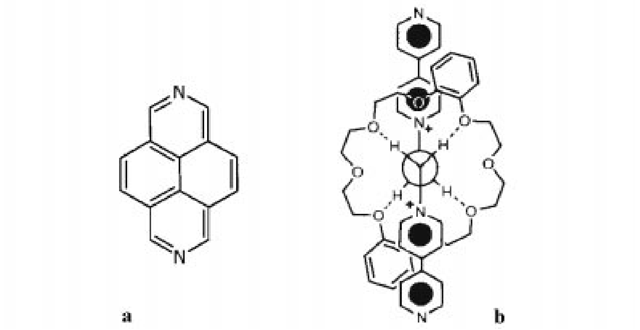


Figure 2. Interporphyrin networking and stacking in **2**: (a) two-dimensional layered arrays of the Zn^{II}TCPP building blocks sustained by metal ion auxiliaries (denoted by large open circles); every cation is strongly coordinated to the carboxylic functions of four different porphyrin units [forming an Na$^+$(COOH)$_4$ interaction synthon] and to the benzoate anion; molecules of the ethyl benzoate solvent are located, and diffused, within the interporphyrin cavities; the latter combine into straight channels in (b) the tightly stacked arrangement of the wavy multiporphyrin layers, at 4.3 Å intervals, along the *a* direction of the unit cell; the benzoate anion and the solvent species are omitted for clarity



Scheme 2. The mononuclear and binuclear sodium−polycarboxyl synthons in **2** (left) and **3** (right); every carboxylic or carboxylate group shown is part of a different Zn^{II}TCPP unit



Scheme 3. The 2,7-diazapyrene (left), and [2]pseudorotaxane (right) ligands

domed conformation with the zinc ion slightly displaced from the porphyrin plane (0.27 Å above the N_4 plane), and bearing a methanol species as an axial ligand. The diazapyrene spacer (also located on inversion) is inserted between, and aligned parallel to, the concave surfaces of two inverted porphyrin species. The mean separation distance of the former from the N_4 planes of the latter is 3.4 Å. The sodium ion auxiliaries link the enclosing porphyrin moieties on opposite sides, locking the diazapyrene inside a "sandwich"-type trimeric cluster (Figure 3a). A single dinuclear sodium carboxylic/carboxylate synthon interconnects two neighboring trimers displaced along the $a+c$ axis of the crystal (parallel to the porphyrin plane), and two additional trimers displaced along a nearly perpendicular $a+2b+c$ direction (Figure 3b,c). This gives rise to the formation of an extended coordination polymer, as every porphyrin unit takes part in three different coordination sites of this type. Adjacent trimers are further connected to each other sideways (along $a+b$) by hydrogen bonding. The N sites of the sandwiched diazapyrene entity act as good acceptors for the carboxylic groups of neighboring porphyrin moieties (OH···N 2.76 Å). In addition, the axial methanol ligands oriented perpendicularly to the porphyrin surface (roughly along $a-c$) provide proton-accepting sites for hydrogen bonds from other species located above and below (OH···O 2.71 Å). The concerted coordination polymerization and directional hydrogen bonding (all potential sites for intermolecular binding are utilized almost to capacity) yield a uniquely structured single framework lattice in which all porphyrin, diazapyrene and sodium components are interconnected to each other in three dimensions (Figure 3b,c). The resulting lattice is perforated by straight, ca. 4.5 Å wide, channels which are filled in this structure by diffused molecules of the ethyl benzoate solvent (three molecules of solvent per one porphyrin unit).

It should be pointed out that the different modes of interporphyrin coordination through the sodium ions in **2** and **3** occurred spontaneously, and could not be predicted or controlled. Yet, this and our previous[4a][5a] studies confirm that alkali metal auxiliaries readily induce the formation of TCPP-based coordination polymers. Evidently, the dominant nature of these ion-pairing interactions in **3** prevents the diazapyrenes from aligning perpendicular to the porphyrin plane and thus from acting as bridging ligands between adjacent porphyrin macrocycles.

Another variant of simultaneous coordination polymerization and hydrogen bonding is represented by compound **4**

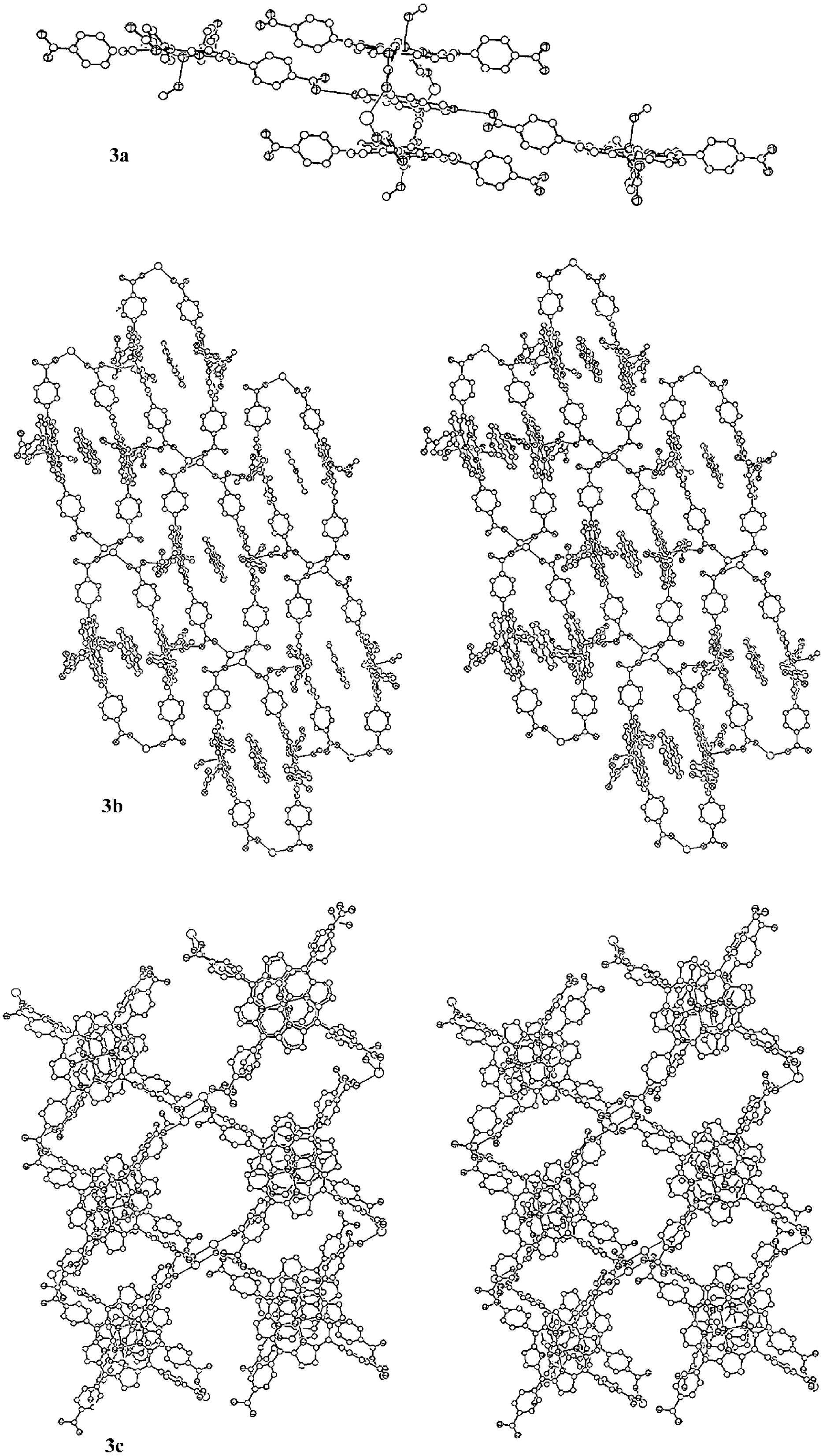


Figure 3. The complex intermolecular binding in **3**: (a) the 2,7-diazapyrene spacer held between four surrounding porphyrin units (by π−π stacking at 3.4 Å, as well as by hydrogen bonding) and two sodium cations (shown as large open circles); (b) stereoview of the structure parallel to the plane of the aromatic fragments, showing the concerted coordination and hydrogen bonding in a direction perpendicular to the porphyrin plane; (c) stereoview of the structure approximately down the open channels (the solvent molecules accommodated therein are omitted for clarity), showing interporphyrin coordination through the sodium ion auxiliaries in the equatorial direction

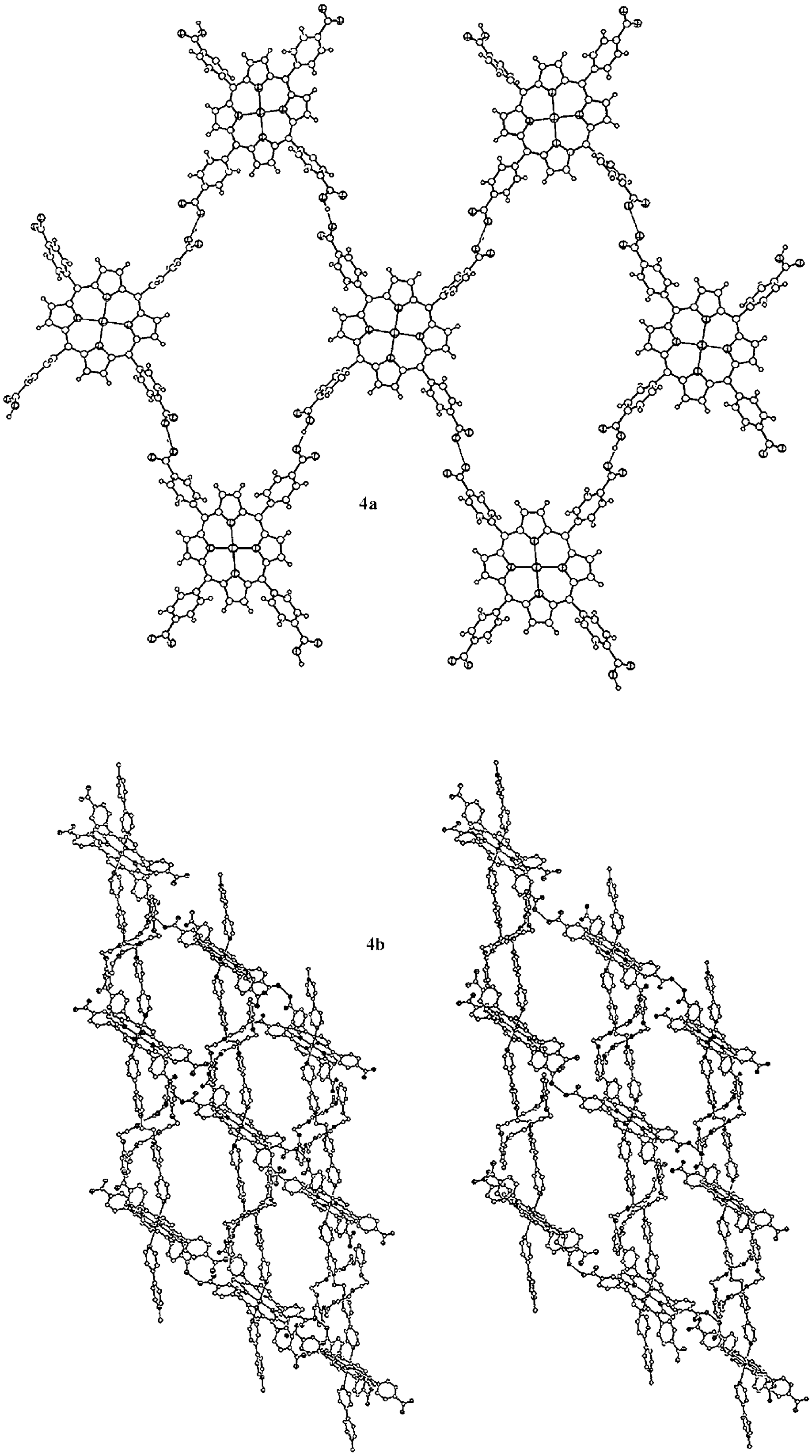


Figure 4. (a) β-Molecular networks of the Zn^{II}TCPP units in **4**; every porphyrin hydrogen atom bonds to four neighboring units and to four additional molecules of water; the van der Waals width of the interporphyrin voids is about 12 Å; (b) stereoscopic illustration of the linear coordination polymers in **4** and the cross-linking between them by interporphyring hydrogen bonds; the Zn, N and O atoms in the porphyrin and ligand moieties are denoted by dark circles

[the crystalline hydrate of the 1:1 complex between $Zn^{II}TCPP^{2-}$ and 1,2-bis(4,4′-bipyridinio)ethane−dibenzo-24-crown-8]. This involves coordination through the metal ion in the porphyrin center of Zn^{II}TCPP without resorting to external auxiliaries. Indeed, earlier studies confirm that Zn^{II} may adopt a six-coordinate environment in the presence of pyridyl-type ligands, and that linear multiporphyrin oligomers and polymers may be obtained in solution as well as in the solid state with bridging bidentate ligands of this type.[7a,15] They have also indicated that a deprotonated TCPP is a better building block for the formation of robust anionic networks than the neutral unit.[7] These observations guided us to choose a cationic bidentate ligand for this synthesis. The [2]pseudorotaxane dication 1,2-bis(4,4′-bipyridinium)ethane−dibenzo-24-crown-8 (Scheme 3), which has been used in the synthesis of other supramolecular systems,[16,17] was assumed to be a perfect candidate to this aim. It is a linear doubly charged species containing a pyridyl fragments at both ends. The macrocyclic crown ring threaded on the molecular axle adds bulkiness and limits the conformational flexibility of the system. Figure 4b illustrates the structure of the anticipated polyrotaxane coordination polymer that forms. Along the linear polymer the pyridyl N atoms coordinate from both sides to the zinc ions in the porphyrin core at 2.691 Å, the Zn−N(pyridyl) bond forming an angle of about 78° with the porphyrin plane. Simultaneously, the deprotonated porphyrin units (located on crystallographic inversion) associate into continuous open networks through cooperative hydrogen bonding between their carboxylic/carboxylate groups (Figure 4a). Each of the latter is involved in one hydrogen bond to another porphyrin species (at $OH\cdots O^-$ 2.451 Å) and another H bond to an external molecule of water (at $OH\cdots O$ 2.679 and 2.789 Å). Every Zn^{II}TCPP unit in this net is linked to four neighboring molecules at the corners of the square framework. The spacing between the molecular surfaces of adjacent units located across the width of the interporphyrin voids is about 12.0 Å. In the absence of a suitable template to fill such a large void space, the linear coordination polymers that propagate in a direction roughly perpendicular to the porphyrin plane interpenetrate through the hydrogen-bonded porphyrin networks. The [2]pseudorotaxane ligands that are embedded within a given layer, link to porphyrin units of neighboring layers located above and below. The resulting structure consists, therefore, of interlocked multiporphyrin β-molecular networks and linear [2]pseudorotaxane coordination polymers. The single-framework lattice is not porous in this case, as the crown-ether macrocycle framework threaded on the ligand molecular axle fills effectively the space available within the layered porphyrin arrays.

The above examples demonstrate useful synthetic tools that can be successfully applied in diverse combinations for the crystal engineering of porphyrin-based network solids. The metalated TCPP building block was found to be particularly attractive for this aim, as it allows the tessellation of multiporphyrin arrays in various ways, including through extensive hydrogen bonding, inter-coordination through external metal ion auxiliaries, and coordination polymerization assisted by bipyridyl-type axial ligands bridging between core metal ions of adjacent porphyrin units. The concerted utilization of coordination (of either type) and hydrogen bonding features yields network molecular solids with fascinating 3-D architectures. It is noteworthy that these formulations are directed primarily by specific noncovalent intermolecular interactions, and not by virtue of dispersion forces as is commonly observed in molecular crystals. Many of the multiporphyrin lattices obtained in this way contain channels accessible to other species that are not part of the supramolecular framework, providing useful models of microporous solids that may bear structural and functional resemblance to the inorganic zeolites. A priori prediction of the actual crystal structure that may form from solution in a particular case (and the detailed stoichiometric content of the interacting components in it) is still beyond reach, as many other factors are involved in the crystallization process (e.g., solubility problems, kinetic vs. thermodynamic control of crystal growth, composition and chemical reactivity of the crystallization environment, etc.). However, the above studies provide useful examples for an effective synthesis of supramolecular arrays with multidimensional architectures, and demonstrate effective tools for the solid-state synthesis of 2-D and 3-D multiporphyrin assemblies. They add to our previous reports on porphyrin-based molecular sieves and zeolite analogues with tunable architectures, and together represent an important step towards the programmed formulation of new molecular materials with useful properties.

Experimental Section

Materials: Zn^{II}TCPP ($C_{48}H_{28}N_4O_8Zn$) and Mn^{III}TCPP·Cl ($C_{48}H_{28}N_4O_8MnCl$) were purchased from Porphyrin Systems GbR, and used as received. The dibenzo-24-crown-8, common solvents and other starting materials were purchased from Aldrich and used as received.

Preparative Procedures: The porphyrin phase used for the crystallizations was obtained by dissolving the commercial Zn^{II}TCPP or Mn^{III}TCPP·Cl materials in hot wet methanol. Ethyl benzoate was found to be an effective crystallization solvent for obtaining X-ray quality crystals of compounds **1−3** by filling the voids in the open multiporphyrin lattices that formed. A series of different experiments is reported below to illustrate the versatile inter-porphyrin binding modes possible in these materials: (a) crystallization of TCPP networks without resorting to external ligands or metal ion auxiliaries, (b) reaction of the tetrakis(carboxy)porphyrin with sodium ion auxiliaries to effect lateral inter-coordination, also in the presence of a large aromatic spacer, and (c) crystallization of these building bocks with [2]pseudorotaxane dication (Scheme 3) as an effective bridging ligand between the porphyrin centers. They yielded four new supramolecular materials.

Compound 1 [$(C_{48}H_{27}N_4O_8Mn)\cdot(CH_3OH)\cdot(H_2O)\cdot 1.5(C_9H_{10}O_2)$]: A methanol solution (2 mL) of Mn^{III}TCPP·Cl (8.8 mg, 0.01 mmol) was heated to boiling (expelling HCl), and 0.2 mL of ethyl benzoate was added. The resulting solution was allowed to stand in ambient air until large, dark-red crystals were formed (ca. 2 mg).

Compound 2 [$(C_{48}H_{28}N_4O_8Zn)\cdot(C_9H_{10}O_2)\cdot Na^+\cdot(C_7H_5O_2)^-$]: A methanol solution (2 mL) of Zn^{II}TCPP (8.6 mg, 0.01 mmol) was heated to boiling in the presence of sodium chloride (one grain), and 0.1 mL of ethyl benzoate was added. This procedure was associated with partial degradation of the ethyl benzoate to benzoic acid and expulsion of HCl. The resulting solution was allowed to stand in ambient air, until a mixture of a small number of dark red crystals with mostly polycrystalline material was deposited in the reaction test tube.

Compound 3 [$(C_{48}H_{27}N_4O_8Zn)^-\cdot Na^+\cdot(CH_3OH)\cdot 0.5(C_{14}H_8N_2)\cdot 3(C_9H_{10}O_2)$]: 2,7-Diazapyrene (4.0 mg, 0.02 mmol) was added to a methanol solution (2 mL) of Zn^{II}TCPP (8.6 mg, 0.01 mmol), the mixture heated to boiling in the presence of sodium chloride, and 0.2 mL of ethyl benzoate added. In this case the preparative procedure was associated with deprotonation of the porphyrin molecule and expulsion of HCl. The resulting solution was allowed to stand in ambient air until dark red crystals were formed after a few days in relatively high yield (ca. 3 mg).

Compound 4 [$(C_{48}H_{26}N_4O_8Zn)^{2-}\cdot(C_{22}H_{20}N_4)^{2+}\cdot(C_{24}H_{32}O_8)\cdot 4(H_2O)$]: The 1,2-bis(4,4′-bipyridinio)ethane dibromide was synthesized first according to a known literature procedure and confirmed by NMR, UV and MS spectroscopy.[16] Then, a 1:4 mixture of this ligand (4 mg, 0.008 mmol) and dibenzo-24-crown-8 (15 mg, 0.033 mmol) was dissolved in chloroform (1.5 mL), and allowed to stand in air for a few days to yield a [2]pseudorotaxane (Scheme 3) in which the ligand is inserted in the crown ether ring (its formation was monitored by ^{1}H NMR spectroscopy).[17] In the next step, a methanolic solution (2 mL) of Zn^{II}TCPP (8.6 mg, 0.01 mmol) was carefully layered over the chloroform phase and allowed to stand. Slow diffusion produced numerous dark-red prisms of the composite crystals of compound **4** layered on the walls of the test tube.

Due to the small preparative scale (see above), the high content of volatile solvents in these crystals, and presence of metal ions therein, it was difficult to obtain reliable elemental analytical data. However, all the obtained crystalline compounds were unequivocally characterized by crystallographic techniques.

X-ray Crystallography: All diffraction measurements were carried out with a Nonius Kappa CCD diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.7107 Å). The crystalline samples of the analyzed compounds were covered with a thin layer of light oil and cooled to 110 K in order to minimize structural disorder and thermal motion effects, and increase the precision of the results. This allowed us to locate most of the hydrogen atoms of the porphyrin network in residual electron-density maps. The structures were solved using direct methods (SHELXS-97 and SIR-92) and refined by full-matrix least squares on F^2 (SHELXL-97).[18] Hydrogen atoms were refined using a riding model with fixed thermal parameters [U_{ij} = 1.2 U_{ij} (equiv.) for the atom to which they are bonded].

1: $(C_{48}H_{27}N_4O_8Mn)\cdot(CH_3OH)\cdot(H_2O)\cdot 1.5(C_9H_{10}O_2)$, M = 1118.0, monoclinic, space group $P2_1/c$, a = 11.5160(1), b = 22.2430(2), c = 21.8340(2) Å, β = 97.95(1)°, V = 5539.05(9) Å^3, T = 110(2) K, Z = 4, $D_{calcd.}$ = 1.341 g·cm^{-3}, μ(Mo-K_α) = 0.31 mm^{-1}, 12828 unique reflections to $2\theta_{max}$ = 55.7°, R_1 = 0.068 for 9747 observations with $I > 2\sigma(I)$, R_1 = 0.097 (wR_2 = 0.214) for all unique data.

2: $(C_{48}H_{28}N_4O_8Zn)\cdot 3(C_9H_{10}O_2)\cdot Na^+\cdot(C_7H_5O_2)^-$, M = 1448.7, monoclinic, space group $P2_1$, a = 9.9730(2), b = 32.1410(6), c = 11.2750(2) Å, β = 110.80(1)°, V = 3378.5(1) Å^3, T = 110(2) K, Z = 2, $D_{calcd.}$ = 1.424 g·cm^{-3}, μ(Mo-K_α) = 0.45 mm^{-1}, 6052 unique reflections to $2\theta_{max}$ = 50.8°, R_1 = 0.057 for 4761 observations with $I > 2\sigma(I)$, R_1 = 0.079 (wR_2 = 0.157) for all unique data. The structure is a racemic twin.

3: $(C_{48}H_{27}N_4O_8Zn)^-\cdot Na^+\cdot(CH_3OH)\cdot 0.5(C_{14}H_8N_2)\cdot 3(C_9H_{10}O_2)$, M = 1460.8, triclinic, space group $P\bar{1}$, a = 13.7460(2), b = 15.5400(2), c = 18.2670(4) Å, α = 108.422(1), β = 93.223(1), γ = 108.670(1)°, V = 3453.1(1) Å^3, T = 110(2) K, Z = 2, $D_{calcd.}$ = 1.405 g·cm^{-3}, μ(Mo-K_α) = 0.44 mm^{-1}, 12717 unique reflections to $2\theta_{max}$ = 52.0°. Conventional refinement converged at R_1 = 0.095 for 8205 observations with $I > 2\sigma(I)$, R_1 = 0.141 (wR_2 = 0.279) for all unique data. It indicated severe disorder of the three ethyl benzoate solvent molecules within the interporphyrin voids of the crystal lattice, which could not be modeled with an adequate precision. Subtraction of their contribution to the diffraction pattern by the Bypass[19] procedure resulted in a considerably improved convergence of the main supramolecular framework at R_1 = 0.065 for 8205 observations with $I > 2\sigma(I)$, R_1 = 0.099 (wR_2 = 0.185) for 12717 unique data.

4: $(C_{48}H_{26}N_4O_8Zn)^{2-}\cdot(C_{22}H_{20}N_4)^{2+}\cdot(C_{24}H_{32}O_8)\cdot 4(H_2O)$, M = 1713.1, monoclinic, space group $P2_1/n$, a = 8.070(1), b = 23.570(1), c = 22.314(1) Å, β = 98.68(1)°, V = 4195.7(2) Å^3, T = 110(2) K, Z = 2, $D_{calcd.}$ = 1.356 g·cm^{-3}, μ(Mo-K_α) = 0.37 mm^{-1}, 7181 unique reflections to $2\theta_{max}$ = 50.8°. Conventional refinement converged at R_1 = 0.105 for 4823 observations with $I > 2\sigma(I)$, R_1 = 0.147 (wR_2 = 0.323) for all unique data. It indicated a low data-to-parameters ratio and severe disorder of the crown ether species, the atomic positions of which could thus be assigned with isotropic U only and determined with low precision.

Despite the considerable disorder in structures **3** and **4**, the supramolecular framework structures could be reliably determined. The observed covalent and coordination bond lengths and angles in the ordered fragments conform to normally observed values in related porphyrin compounds, as documented in the literature. This includes also clear distinction in most cases between C−O bond lengths in a carboxylic residue (one short, near 1.2 Å, and one long, near 1.3 Å), and in a carboxylate anion (roughly equal bond lengths usually within 1.24−1.27 Å), as well as between distances of carboxyl−carboxyl, and carboxyl−carboxylate hydrogen bonding interactions.[4b,10]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-160614 (**1**), -160615 (**2**), -160616 (**3**) and -160617 (**4**). Copies can be obtained free of charge on the application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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