Solid-state supramolecular chemistry of porphyrins. Stacked and layered heterogeneous aggregation modes of tetraarylporphyrins with crown ethers

Yael Diskin-Posner, R. Krishna Kumar and Israel Goldberg*

School of Chemistry, Sackler Faculty of Exact Sciences, Tel Aviv University, 69978 Ramat Aviv, Tel Aviv, Israel. E-mail: goldberg@post.tau.ac.il

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New crystalline materials of mixed composition based on the interaction between tetraarylporphyrin and 18-crown-6 derivatives have been prepared and characterized by X-ray diffraction analysis. Free crown ether macrocycles (18-crown-6 and dibenzo-18-crown-6) associate to manganese- or zinc-tetraphenylporphyrin in aqueous solution through a bridging molecule of water which simultaneously coordinates to the axial site of the porphyrin metal core and hydrogen bonds to the oxygens of the crown ether. This ternary mode of self-assembly can lead to the formation of monomeric, oligomeric and stacked polymeric entities, depending on the symmetry of the crown structure and the preferred coordination geometry of the metal ion. Sodium or potassium 18-crown-6 chlorides were found to be excellent templates for the construction of non-interpenetrating β-molecular networks from zinc-tetra(4-carboxyphenyl)porphyrin building blocks. The resulting layered motifs incorporate the crown ether moieties within the interporphyrin cavities. These arrays are stabilized by strong hydrogen bonds between the self-complementary carboxylic groups as well as by ion pairing, as their formation is associated with proton transfer from one of the carboxylic groups to the chloride anion and expulsion of hydrochloric acid. Molecules of the methanol solvent, which coordinate axially to the central metal ions of the porphyrin and crown ether moieties in one layer while hydrogen bonding to the carboxylic groups of another layer, contribute to the tight packing of the molecular layers along the third dimension. The experimentally established geometries and packing modes of these aggregates provide useful information for further crystal engineering efforts of networked multi-porphyrin domains.

A remarkable effort has been directed in the past towards the design of new metalloporphyrin-based nanostructures as models and components for photonic devices, chemical sensors and novel receptors for selective catalysis.[1] This effort relied mostly on covalent chemistry, while the construction of stable multi-porphyrin arrays by supramolecular synthesis has remained a relatively unexplored approach.[2] Nano-fabrication of materials by self-assembly processes has gained, however, a considerable attention in more recent years. The diverse molecular recognition algorithms that can be readily incorporated into the porphyrin species make them very attractive building blocks in this type of chemistry. The present study is part of an extensive evaluation of structural motifs of supramolecular multi-porphyrin domains in the solid state, aiming at the design of new molecular materials by the noncovalent approach and assessment of their potential utility as solid state receptors and molecular sensors.

Tetraarylporphyrins rarely crystallize as pure materials. Rather, they show high affinity for incorporation of additional molecular species into the crystal lattice. Earlier studies of a large number of tetraarylporphyrin-based lattice clathrates have shown that the organization of the porphyrin building blocks is largely determined by their molecular shape,[3] being strongly conserved in two dimensions to optimize intermolecular van der Waals attraction.[4] More recent investigations by us, among others, have shown that this can be readily modified by utilizing directional interactions. Correspondingly, a variety of crystalline oligomers, polymers and networks of different structural characteristics have been rationally designed from these metallomacrocycles by selection of the coordination geometry of metals, suitable functionalization of the porphyrin framework, and the geometry of multidentate ligands involved in the supramolecular synthesis.[5,6]

It has been shown that the directed modes of interporphyrin aggregation affect the porosity of the molecular organization, and consequently the selectivity of the porphyrin lattice toward a suitably sized guest component, as well as the stability of the assembled structure. As part of this general effort we have examined the structural features of several mixed porphyrin–crown ether systems in a search for new patterns of supramolecular organization. This report focuses on the complexes of axially coordinated zinc tetraphenylporphyrin (ZnTPP) with 18-crown-6 and dibenzo-18-crown-6, and on mixed layered mosaic architectures of zinc tetra(4-carboxyphenyl)porphyrin (ZnTCPP) with sodium and potassium 18-crown-6. The latter systems are of particular interest in the context of formulation of stable hollow β-molecular networks from laterally functionalized tetraphenylporphyrin frameworks, as demonstrated recently in a preliminary publication.[5a] Only a few scattered examples of related supramolecular materials composed of porphyrins and crown ethers have been reported.[7]

Experimental

The essential starting materials were obtained from Aldrich. ZnTPP and ZnTCPP were prepared by standard procedures of porphyrin synthesis adapted from the literature.[8] Adducts of ZnTPP with dibenzo-18-crown-6 (**1**) and with 18-crown-6 (**2**) (the crown compounds are very hygroscopic and contain water) were obtained by dissolving stoichiometric amounts of ZnTPP and the corresponding crown ether in a hot ethyl ester of benzoic acid. Adducts of anionic (mono deprotonated) ZnTCPP$^-$ with cationic [Na-18-crown-6]$^+$ (**3**) and [K-18-crown-6]$^+$ (**4**) were prepared by dissolving the porphyrin and 18-crown-6 components in hot methanol in the presence of sodium or potassium chloride accompanied by expulsion of HCl. Slow evaporation of these solutions under controlled conditions led to single crystals of the composite materials.

Crystal data

The crystallographic data for the analyzed[9–11] structures **1**–**4** follows.

1, $(C_{44}H_{28}N_4Zn)\cdot(H_2O)\cdot(C_{20}H_{24}O_6)$: M 1056.5, triclinic, space group $P\bar{1}$, $a = 10.207(1)$, $b = 14.450(1)$, $c = 17.827(1)$ Å, $\alpha = 81.98(1)$, $\beta = 85.97(1)$, $\gamma = 88.87(1)°$, $V = 2597.0(3)$ Å^3, $Z = 2$, $T = 295$ K, $D_{\text{calc}} = 1.351$ g cm^{-3}, μ(Mo-Kα) = 0.53 mm^{-1}, 17173/9425 measured/unique reflections ($R_{\text{int}} = 0.076$), $R1 = 0.063$ for 4379 observations with $F_0 > 4\sigma(F_0)$, $R1 = 0.170$ ($wR2 = 0.147$) for all unique data, $|\Delta\rho| \leqslant 0.40$ e Å^{-3}.

2, $(C_{44}H_{28}N_4Zn)\cdot(H_2O)\cdot\frac{1}{2}(C_{12}H_{24}O_6)\cdot(C_9H_{10}O_2)$: M 978.4, triclinic, space group $P\bar{1}$, $a = 12.182(1)$, $b = 12.431(1)$, $c = 17.077(1)$ Å, $\alpha = 70.65(1)$, $\beta = 83.00(1)$, $\gamma = 87.55(1)°$, $V = 2421.8(3)$ Å^3, $Z = 2$, $T = 120$ K, $D_{\text{calc}} = 1.342$ g cm^{-3}, μ(Mo-Kα) = 0.56 mm^{-1}, 15174/9878 measured/unique reflections ($R_{\text{int}} = 0.084$), $R1 = 0.076$ for 4371 observations with $F_0 > 4\sigma(F_0)$, $R1 = 0.200$ ($wR2 = 0.160$) for all unique data, $|\Delta\rho| \leqslant 0.80$ e Å^{-3}. The ethyl residue of the solvent component was found to be disordered between two orientations. Correspondingly, two equally populated positions were assumed for the terminal methyl in the final refinement.

3, $(C_{48}H_{27}N_4O_8Zn)^-\cdot(C_{12}H_{24}O_6)Na^+\cdot(CH_4O)_4$: M 1268.6, triclinic, space group $P\bar{1}$, $a = 9.019(1)$, $b = 10.747(1)$, $c = 16.206(1)$ Å, $\alpha = 83.07(1)$, $\beta = 80.65(1)$, $\gamma = 77.57(1)°$, $V = 1507.6(2)$ Å^3, $Z = 1$, $T = 120$ K, $D_{\text{calc}} = 1.397$ g cm^{-3}, μ(Mo-Kα) = 0.49 mm^{-1}, 9289/6247 measured/unique reflections ($R_{\text{int}} = 0.034$), $R1 = 0.061$ for 4423 observations with $F_0 > 4\sigma(F_0)$, $R1 = 0.097$ ($wR2 = 0.167$) for all unique data, $|\Delta\rho| \leqslant 0.95$ e Å^{-3}. In the assumed centrosymmetric space group, which was strongly indicated by intensity statistics, the molecular units of the complex are located on crystallographic inversion. This requires a structural disorder between one MeOH species which axially binds to the five-coordinate zinc of the porphyrin core and another non-coordinating MeOH moiety which is positioned close to the concave site of the porphyrin framework.

4, $(C_{48}H_{27}N_4O_8Zn)^-\cdot(C_{12}H_{24}O_6)K^+\cdot(CH_4O)_4$: M 1284.7, triclinic, space group $P\bar{1}$, $a = 12.448(1)$, $b = 15.412(1)$, $c = 16.307(1)$ Å, $\alpha = 100.55(1)$, $\beta = 90.83(1)$, $\gamma = 100.27(1)°$, $V = 3022.8(4)$ Å^3, $Z = 2$, $T = 120$ K, $D_{\text{calc}} = 1.411$ g cm^{-3}, μ(Mo-Kα) = 0.55 mm^{-1}, 20312/14874 measured/unique reflections ($R_{\text{int}} = 0.041$), $R1 = 0.082$ for 8122 observations with $F_0 > 4\sigma(F_0)$, $R1 = 0.167$ ($wR2 = 0.240$) for all unique data, $|\Delta\rho| \leqslant 1.39$ e Å^{-3}. The methanol located on the concave face of the porphyrin framework is not coordinated.

The crown ether rings, as well as the solvent moieties incorporated into the crystal lattice, tend to be partially disordered even at 120 K [as reflected in a relatively low percentage of significant observations above the threshold of $2\sigma(I)$ and somewhat high R-values for the weakest reflections in structures **2**–**4**], which lowered slightly the precision of the crystallographic determination. The resulting structural models of the four compounds are nevertheless still quite reliable, and the observed covalent and coordination bond lengths and angles conform to normally observed values documented in the literature. As stated at the outset, the subsequent discussion focuses mainly on aspects of the supramolecular association and intermolecular organization.

CCDC reference number 440/125. See http://www.rsc.org/suppdata/nj/1999/885/ for crystallographic files in .cif format.

Results and discussion

Supramolecular aggregation of crown ether and porphyrin derivatives can be achieved in several ways, two of which will be discussed below. The first examples involve a stacking face-to-face arrangement of the two types of macrocyclic and roughly planar species, which is facilitated by the presence of metal ion in the porphyrin center. Axial coordination of the 18-crown-6 derivative to the metalloporphyrin may occur effectively only through a third component capable of binding simultaneously both to the metal center of the porphyrin core as well as to the oxygen sites in the crown ether rings. The high affinity of water to coordinate to metal ions through the lone pair electrons of its oxygen [relevant examples to this study include five-coordinate H_2O–ZnTPP and six-coordinate $(H_2O)_2$–MnTPP complexes],[12,13] as well as to associate by hydrogen bonding through its protons to oxygen nucleophiles of the 18-crown-6 moiety,[14] makes it a readily accessible ligand for this purpose. The different monomeric, oligomeric and polymeric porphyrin–water–crown ether motifs obtained in this work are illustrated in Fig. 1.

Compound **1** represents a 1 : 1 supramolecular adduct of ZnTPP with dibenzo-18-crown-6 linked to one another through an H_2O bridge [Fig. 1(a)]. The coordination of water to the porphyrin and crown ether components is characterized by the respective distances: H_2O–Zn = 2.141(3), $OH_2\cdots$O(crown ether) = 3.054(5) and 3.115(5) Å, reflecting a strong interaction with the former and a weaker association (mostly due to the poor nucleophilicity of ethereal O-atoms) with the latter. The constraints introduced by the aromatic substituents cause the dibenzo-18-crown-6 to have a slightly bent shape. The water ligand is perching on the convex surface of the crown moiety, lying in close proximity to four of the ethereal oxygens and donating its protons to two of them. This combination of steric, electrostatic and H-bonding interactions stabilizes an open and stable conformation of the crown ether ring. The five-coordinate zinc ion has a typical square-pyramidal coordination geometry, deviating from the mean plane of the four pyrrole nitrogens towards the axial water ligand by 0.28 Å. Fig. 2 demonstrates the crystal packing of the monomeric complexes in this structure. Two significant details of this arrangement deserve particular attention. Thus, adjacent complexes are rather closely packed in the crystal, the peripheral phenyl groups of one component (either of the porphyrin or of the crown ether) effectively filling

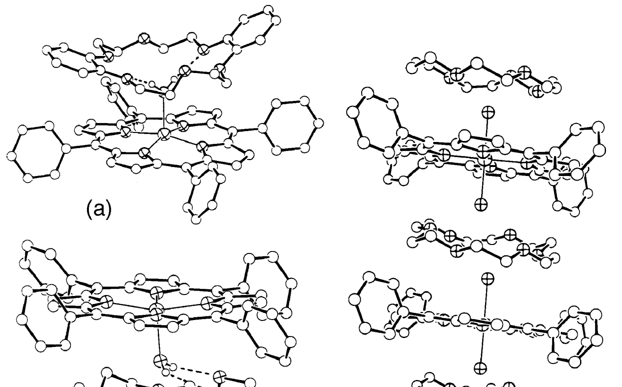

Fig. 1 Supramolecular structures of the water mediated porphyrin–crown ether adducts in: (*a*) **1**, (*b*) **2**, and (*c*) the polymeric structure involving MnTPP.[18]

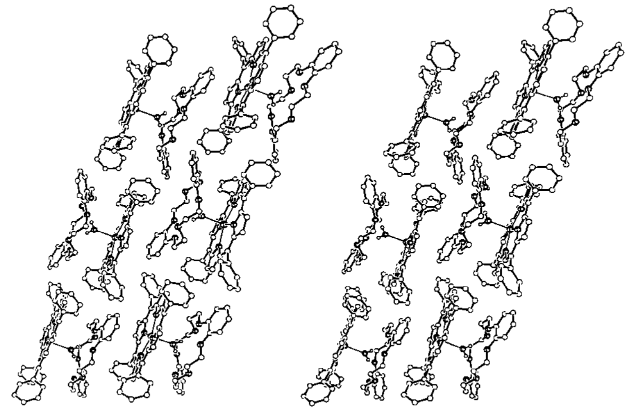

Fig. 2 Stereoview of the crystal structure of **1**, illustrating the layered arrangement of the component species and the effective packing.

the space in the concave molecular surface of a neighboring component. Moreover, this structure maintains the same characteristics of intermolecular organization as observed in other TPP clathrates. The crystal structure (typically of $P\bar{1}$ symmetry) is composed of mixed flat layers of the component macrocyclic moieties, which are stacked in the lattice one on top of the other in an offset manner.[3]

Interaction of ZnTPP with the unsubstituted 18-crown-6 component allows the formation of a more extended oligomeric entity [Fig. 1(b)]. The 18-crown-6 in its open form has two equivalent faces, and can associate simultaneously with two neutral guests.[15] In the resulting structure, the 18-crown-6 is thus sandwiched between two complexes of H_2O–ZnTPP, forming a centrosymmetric aggregate [H_2O–Zn = 2.130(4), $OH_2\cdots$O(crown ether) = 2.918–3.075(5), deviation of Zn from the pyrrole nitrogen's plane 0.30 Å]. We have analyzed recently a series of similar 'dimers' of ZnTPP bridged by different bidentate ligands.[16] The various ligand spacers maintained the two porphyrin components in each such oligomer at a distance ranging from 9.4 to 14.0 Å. The corresponding spacing between the porphyrin frameworks (*i.e.*, between the planes defined by the four pyrrole nitrogens in each molecule) in **2** is 8.1 Å. The conformation of the 18-crown-6 has an approximate D_{3d} symmetry, with all *gauche* O–C–C–O and *anti* C–C–O–C torsion angles. A very similar molecular structure has been, in fact, already described in an earlier report.[7f] Nevertheless, we have chosen to include our own observations in this paper for the sake of completeness of the discussion. Moreover, this and the previous characterizations refer to two different pseudo-polymorphic crystal structures. The crystalline form in the present case is triclinic and contains molecules of ethyl benzoate, while the previous investigation relates to a (much less common for porphyrin clathrates) monoclinic $C2/c$ modification of the dichloromethane solvate. The crystal packing of **2** is depicted in Fig. 3, showing a layered organization of the crown ether and porphyrin molecular components similar to that observed in **1**. The mixed molecular layers are interspaced in **2** by channels (propagating along the *a*-axis of the crystal) occupied by molecules of the solvent.

Next, we have attempted the preparation of the corresponding polymeric assembly by replacing the Zn(II) ion in the porphyrin core by Mn(III), which reveals high affinity for a six-coordinate environment.[13,17] The resulting crystal structure[18] was confirmed to consist of a linear multicomponent array based on the repeating motif [H_2O—MnTPP·ClO_4—H_2O—18-crown-6] [Fig. 1(c)]. The overall interaction scheme between the different molecules along the polymeric chain [H_2O–Mn = 2.28–2.30, $OH_2\cdots$O(crown ether) = 2.90–3.04 Å] is quite similar to that observed in structure **2**, except for the planarity of the MnTPP framework in the present case. Close packing of these one-dimensional polymeric assemblies is hindered by the presence of separate anions, leading to the inclusion of four molecules of ethyl benzoate in the unit-cell. Severe structural disorder of the 18-crown-6 ring and of the solvent species (even at 120 K) prevented, however, precise refinement and more detailed characterization of this structure.

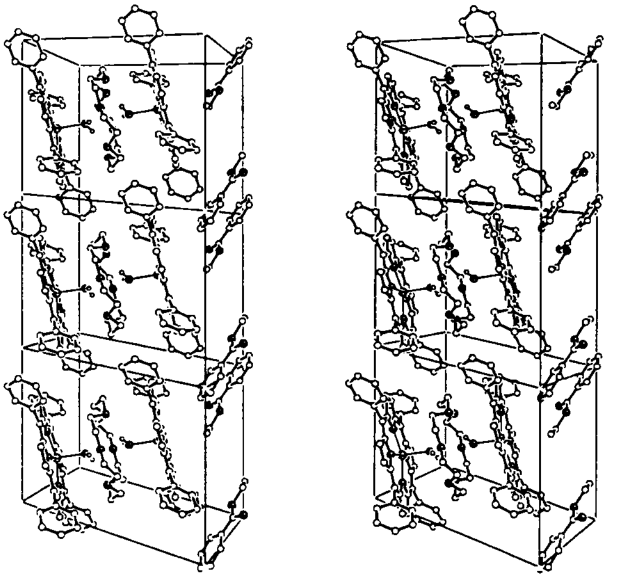

Fig. 3 Stereoview of the crystal structure of **2** (three unit cells along the *a*-axis are shown). Note the corrugated layers of the porphyrin moieties, typically observed in porphyrin clathrates. Molecules of the ethyl benzoate solvent interspace between the concave surfaces of the metalloporphyrins of adjacent layers.

In an attempt to combine the observed axial coordination features with potential lateral hydrogen bonding interactions between the porphyrin species, and thus extend the supramolecular assembly in three dimensions, the ZnTPP and MnTPP moieties were replaced in the next series of experiments by the corresponding TCPP analogs. It has been shown very recently that the TPP building blocks, when substituted by self-complementary recognition sites at the peripheral 4-position of the phenyl ring, may yield hollow network architectures sustained by hydrogen bonds.[5a] Formulation of β-molecular networks composed of zinc tetra(4-amidophenyl)porphyrin (ZnTAPP) provides a suitable example. These networks do not interpenetrate, and have interporphyrin cavities of van der Waals dimensions of about 5.9 by 10 and 6.8 by 10 Å.[5a] The ZnTCPP entity was shown also to form uniquely structured two-dimensional molecular networks through $(COOH)_2$ pairwise hydrogen bonding between the terminal carboxylic functions of adjacent porphyrins.[5d] Yet, the latter have much larger cavities (approximately 16 × 21 Å) and mutually interlock into one another.[19] The capacity of carboxylic acids to exhibit chain polymeric as well as cyclic dimeric modes of self-assembly,[20] combined with utilization of a suitably shaped template, led in this work to the construction of non-interpenetrating TCPP-based molecular layers as well. Related formulations of metalloporphyrin networks with the TCPP building blocks have been attempted most recently by others.[21]

Reaction of ZnTCPP or MnTCPP with the free 18-crown-6 derivatives in different solvents failed to produce crystalline materials. On the other hand, sizeable crystals could be obtained from a methanol solution of ZnTCPP when the 18-crown-6 component was replaced by its sodium or potassium salt (presence of a metal ion inside the crown ether ring rigidifies its fully open D_{3d} conformation). Fig. 4 illustrates the structure of the observed porphyrin β-networks in compounds **3** and **4** (the intermolecular organization in the two crystals is

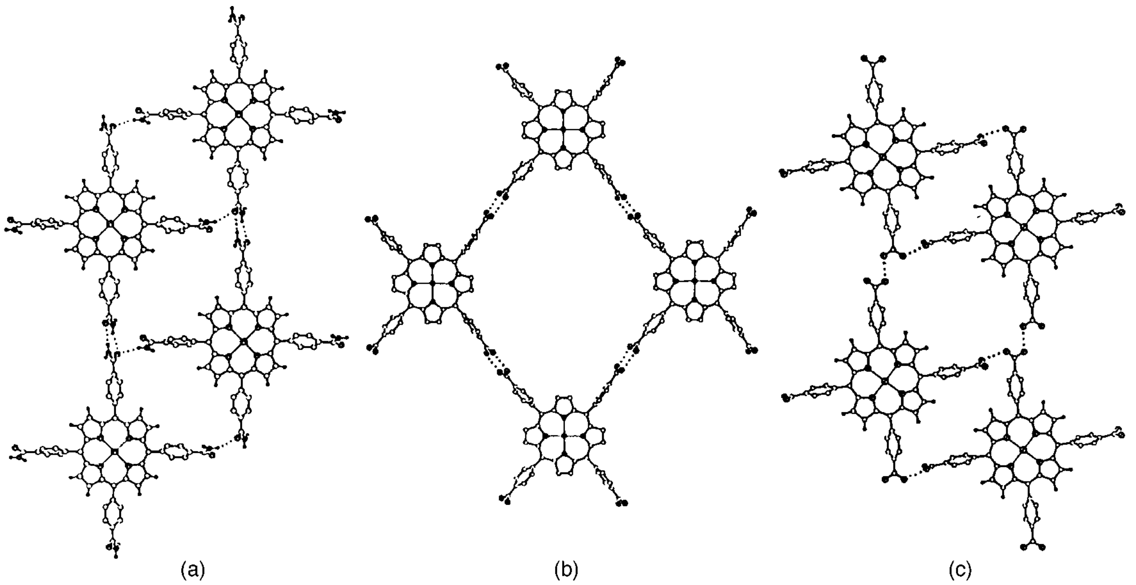

Fig. 4 Self-assembly of tetraarylporphyrin species containing self-complementary recognition sites. Open networks of (*a*) ZnTAPP with inter-porphyrin van der Waals cavities of nearly equal size [approximately 5.9 by 10 Å and 6.8 by 10 Å],[5a] (*b*) ZnTCPP formed by cyclic dimerization of the carboxylic functions, with very large cavities [16 × 21 Å],[19] and (*c*) anionic ZnTCPP induced by chain polymeric hydrogen bonding, with one large [8.5 × 11 Å] and one small cavity [3 × 6.5 Å] (present work). Hydrogen bonds are indicated by dotted lines.

essentially iso-structural despite the difference in the crystal data of the two solids), in comparison with the aggregation patterns of the ZnTAPP and ZnTCPP building blocks found earlier. As in the previous examples, the porphyrin arrays in **3** and **4** are stabilized by strong hydrogen bonding between the sensor groups of adjacent units. These networks are anionic, as the positive charge of the (18-crown-6 sodium)$^+$ and (18-crown-6 potassium)$^+$ ions is balanced by abstraction of one proton from the ZnTCPP moiety during crystallization (accompanied by expulsion of HCl). This is in line with the observed distribution of C–O bond distances in the carboxylic functions of ZnTCPP (Table 1). In compound **4**, three out of the four COOH groups have one short [1.205(5)–1.225(5) Å] and one long [1.307(5)–1.321(5) Å] C–O bond as in an ordered carboxylic residue, while the fourth group has nearly equal bonds [1.259(5) and 1.272(5) Å] as in a carboxylate anion.[22] A similar distinction applies to **3** although in this structure the ZnTCPP is positioned on, and disordered about, the crystallographic inversion, and the asymmetric unit contains only two functional residues. One of them corresponds to an ordered COOH group with single [1.311(4)] and double [1.225(4) Å] C–O bonds, while the other most likely represents an average between the (inversion related) COOH and COO$^-$ moieties [1.257(4) and 1.279(4) Å]. This is further supported by the observed carboxyl–carboxylate and carboxyl–carboxyl hydrogen bonding interactions in the network assembly of the ZnTCPP. The observed OH···O distances are rather short for the former (2.48–2.55 Å in **3** and **4**)[23] and somewhat longer for the latter (2.63 Å in **4**), each of the carboxylate oxygen atoms serving as a proton acceptor from a different neighboring unit (Table 1). Two of the carboxylic groups are oriented perpendicular to the porphyrin plane, and are involved in hydrogen bonds between neighboring porphyrin networks (see below).

The layered multi-porphyrin motif in **3** and **4** contains open spaces between the connecting units (Fig. 4). They have approximate van der Waals dimensions of 8.5 × 11 and 3 × 6.5 Å. The [18-crown-6 sodium]$^+$ and [18-crown-6-potassium]$^+$ moieties, with van der Waals diameter of about 10.5–11.0 Å, conveniently fit within the width of the larger interporphyrin cavity (being slightly tilted in the other direction due to the shorter 8.5 Å spacing available along it), and

Table 1 Hydrogen bonding and coordination distances (Å) in structures **3** and **4**

Compound **3**[a]			
C19–O20	1.279(4)	C19–O21	1.257(4)
C28–O29	1.225(4)	C28–O30	1.311(4)
O20···O20 (at −2 − *x*, −*y*, 1 − *z*)	2.548(5)	OH(30)···O21 (1 + *x*, 1 + *y*, *z*)	2.535(5)
OH(42)···O30 (−*x*, 1 − *y*, −*z*)	2.744(6)	OH(44)···O29 (*x*, *y*, *z*)	2.728(5)
Zn–O42	2.141(5)	Na–O44	2.330(2)
		Na···O(crown ether)	2.702(3)–2.798(3)
Compound **4**[b]			
C31–O32	1.259(5)	C31–O33	1.272(5)
C40–O41	1.321(5)	C40–O42	1.205(5)
C49–O50	1.316(5)	C49–O51	1.221(5)
C58–O59	1.307(5)	C58–O60	1.225(5)
OH(41)···O51 (at *x*, *y* − 1, *z*)	2.628(5)	OH(50)···O32 (1 + *x*, 1 + *y*, 1 + *z*)	2.554(5)
OH(59)···O33 (*x*, 1 + *y*, *z*)	2.476(5)	OH(81)···O59 (−*x*, 1 − *y*, 2 − *z*)	2.786(6)
OH(83)···O60 (*x*, *y* − 1, *z*)	2.706(6)	OH(85)···O42 (*x*, *y*, *z* − 1)	2.747(5)
Zn–O81	2.155(3)	K···O(crown ether)	2.748(3)–2.829(3)
K–O83	2.484(4)	K–O85	2.485(5)

[a] Labels C19, O20, O21 and C28, O29, O30 represent atoms in the two independent carboxy groups; O42 and O44 represent the oxygen atoms of the axial methanol ligands coordinated to the zinc and sodium metal ions, respectively. [b] Labels C31, O32, O33; C40, O41, O42; C49, O50, O51; C58, O59, O60 represent atoms in the carboxy groups; O81 represents the methanol oxygen site ligated to zinc, while O83 and O85 the oxygen atoms of the methanol ligands coordinated to the potassium ion.

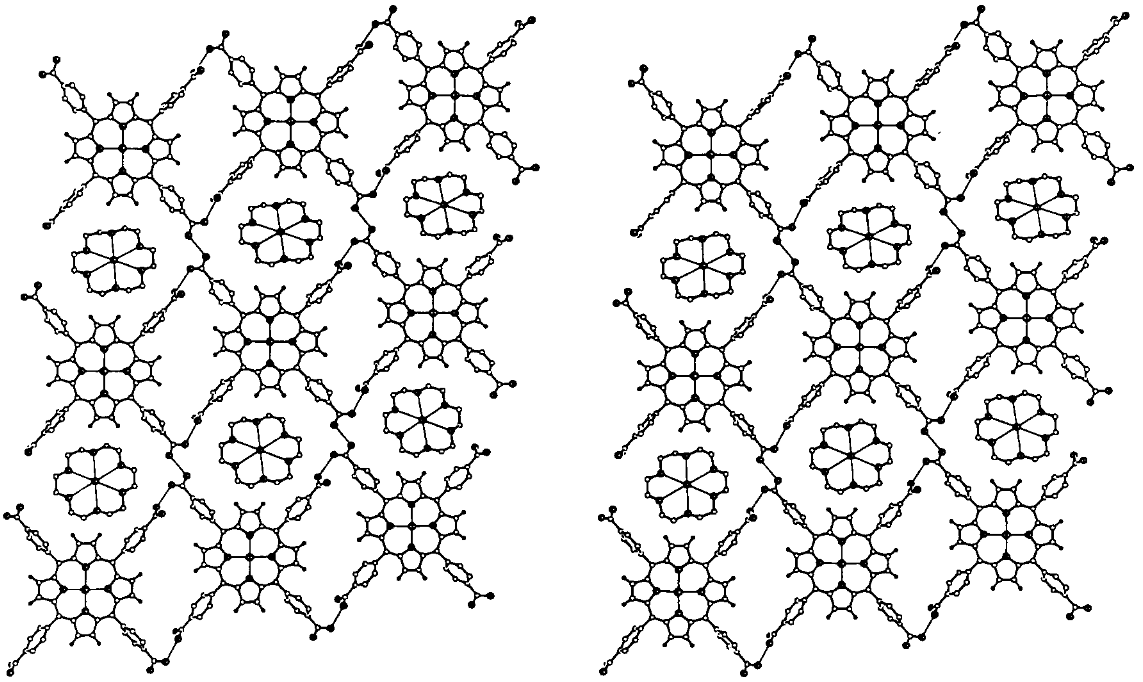

Fig. 5 Stereoview of the β-molecular networks observed in structures **3** and **4**. The metal ion in the porphyrin center is Zn(II); that in the center of the 18-crown-6 is either Na(I) or K(I). Note the intra-layer hydrogen bonding (thin lines between crossed circles), and the tilt of the 18-crown-6 moiety with respect to the plane of the layered arrangement in order to fit within the interporphyrin cavities. The methanol ligands coordinated axially to the central metal ions of the macrocyclic entities are omitted for clarity.

turn out to be excellent templates for this mode of layered porphyrin–crown ether assembly (Fig. 5). The zinc ions within the porphyrin, as well as the alkali ions within the 18-crown-6, are axially coordinated by either one (to Zn^{2+}) or two (to Na^+ or K^+) molecules of the methanol solvent. As in the previous examples the zinc ion is five-coordinate and deviates slightly from the planes of the porphyrin core (by 0.18 and 0.22 Å in **3** and **4**, respectively), the concave side of the porphyrin being approached by another molecule of non-coordinating solvent. This preserves the pseudo-centric environment around the component species, and the centrosymmetric intermolecular arrangement.

An effective crystal packing of the molecular layers is facilitated by the absence of separate anionic entities in the lattice and the additional hydrogen bonding capacity of the methanol molecules. Thus, the mixed porphyrin–crown ether layers stack in the crystal in an offset manner with an average spacing of 5.08 Å (Fig. 6). This allows the axial methanol ligands of one layer to perch on the smaller cavities (which are too narrow to fully accommodate a molecular species or even a methyl group) of an adjacent layer, and to form interlayer hydrogen bonds. These interactions involve the metal-ligating hydroxyl groups (as proton donors) and the carboxylic functions (as proton acceptors) which are oriented perpendicular to the molecular layers. The corresponding OH···O distances range from 2.71 to 2.79 Å, significantly longer than those involving the carboxylate groups. Each porphyrin unit is thus involved in six intra-layer and three inter-layer hydrogen bonding interactions. Table 1 summarizes the O···O hydrogen bonding distances in **3** and **4**, showing also that all potential proton donor and proton acceptor sites (except in the non-coordinating methanol) are effectively used in these interactions. The stacking distance in these structures conform to previous observations that an offset layered arrangement of the roughly flat porphyrin species at a narrow distance range near 4.5–5 Å is a fundamental property of the porphyrin–porphyrin interaction required to optimize van der Waals stabilization in these solids.[3,5b]

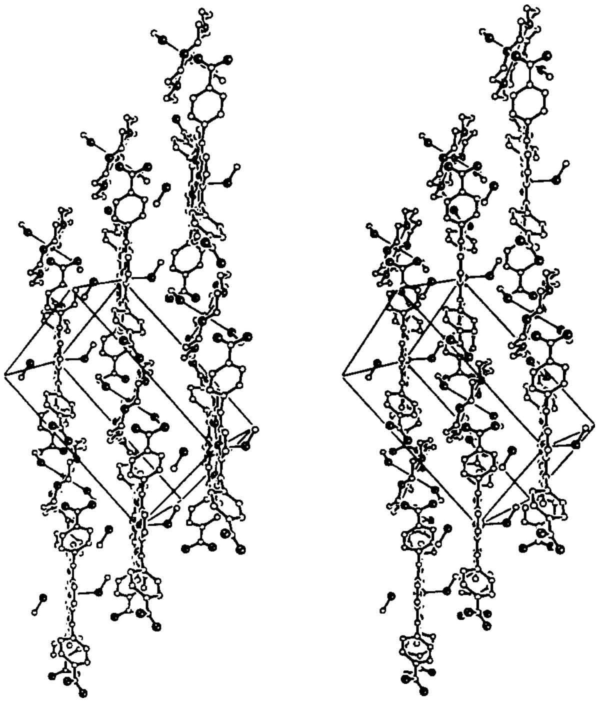

Fig. 6 Side view (stereo) of the crystal structure of **3**, illustrating the efficient offset stacking of neighboring molecular layers (crystal packing in **4** is isostructural). It shows also the relative disposition of the methanol ligands which take part in hydrogen bonding between these layers (see Table 1).

Our long range target in this series of investigations is to crystal-engineer cross-linked open networks of multi-porphyrin aggregates with high structural integrity, which provide a promising perspective for new materials with interesting and useful properties. This study confirms previous observations that functionalized metalloporphyrin macrocycles provide (in an appropriate environment) excellent building blocks for the assembly of molecular aggregates, by utilizing the molecular recognition features of the metal core ion and the peripherally substituted sensors. In this context, formulations of linear coordination polymers and β-molecular networks are of a particular interest as they represent successful applications of known synthons to the supramolecular synthesis of molecular solids. It appears, however, that the strong tendency of the TPP derivatives to form an offset stacked arrangement in the close-packed solid phase, is a major obstacle on the road to the construction (through simultaneous coordination along the axial and lateral directions) of robust multi-porphyrin architectures by non-covalent synthesis. Further efforts are currently underway with other ligands that may optimize stronger cross-linking of the molecular layers in the axial direction through coordination polymerization.

Acknowledgements

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