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Crystal engineering of metalloporphyrin assemblies. New supramolecular architectures mediated by bipyridyl ligands

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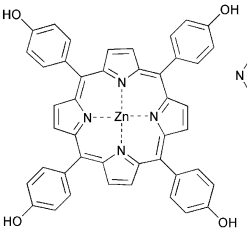
Received (in Cambridge, UK) 20th March 2002, Accepted 24th May 2002
First published as an Advance Article on the web 5th June 2002

Targeted synthesis of new supramolecular motifs of metalloporphyrins in crystals by a concerted mechanism of molecular recognition in three dimensions, aided by organic ligands, is presented; it involves induced assembly of [tetrakis(4-hydroxyphenyl)porphyrinato]zinc species by a combination of axial coordination through bridging bipyridyls and of lateral hydrogen bonding.

Solid-state supramolecular synthesis of stable network materials, by design, presents an exciting challenge in molecular chemistry.[1,2] It requires suitably instructed building blocks that are programmed by virtue of their structure and functionality to self-assemble spontaneously into two- or three-dimensional polymeric arrays.[3] Tetraarylporphyrins, due to their square shape and thermal and oxidative stability, were found to be extremely useful to this end, and were subjected to a systematic investigation.[4] We have demonstrated recently successful syntheses of molecular sieve-type structures based on the [tetra(4-carboxyphenyl)porphyrinato]zinc framework with pores of nano-sized dimensions, utilizing either interporphyrin cooperative hydrogen bonding or coordination through organic ligands and external metal ions.[5,6] In this paper we communicate new uniquely structured formulations of three-dimensional supramolecular networks with [5,10,15,20-tetrakis-(4-hydroxyphenyl)porphyrinato]zinc (**1**), by a simultaneous expression of axial coordination as well as equatorial hydrogen-bonding interactions. The former involves ligand-mediated [*N*,*N*′-bis(4-pyridylmethylidyne)hydrazine (**2**) or 4′4′-bipyridyl (**3**)] coordination between the porphyrin cores. The latter is represented by two different interaction motifs. In one example the porphyrin units are inter-connected through ligand-**2** spacers, while in the second case they hydrogen bond directly to each other. These results illustrate yet another successful realization of supramolecular multiporphyrin assembly *via* new synthons of extended non-covalent connectivity in three dimensions.



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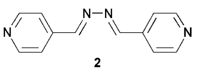

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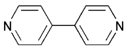

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The preparative procedures of the new materials were guided by the following considerations. Due to the high affinity of **1** for attracting water and methanol either to the peripheral hydroxy groups or the zinc ion in the porphyrin core,[7] special precautions needed to be undertaken to prevent the blockage of these functions to the desired porphyrin or ligand binding. This was achieved in this study by introducing dibenzo-24-crown-8 to the reaction mixture, as a water and methanol trap. Moreover, significant amounts of nitrobenzene were incorporated into the crystallization environment as well, due to its excellent templating role in the stabilization of open multiporphyrin assemblies.[6,8]

Compounds **4** and **5** were obtained by reacting **1** with **2** or **3**, respectively.† They represent two different modes of the supramolecular interaction, both containing, however, similar motifs of ligand-bridged assembly of **1** (Fig. 1). The structure of **4** can be best described as consisting of linear arrays of the porphyrin species, held together by OH···OH hydrogen bonds (O···O 2.810 Å) between the *cis*-related hydroxyphenyl arms on both sides of every unit. Every porphyrin is thus hydrogen-bonded to two adjacent moieties. Parallel porphyrin arrays are then tessellated together by coordination through the bipyridyl ligands (Zn···N 2.159 Å, the zinc ion being five-coordinated and slightly displaced from the porphyrin plane towards the axial ligand) that bridge effectively between their metal centers, thus yielding a ladder-type polymer sustained by coordination as well as hydrogen bonding (Fig. 1). The distance between the ligand-bridged porphyrin cores is nearly 16 Å. The ladder assemblies are organized in the triclinic structure in an offset (sideways as well as upwards or downwards) parallel manner. They are further interconnected diagonally to the next-nearest ladders on both sides by OH···N hydrogen bonding (O···N 2.654 Å). This involves the second OH proton donor at every OH···OH binding site, and additional bipyridyl moieties. The long thin ligands interpenetrate through the narrow (approx. 4 Å-wide space between the H-bonded units) interporphyrin voids of the nearest ladder assembly in order to reach the next-nearest entities. This results in the formation of a single-framework concatenated architecture of the porphyrin and bipyridyl components (Fig. 2). The distance between porphyrin-

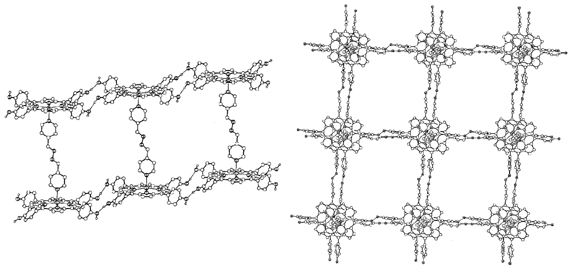

Fig. 1 Assembly of the ligand-bridged coordination motifs of porphyrin **1**. (Left) Side view of the linear array of H-bonded units in **4**. (Right) Top view of the open bilayered array of H-bonded (porphyrin–axial ligand–porphyrin) units in **5**.

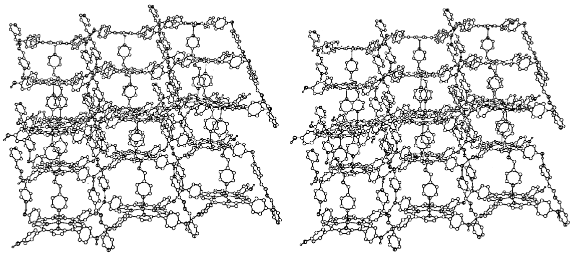

Fig. 2 Stereoview of the interwoven supramolecular networks in **4**. The solvent-accessible space represents 53% of the crystal volume.

DOI: 10.1039/b202791g

coordinated bipyridyl pillars in adjacent ladders, which are parallel to one another, is about 10 Å. This space (roughly 6.5 Å in van der Waals diameter) is filled in the crystal by the nitrobenzene solvent.

Replacement of **2** by a shorter ligand **3**, has a considerable effect on the self-assembly process and the resulting intermolecular organization described above. Structure **5**, obtained by reaction of **1** with 4,4′-bipyridyl, also consists of ligand-bridged porphyrin dimers, in which ligand **3** is sandwiched between two porphyrin macrocycles. The observed coordination Zn–N distances are 2.134 and 2.144 Å. These trimers are extensively linked to one another by direct (rather than through the ligand, as in the previous example) porphyrin–porphyrin OH···OH hydrogen bonds at O···O distances within the range of 2.64–2.70 Å. This includes formation of two-dimensional bilayer arrays with very large square voids between adjacent units of van der Waals width of about 15 Å. (Fig. 1).

Within the bilayers, every porphyrin is hydrogen bonded through its hydroxy groups to four (rather than two, as in the earlier example) different neighboring moieties. Adjacent bilayers are arranged in an offset manner to place the porphyrin frameworks of one bilayer above the void space of another bilayer. Moreover, they interpenetrate into, and further hydrogen bond to, each other, utilizing almost to capacity the hydrogen bonding potential of the hydroxyl functions. To facilitate the latter, one of the porphyrin cores in the ligand-bridged porphyrin dimer is inclined by 25° from being perpendicular to the main axis of the bridging ligand. The extended intermolecular connectivity through ligand coordination and interporphyrin hydrogen bonding, thus formed in the crystal structure, is illustrated in Fig. 3. The solvent accessible void space created between the bipyridyl bridges and between the concave surfaces of the ligand-bridged porphyrin dimers was assessed to comprise 62% of the crystal volume and is filled in the structure by diffuse nitrobenzene solvent.

In the two solids, a combined mechanism of axial coordination and lateral multiple hydrogen bonding provides the organizing force for the supramolecular assembly of the metalloporphyrin and bipyridyl entities. The thermodynamically labile nature of these interactions allows for spontaneous interpenetration of the networked arrays and full utilization of the self-complementary molecular recognition elements during crystallization. Successful formulations of multiporphyrin arrays in solution relied in the past mostly on the use of external metal ions as linkers between porphyrin units,[9] and more scarcely on cooperative hydrogen bonding.[10] The above described tools of supramolecular synthesis provide another mechanism that can be also useful in the design of stable porphyrin-based nanostructures, possible biomimetic photonic models and other molecular devices.

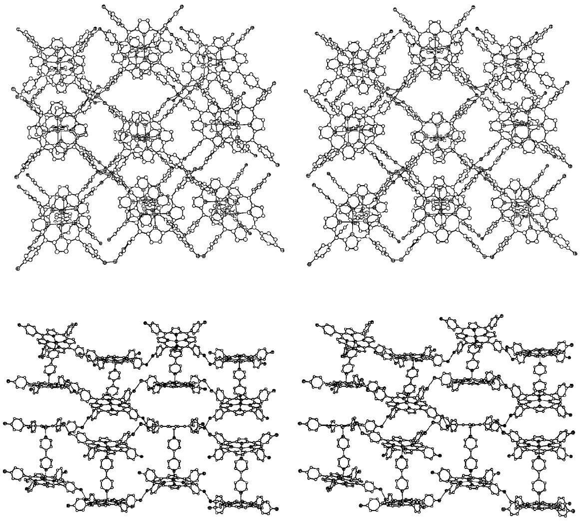
Fig. 3 Stereoviews of the supramolecular organization in **5**. (Top) Two interpenetrating bilayered arrays. Note the void space between the bipyridyl pillars. (Bottom) Side view of the interconnected porphyrins. The mean distance between the concave surfaces of the vertically displaced ligand-bridged units is 9 Å.

This research was supported in part by The Israel Science Foundation (68/01), as well as by the US–Israel Binational Science Foundation (BSF), Jerusalem, Israel (Grant No. 1999082).

Notes and references

† Compounds **4** and **5** were obtained by reacting equimolar (0.01 mmol) amounts of the porphyrin and the organic ligand components in 4 ml of hot methanol. To the resulting solutions was added 0.25 ml of nitrobenzene and 0.01 mmol of dibenzo-24-crown-8 to effect solubility, and provide suitable templates for inducing an open intermolecular organization. The competitive nature of the OH···OH and OH···N hydrogen bonds leads to structures of different porphyrin:ligand stoichiometries. Single crystals were obtained either by slow evaporation, or by the three-phase diffusion technique described earlier.[6] Both crystals turned out to contain a considerable amount of nitrobenzene solvent, mostly ordered in **4**, but heavily disordered in **5**.

Crystal data: **4**: $[2(C_{44}H_{28}N_4O_4Zn)\cdot 3(C_{12}H_{10}N_4)\cdot 13(C_6H_5NO_2)]$: M = 3715.30, triclinic, space group $P1$, a = 13.6390(3), b = 14.9790(3), c = 23.0890(6) Å, α = 79.385(1), β = 75.360(1), γ = 87.380(1)°, V = 4485.80(18) Å^3, Z = 1, T = 110 K, D_c = 1.375 g cm^{-3}, μ(Mo-Kα) = 0.35 mm^{-1}, 19762 unique reflections ($2\theta_{max}$ = 55.8°). The final $R1$ = 0.074 for 12479 observations with $F_o > 4\sigma(F_o)$, $R1$ = 0.131 ($wR2$ = 0.201) for all unique data, $|\Delta\rho| \leq 1.14$ e Å^{-3}.

5: $[2(C_{44}H_{28}N_4O_4Zn)\cdot(C_{10}H_8N_2)\cdot n(C_6H_5NO_2)]$: orthorhombic, space group *Cmca*, a = 28.2500(6), b = 26.4570(9), c = 41.4810(13) Å, V = 31003.3(2), Z = 8, T = 110 K, 14428 unique reflections ($2\theta_{max}$ = 51.4°). For n = 12 (see below) M = 3117.65, D_c = 1.336 g cm^{-3}, μ(Mo-Kα) = 0.39 mm^{-1}. Routine refinement of the solved structure converged only at $R1$ = 0.151 for 5275 reflections with $F > 4\sigma(F)$, $R1$ = 0.32 and $wR2$ = 0.39 for all the data. The structure of the six molecules of the nitrobenzene solvent could not be reliably modeled, and its contribution was thus subtracted from the diffraction pattern by the 'Squeeze' method.[11] This refinement converged at final $R1$ = 0.078 for 4448 observations with $F_o > 4\sigma(F_o)$, $R1$ = 0.183 ($wR2$ = 0.222) for all unique data, $|\Delta\rho| \leq 0.37$ e Å^{-3}. The molecular entities are located in the crystal on mirror symmetry elements, and the supramolecular framework is well defined. The integrated total residual electron density (48% of the overall electron count) is consistent with six nitrobenzene species per asymmetric unit.

CCDC reference numbers 182545 (**4**) and 182546 (**5**). See http://www.rsc.org/suppdata/cc/b2/b202791g/ for crystallographic data in CIF or other electronic format.

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11 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.