

Crystal engineering of porphyrin framework solids

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This article describes recent achievements made by us and other groups in targeted synthesis of porphyrin-based framework solids by various non-covalent mechanisms of molecular recognition. The self-assembly processes are effected in a tunable manner either by direct association of suitably designed porphyrin building blocks, or by their supramolecular aggregation through external linkers as metal ions and organic bi-dentate ligands. Many of these crystalline porphyrin materials exhibit open architectures and remarkable structural integrity, and their potential application for selective guest storage and molecular sieving is highlighted.

1 Introduction

Molecular self-assembly has been touted as a stratagem for the nano-fabrication of new “soft” materials. It involves the spontaneous aggregation of small molecular entities into specific structures in liquid or solid environments, using a variety of cooperative and directional intermolecular interactions. In doing so, this process accomplishes the most difficult steps of ordering molecular components in space to form supramolecular entities with predefined dimensionality and connectivity. The deliberate synthesis of crystalline framework solids has long been motivated by prospects of obtaining ordered materials with preconceived structure and desirable properties. While the field of an *a priori* prediction of crystal structures is at the beginning of the 21st century still in its infancy, *empirical* formulations by design of a wide variety of interesting innovative and potentially useful materials, based on carefully selected building blocks, represent a rapidly developing field of study.^{1,2} Attractive examples are provided by a series of successful constructions of open-framework structures based on organic or organometallic molecular building blocks, which are tessellated by a concerted array of non-covalent interactions, and reveal high structural rigidity.¹ The porous architectures, which sustain large amounts of

empty space can be used in selective inclusion, storage and transport processes, as well as in catalyzed molecular transformation reactions. The chemical and structural diversity of the molecular building-block species allow us to reasonably control the self-assembly process and to alter systematically the composition, topology, porosity and functionality of the supramolecular frameworks. Applications of this crystal engineering approach to the systematic development of open chiral crystalline environments have been envisioned as well.^{1a}

The tetrapyrrolic macrocycles (porphyrins and related compounds) can play an important role in the design of extended supramolecular lattices, which derives from their robust structure, remarkable thermal and oxidative stability, and unique photo-physical and electrochemical properties. Multi-porphyrin arrays can be made both *via* covalent as well as non-covalent synthetic methodologies. However, the covalent-synthesis procedures are in general effective only in the construction of *small* supramolecular aggregates. On the other hand, the non-covalent approaches are considerably more useful in the syntheses of well-ordered *polymeric* assemblies. The latter are based on thermodynamically labile intermolecular bonds, which facilitate the construction of defect-free large periodic arrays. Interest in self-assembled systems of the porphyrin chromophores has been traditionally centered in the past mostly on the electron and energy transfer processes and homogeneous catalysis. However, the supramolecular entities have a useful potential also in other applications, and our own efforts during the last decade have been directed at a *systematic design* of new multi-porphyrin assemblies in ordered crystalline solids. Such materials can act *e.g.*, as molecular sieves, sensors, actuators, heterogeneous catalysts and nanosized reactors within a confined environment. The crystalline state imparts long-range translation symmetry to the supramolecular organization, and allows precise characterization by diffraction techniques of its microscopic structure in relation to the macroscopic properties of these materials. Hence, this paper is about targeted crystal engineering of porphyrin-based architectures that represents an attractive “*bottom-up*” strategy to tailoring extended lattice materials and organic zeolite analogs from molecular building blocks.

Israel Goldberg was born in Poland in 1945, and received his BSc, MSc and PhD (1973) degrees from Tel Aviv University, Israel. He then worked for two years with Professor K.N. Trueblood and Professor D. J. Cram, at the University of California in Los Angeles, as a post-doctoral research associate. In 1975 he joined the faculty at the School of Chemistry of Tel Aviv University, and was promoted to Professor in 1991. The research interests of his group include: supramolecular chemistry, crystal engineering, nanotechnology, structural chemistry and X-ray crystallography, with current emphasis on porphyrin framework materials, porous solids, and nanosized assemblies. Professor Goldberg has published over 250 peer reviewed papers and chapters in collective volumes on research in these fields. He currently serves on the Editorial Board of the Journal of Inclusion Phenomena and Macrocyclic Chemistry, the International Advisory Editorial Board of Crystal Engineering Communications, and the Scientific Board of the International Symposia Series on Supramolecular Chemistry.

Successful solid-state synthesis of the desired materials relies on the correct choice of the molecular building blocks. These are designed by virtue of their structure and functionality to assemble themselves into large polymeric arrays *via* non-covalent bonds, either directly or through auxiliary bridging components. Based on earlier experience with porphyrin clathrates and their structural systematics, and on our expertise in clathrate chemistry,³ we have applied to this end as a platform the most readily available representative of the porphyrinoids, the *meso*-tetraphenylporphyrin moiety, in its free-base (H₂-TPP) as well as core-metalated (M-TPP) forms (Fig. 1). We anticipated that when activated by functional substituents, these macrocycles may provide robust building blocks that can self-assemble into polymeric patterns in crystals through reliable motifs of intermolecular coordination, hydrogen-bonding and π - π stacking, and demonstrated the feasibility of these ideas in several earlier publications on this subject.^{4,5a} The coordination properties of the metal entity in the center of the metalloporphyrin ring and nature of the potential axial ligands linked to it, along with deliberate functionalization on the porphyrin periphery by substituents with specific molecular recognition features, provide diverse binding tools for imposing directed self-assembly and self-organization of the porphyrin entities into network arrays and crystalline framework solids. The extended aromatic system of the porphyrin entity adds a degree of functionality unobtainable with many other natural or synthetic macrocycles, often inducing characteristic stacking ordering of these building blocks and π - π attraction of other components.⁶

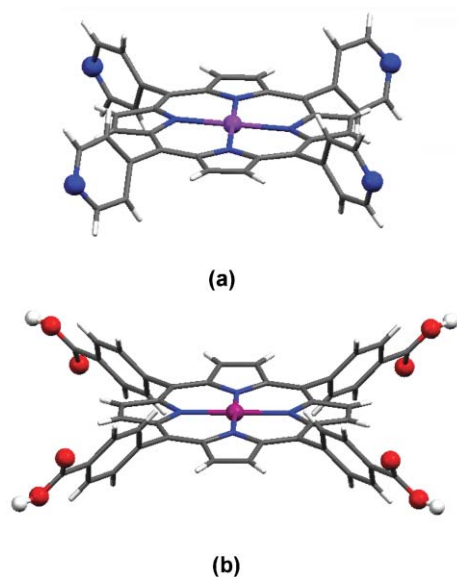


Fig. 1 Metalated porphyrin building blocks of approximate square-planar symmetry most commonly used in the self-assembly of extended frameworks: (a) tetra(4-pyridyl)porphyrin (TPyP), and (b) tetra(4-carboxyphenyl)porphyrin (TCPP). Small spheres mark the metal centers and the peripheral functional groups utilized for interporphyrin tessellation.

2 Key developments related to porphyrin framework solids

In the narrow context of the porphyrin-based network solids a number of uniquely interesting discoveries have been reported since the early 1990s. They relate *e.g.*, to the “porphyrin sponges” which represent expandable lattice clathrates stabilized mostly by virtue of van der Waals forces between the individual metallomacrocyclic molecules or their five-coordinate or six-coordinate complexes with axial ligands (thus referred to as zero-dimensional frameworks), yet revealing a considerable conservation of the host structure.³ Other studies focused on a series of one-dimensional coordination polymers (electron-transfer complexes) composed of alternating manganese porphyrin donor and a strong cyano-carbon acceptor (*e.g.*, TCNE or TCNQ), which represent magnetically ordered materials (the latter have been developed further in more recent years).⁷ At about the same time, the synthesis and characterization of infinite two-dimensional and three-dimensional supramolecular networks (including those involving the TPPs as building blocks) sustained by specific directional interactions has become an area of rapid growth that attracted wide attention. In 1994 we pioneered the synthesis of the first genuine porphyrin-based molecular-sieve-type solid, by assembling a single-framework three-dimensional coordination polymer of tetra(4-pyridyl)-metalloporphyrin (M-TPyP) of open but highly robust honeycomb architecture by direct inter-coordination (Fig. 2a).^{5a} This framework material (with M = Zn, Co or Mn) reveals unprecedented high thermal stability (preserving its open lattice structure up to above 300 °C), and being perforated by 0.6 nm wide lattice channels, exhibits remarkable and size-selective molecular sorption and desorption features towards small inert and polar species.^{5a,b} It represents the first realization of a porphyrin-based organic zeolite analog. Concurrently, a “porous” M-TPyP framework sustained by inter-coordination through external copper ions (which collapsed, however, upon the removal of the adsorbed solvent) was reported by another group.⁸ These discoveries stimulated other researchers to investigate formulations of two- and three-dimensional metal-bridged frameworks of the readily accessible tetrapyrrolyl chromophore. Indeed, a number of TPyP-based polymeric materials of different (but often unpredictable) topologies and varying porosity have been prepared consequently in a sporadic manner by different researchers, utilizing Cu, Fe, Cd, Hg, Pb and Ag metal ions as convenient exocyclic linkers (see below).⁹ Many of the above assemblies turned out to be quite rigid, but their porosity features are often diminished by the need to incorporate counter ions within the interporphyrin voids of crystal lattice in order to balance the excessive charge introduced by the metal ion linkers. This severely limits the potential function of those materials as solid-state receptors or in molecular sieving applications.

Being aware of the latter problem already at the initial stages of our studies on this project, and in order to circumvent this deficiency, we introduced in 1996 the uniquely attractive tetra-(carboxyphenyl)porphyrin (TCPP) platform as an optimally versatile building block for the supramolecular synthesis of

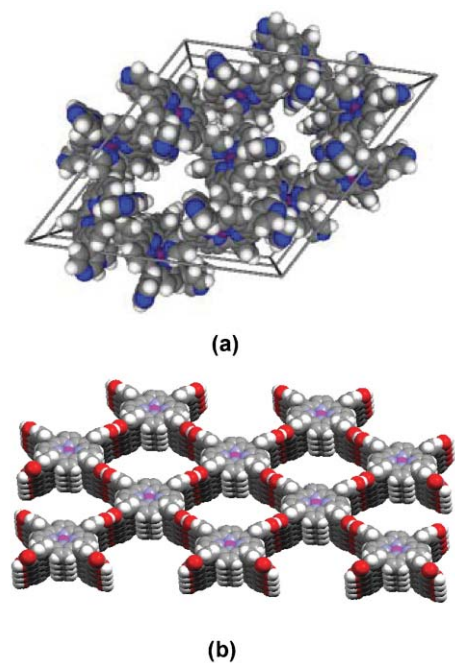


Fig. 2 Space-filling illustrations of: (a) the honeycomb molecular sieve structure with 0.6 nm wide channels, characterizing the 3D coordination polymer of M-TPyP;⁵ (b) molecular-sieve-type structure based on stacked-layered 2D hydrogen-bonding polymers of M-TCPP with 1.5 nm wide vertical channels.¹⁰

multi-porphyrin arrays.^{4a} We were motivated by the potential ability of this building block to self-assemble not only by multiple complementary hydrogen-bonding motifs, but also by self-coordination or coordination through external metal ion bridges. Utility of the former in the construction of an open lattice was confirmed by us (among other examples) in 1999 by a successful formation of extensively H-bonded non-interpenetrating porphyrin networks with very wide interporphyrin voids and their self-organization into a unique porphyrin-sieve architecture that consists of tightly stacked overlapping arrangement of the open arrays (Fig. 2b).¹⁰ The layered structure is thermally stable up to 80 °C. It is perforated by 1.5 nm wide channels, and is accessible to other species that can be incorporated within the porphyrin lattice. The construction of such open interporphyrin organization required a suitably large template around which the open frameworks can assemble, and to prevent interpenetration of the network arrays (see below). The TCPP platform has turned out advantageous to the TPyP scaffold in formulations of hybrid coordination polymers mediated by exocyclic metal ion bridges. The carboxylic acid groups can be subjected to one-, two-, three- or four-fold deprotonation, thus accounting for the desired charge balance and eliminating the need to incorporate other ions. This also leads to enforced coordination (by electrostatic attraction) between the anionic chromophores and the cationic linkers, and enhances the propensity of forming more stable crystalline architectures with better-defined nano-porosity. Our first realizations of this concept (reported in 2000), confirmed the attractive utility of the M-TCPP unit in the construction of hybrid organic–inorganic

coordination polymers as well as of new porphyrin-based zeolite analogues.¹¹ It opened a new burgeoning field of studies, attracting other researchers and eventually leading two to three years later to formulation of *functional* organic zeolite materials of this type.¹² In parallel, we have incorporated onto the TPP framework additional molecular recognition functions (other than the pyridyl and carboxylic groups) and utilized diverse external bridging reagents, for evaluation of their networking capacity. The crystal-engineering concepts that have led us to successful syntheses of structures with initially two-dimensional and then three-dimensional supramolecular porphyrin domains are evaluated below. They could be realized by diverse methods of the crystal synthesis, most successfully in this laboratory by resorting to diffusion and solvothermal techniques.

3 Assembly of two-dimensional arrays

Typically, the square-planar functionality of the TPP framework is ideal for fabrication of flat networks, which propagate in the $\pm x$ and $\pm y$ equatorial directions parallel to the porphyrin plane. This is particularly so when incorporation of molecular recognition features on the porphyrin periphery (e.g., at the 4-positions of the *meso*-phenyl groups) preserves the square-planar symmetry to allow multiple and divergent intermolecular associations. Primarily, the functional substituents can be either nucleophiles capable of coordinating to metal centers, or groups with complementary hydrogen-bonding capacity (Fig. 1). Their particular shape and functionality control the topology and stability of the formed grid of the porphyrin moieties. The use of different porphyrin components with complementary recognition functions in the self-assembly process is also (though less common) an option. Preparation of stable grids of such large molecular building blocks (more than 1 nm long and wide) is a challenging goal, as optimization of the interporphyrin interaction scheme oftentimes may result in the assembly of arrays with considerable void space between the individual units, a feature that is not tolerated favorably by the condensed solid phase.

3.1 Networks sustained by inter-porphyrin hydrogen bonds

Hydrogen-bonding aggregation into ordered architectures is particularly relevant in solids, as in solution it is generally of limited stability. In our crystal engineering efforts we used at the initial stage porphyrins decorated symmetrically at their *meso*-positions with the self-complementary 4-hydroxyphenyl (TOHPP), 4-amidophenyl, 4-carboxyphenyl (TCPP) and 4-(3',5'-diaminotriazino)phenyl groups in different attempts to obtain crystalline network hydrogen-bonding polymers with gradually increasing pore size. The cooperative effect of multiple-hydrogen-bonding is of utmost importance in stabilizing hollow yet ordered network organization in the solid, as the enthalpies of such interactions when considered alone are relatively small (within a typical range of 15–30 kJ mol⁻¹).¹³ Metal ions, when present in the porphyrin core have little, if any (other than making the macrocycle more rigid), effect on the network construction. Thus, the latter could be achieved with metallated as well as free-base porphyrin units.

The actual pattern of the supramolecular assemblies that form in these cases is controlled also by the nature of the crystallization environment (*e.g.*, presence or absence of solvent with competing H-bonding functions and size of the templating agent).¹⁴ For example the self-assembly of the tetraamido and tetracarboxy porphyrins can follow two primary modes of supramolecular interaction, utilizing cyclic dimeric [*e.g.*, (CONH₂)₂, or (COOH)₂] or chain-polymeric (catemeric) interaction geometries, or combination of these two types (Fig. 3).¹⁵ Networks induced by small templates (around which the building blocks organize) are formed in the catemeric fashion (by hydrogen bonding between the *cis*-related arms of adjacent species oriented in nearly perpendicular directions parallel to the porphyrin plane) or in a mixed dimeric/catemeric mode (Figs. 3b,c and 4a). Those induced by adequately large templates involve cyclic-dimeric patterns of the hydrogen bonds (with the interacting functional groups of neighboring species pointing head-to-head at one another) along the four equatorial directions (Figs. 2b and 3a). In both cases a layered arrangement of regularly spaced porphyrin units is attained, due to favorable stacking attractions (a fundamental property of the porphyrin–porphyrin interaction) of the flat extended aromatic surfaces of thus formed nets.^{3a,6}

The former patterns are characterized by 0.7 nm wide (in the tetraamido network templated by dimethylsulfoxide entities)

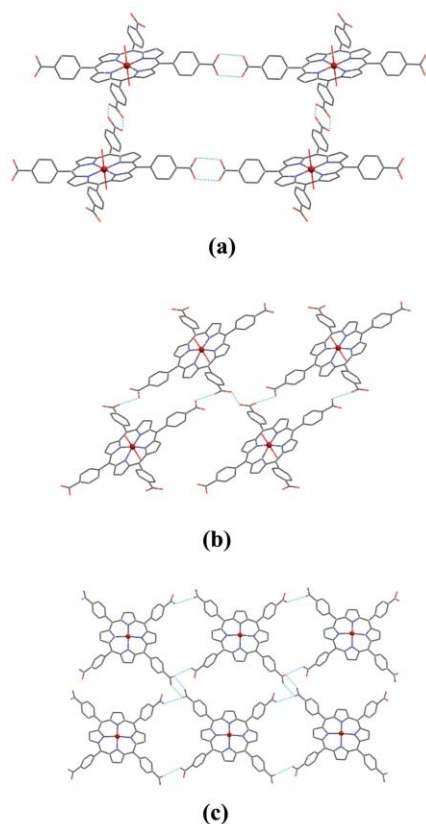


Fig. 3 (a) Cyclic dimeric mode of H-bonding of M-TCPP molecules, yielding a square grid. (b) Catemeric H-bonding of M-TCPP units into layers with smaller void space. (c) Mixed cyclic dimeric and catemeric association of tetra(amidophenyl)porphyrin units into a flat array. The H-bonds are marked by dotted lines.

or 0.85 nm wide (in the tetracarboxy derivative assembled around sodium or potassium 18-crown-6 species) interporphyrin cavities, considerably smaller than the size of the porphyrin molecule, which makes interpenetration of the network arrays improbable.¹⁶ However, variation of the binding mode between the TCPP units from catemeric^{16b} to cyclic-dimeric results in the formation of supramolecular grids with much larger, *ca.* 1.6 nm wide, interporphyrin voids.¹⁰ Here, the interporphyrin space is already wider than a single building block of the hydrogen-bonded polymer, and special attention [*e.g.*, use of sizeable templating reagent with low tendency to interact with the host porphyrin as tetra(4-aminophenyl)porphyrin] is required to prevent concatenation of the open networks during crystallization. In the above examples every building block takes part in several (4–8) hydrogen bonds to its neighboring species, thus imparting relative stability to the network organizations in which the intra-layer voids are readily accessible to guest components (*e.g.*, nitrobenzene, ethyl benzoate, crown-ethers, *etc.*). The hydrogen-bonded layers commonly stack in the crystal in a partly offset manner at a narrow distance range of 4–5 Å,^{3a} yielding in the less offset cases materials with open channels in which the stacked organization of the porphyrin layers occupies only 40–60% of the crystal volume.

The use of tetra-substituted porphyrin scaffolds with either four small hydroxy substituents or four large 4-(3',5'-diaminotriazino) sensor groups effect farther variation of the porphyrin grid size.^{4b,17} Indeed, the latter porphyrins assemble into flat supramolecular networks with unprecedented large voids of 2.2 × 2.2 nm (Fig. 4b), where every porphyrin unit is involved in eight intra-layer hydrogen bonds to four different neighbors. However, as the dimensions of the single porphyrin units are only about *ca.* 1.6 × 1.6 nm, it turned out to be difficult in this case to prevent concatenation of these networks that effectively reduces the amount of empty space in the crystalline lattice.¹⁷ The interweaving of one network into another is further stabilized in this case by multiple hydrogen bonding, utilizing the excessive binding sites not involved in intra-layer interactions. However, the resulting bulk structure still presents a robust molecular-sieve-type architecture revealing 0.6 nm wide channels (these are suitable to accommodate small guest molecules as DMF or DMSO). At the other end, in polymeric chains and networks composed of the TOHPP scaffold the van der Waals width of the intra-layer voids between the porphyrin units is only about 0.35–0.4 nm, to barely allow accommodation of an aromatic guest species edge on.^{4b}

We further diversified the tailoring tools of these networks by adding alternative hydrogen bonding sites to the porphyrin building blocks either through coordination of axial ligands, or by employing asymmetrically rather than symmetrically substituted porphyrin entities (Fig. 5). For example, utilization of the ZnTCPP-[hexamethylenetetraamine (HTMA)]₂ complex as the basic unit for self-assembly introduces to the tetracarboxyporphyrin system several tertiary-N strong proton acceptor sites residing on the axial ligands. The latter have higher affinity for the protons than the carboxylic functions, thus inducing a different supramolecular connectivity scheme than before that involves two COOH⋯N_{HTMA} and two

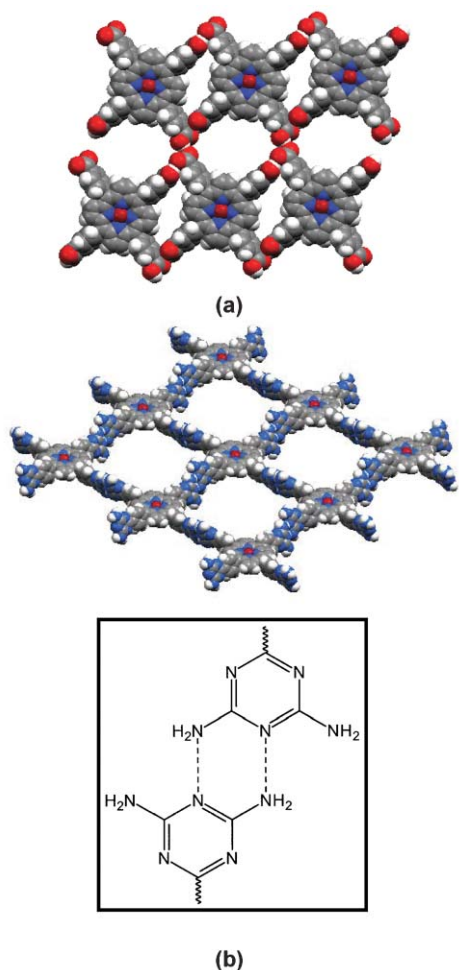


Fig. 4 Space-filling illustrations of: (a) network with small (0.85 nm wide) inter-molecular cavities of M-TCPP sustained by catemeric hydrogen-bonding motifs between the carboxylic groups of adjacent porphyrins.^{16b} (b) Large grids with 2.2 nm wide cavities formed by the tetra[4-(3',5'-diaminotriazino)phenyl]porphyrin scaffold *via* cooperative cyclic dimeric [C(NH₂)–N:]₂ hydrogen bonding motifs (see insert box) which extend in all four directions of the layered array.¹⁷

N_{HTMA}⋯HOOC hydrogen bonds of the lateral carboxyphenyl groups and the axial HTMA ligands. Extension of this binding pattern throughout the crystal yields corrugated two-dimensional layers with intra-layer 0.5 × 0.8 nm void space between adjacent porphyrins in the grid network.^{18a} Tight stacking of the open layers stabilizes the inter-layer structure.

In another example of this section we have modified the TCPP building unit by replacing one of the 4-carboxyphenyl functions by a 3-pyridyl ring, thus creating a less symmetric building block.^{18b} The *N*-pyridyl site is a strong proton acceptor, which can be effectively utilized in intermolecular (carboxyl⋯pyridyl) hydrogen bonding. Indeed, this porphyrin entity self-assembles into polar two-dimensional grids by head-to-head interaction of the four functional substituents of one unit with the lateral substituents of four neighboring species.^{18b} However, the deviation of the *N*-acceptor from the plane of the porphyrin core prevents formation of flat arrays, giving rise instead to wavy networks wherein adjacent units along the COOH⋯N hydrogen bonding direction are related

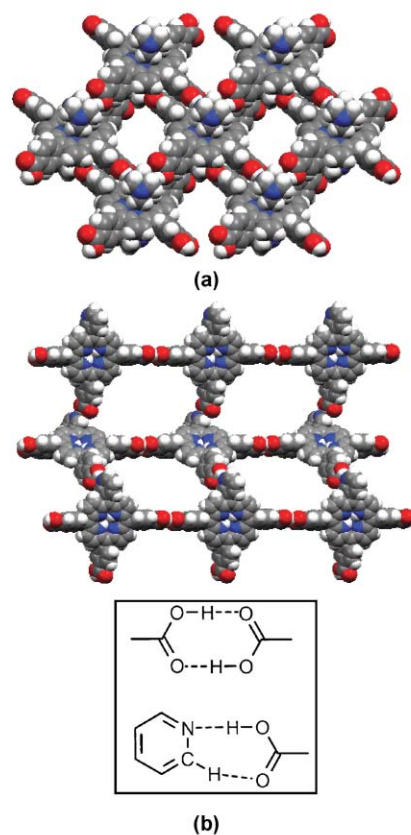


Fig. 5 (a) Section of ZnTCPP–(HTMA)₂-based square network sustained by COOH⋯N_{HTMA} hydrogen bonds, every unit being linked to four neighbors *via* eight H-bonds.^{18a} (b) Wavy grids with 1.2 nm wide cavities formed by the 3-pyridyl-tris(4-carboxyphenyl) porphyrin.^{18b} Each unit associates to adjacent species *via* two *trans*-related cyclic (COOH)₂ H-bonding dimers and two additional sets of hydrogen bonds involving the carboxylic acid and pyridine moieties (see insert box).¹⁵

to one another by a twofold screw axis. They stack one on top of the other very efficiently in the crystalline phase (the convex surfaces of one layer fitting tightly into the concave sections of a neighboring layer), which yields a channeled crystalline architecture. The above change in the symmetric structure of the TCPP building blocks has an evident effect on the intra-layer grid dimensions, which are reduced from 1.6 nm in the TCPP case to 1.2 nm in the present example (corrugated networks with yet smaller inter-porphyrin voids were obtained when the 3-pyridyl substituent was replaced by the 2-quinolyl function^{18c}). The asymmetry feature introduced into the porphyrin moiety by the 3-pyridyl and 2-quinolyl recognition elements is effectively transferred to the corresponding network organizations characterized by twofold axes of screw symmetry, imparting axial polarity (and chirality) to these crystal structures. This may facilitate enantioselective incorporation of guests into the channel voids (currently under investigation), and is an essential property for fabrication of materials with NLO properties.

The above results demonstrate our ability to crystal engineer by design stable materials consisting of network hydrogen bonding porphyrin polymers of *tunable* grid size and porosity.

In the formed aggregates the van der Waals width of the interporphyrin void space varies within *ca.* 0.4–2.2 nm, being tuned by the type, size and disposition of the functional substituents on the porphyrin scaffold. Either tight stacking, or interpenetration, of the layered polymeric arrays contribute to the stability of these solid materials, some of them revealing effective guest sorption and desorption features to be explored further. Noteworthy are several attempts made by others to use M-TPPs with functional octa-substitutions at the 3,5- or 2,6-positions of the peripheral phenyls (instead of the tetra-substituted derivatives at 4-positions). This induced, however, the construction of supramolecular columnar porphyrin motifs (instead of layered networks) with weak associations between the columns.¹⁹ The apparent advantage of the porphyrin columns, held together by links between the side arms at a distance of ≥ 1 nm between successive macrocycles, is that they allow free access to the metalloporphyrin core. The latter feature makes these materials potentially suitable as heterogeneous catalysts, but no useful or practical applications have been reported thus far.

3.2 Networks sustained by metal–ligand coordination

Similar two-dimensional networks have been constructed in our laboratory by inter-coordination of the TCPP units with the aid of external metal ions, taking advantage of the metal-ligating capacity of the carboxylic functions (Fig. 6). The binding energy of coordination bonds is typically within

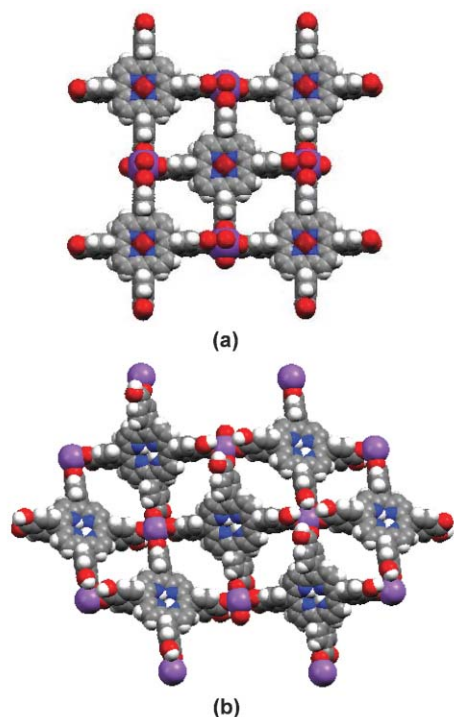


Fig. 6 TCPP-based open networks tessellated by exocyclic metal ion bridges. (a) M-TCPP building blocks inter-connected by hydrated potassium ions into planar arrays.^{20c} (b) Wavy networks of free-base TCPP sustained by inter-coordination through sodium ions.^{11a} The metal connectors are denoted by purple spheres.

120–250 kJ mol⁻¹, making them most effective in the synthesis of stable network arrays. Moreover, the carboxylic groups can be readily deprotonated in neutral and basic environments to yield anionic porphyrin units, and balance the charge introduced by the cationic metal bridges. This eliminates the need to incorporate additional anionic moieties, and enhances the propensity of forming stable *open* architectures. Thus the TCPP and MTCPP (*e.g.*, M = Cu^{II}, Pd^{II}, Pt^{II}, ions in the porphyrin core that lack axial coordination capacity) building blocks, when combined with exocyclic metal ions as linkers (*e.g.*, Na^I, K^I, Cu^{II}) self-assemble into flat (either planar or somewhat wavy) open polymeric grids with about 0.5 nm wide interporphyrin cavities.^{11,20} The immediate environment around each porphyrin unit in these assemblies in characterized approximately by a square-planar symmetry. Tight overlap stacking of such polymeric layers (typically with inter-layer separation of about 4.5 Å) yields extended channel voids which propagate through the crystal normal to the coordinated layers, and are selectively accessible to exchangeable guest molecules that can fit into these voids (*e.g.*, DMF, pyridine, triethylamine, nitrobenzene). With a given TCPP building block, using connectors of different size can diversify the polymeric network formation. Thus *e.g.*, the application of Cu(NH₃)₆ complexes instead of the simple metal ions as bridging ions widens the interporphyrin voids to 0.75 nm, allowing inclusion of larger guest components than in the earlier examples.^{20c}

The tetra-dentate TPYP and MTPyP macrocycles are also excellent building blocks for the synthesis of highly organized polymeric networks of square-planar, as well as other less symmetric, topologies (Fig. 7). Such formulations have been

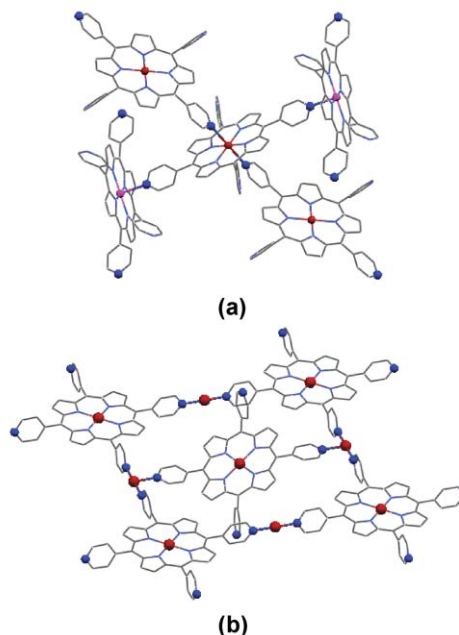


Fig. 7 Two-dimensional networking motifs of the M-TPyP unit (a) by direct interporphyrin coordination through the metalloporphyrin cores (yielding a paddle-wheel like pattern),^{5,9b–c,22} and (b) with the aid of exocyclic metal ions.⁹ The metal ions and the coordinating N-sites are denoted by small circles. Hydrogen atoms are omitted for clarity.

materialized by other groups with the aid of various metal ion linkers such as *e.g.*, Fe, Mn, Cd, Hg, Pb and Ag salts (if fact, the coordination versatility of some of these cations affords a variety of coordination geometries in these compounds: linear two-coordinate, T-shape three-coordinate and the square-planar four-coordinate).⁹ The porphyrin cores within such free-base TPyP-based nets can be further populated with different metal cations without distorting the supramolecular arrangement. The mix-metalated content (metal ions of one type in the porphyrin cores and of another type as external bridges) can be varied, a feature which is particularly relevant to the design of light-harvesting model systems and sensor materials.^{9e} Yet, it should be kept in mind that the interporphyrin voids in these layers are partly or fully occupied by suitable counter-ions needed to balance the charge.

In a similar context, we have synthesized a square-planar heterogeneous network system, which consists of mixed free-base TPyP building blocks and manganese ions embedded within the TPP macrocycle (Mn-TPP) as the linking reagents (Fig. 8a).²¹ Its major significance lies in the fact that further metallation of the free-base porphyrins can result in continuous multiporphyrin patterns with different metal ions and oxidation states, which in turn can be useful in charge-transfer processes. Yet, such systems could not be crystallized as yet.

Homogeneous coordination polymers composed of the M-TPyP and M-TCPP chromophores without the exocyclic linkers have been prepared too, inserting into the porphyrin core metal ions that exhibit high propensity for octahedral coordination (to the pyrrole groups of the porphyrin ligand at the four equatorial positions, and to two pyridine nitrogen

atoms from adjacent porphyrin entities at the axial sites (Fig. 7a)). Suitable examples are provided by Fe-TPyP, Zn-TPyP, Mn-TPyP as well as Mn-TCPP materials, in which the resulting assemblies represent two-dimensional nets composed of hexa-coordinated porphyrins that are nearly orthogonal with respect to one another. Generally, the TPyP-based polymers reveal a remarkable thermal stability due to strong N-metal bonds and an effective interlocking of the layered frameworks, and their open structures remains intact up to 300 °C or so.^{9b-c,22} The two-dimensional frameworks with metallated TCPP or tetra(4-cyanophenyl)porphyrin chromophores turned out much softer materials due to weaker metal-to-ligand bonding.^{3a,22b}

3.3 Arrays mediated by anions

The concept of tailoring porphyrin networks with the aid of cationic linkers related to above can be expanded to involve component species charged in a reversed manner. Namely one can use positively (rather than negatively) charged porphyrin species combined with anionic (rather than cationic) linkers. In fact, pyridyl porphyrins can be readily converted into a cationic moiety by simple alkylation at the pyridyl site. Correspondingly, we have modified the simple TOHPP moiety by replacing one of the hydroxyphenyl groups by a 4-pyridyl ring, which was then alkylated by a chemical reaction with dichloroethane to yield an ethylpyridinium chloride entity.²³ The three remaining divergently oriented hydroxyl groups maintain the capacity of this scaffold to participate in intermolecular hydrogen bonding and associate into networks. Presence of the small chloride anion facilitates the formation of relatively strong charge-assisted O–H⋯Cl[−] hydrogen bonds, commonly expressed in organic crystals (Fig. 8b). As anticipated, the formed assembly consists of layered supramolecular organization of the cationic building blocks, which is sustained by such hydrogen bonds. In a given layer, each chloride anion interacts with three different porphyrin species, while every porphyrin molecule is linked through its hydroxyl groups with three different anions (the threefold connectivity is adequate to preserve a layered intermolecular organization). The open flat aromatic networks thus formed contain voids between the porphyrin units, the net width of these van der Waals cavities being 0.4 nm. They are arranged tightly (also due the ion-pairing interactions) in a partly offset-stacked manner along the normal direction, with interlayer separation of about 4 Å. Extended channels that propagate through the crystal perpendicular to the network arrays impart porosity of the overall architecture, and allow enclathration of inert molecules (*e.g.*, dichloroethane) as guests.²³

3.4 Porphyrin arrays with organic ligand bridges

In principle, it is possible to synthesize network arrays with organic ligands as interporphyrin bridges through lateral hydrogen bonding between the components species. This issue has not been investigated, however, is sufficient depth as yet. In our experience, the competitive porphyrin–porphyrin and porphyrin–ligand hydrogen bonding interactions hamper formulations of such assemblies in a predictable manner.

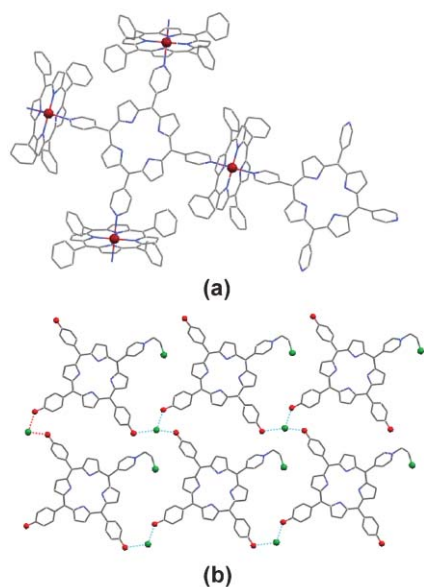


Fig. 8 Motifs of (a) mixed porphyrin networks of TPyP and MnTPP building blocks sustained by two-dimensional coordination,²¹ and (b) networks of alkylated monopyridyl-tris(hydroxyphenyl)porphyrin tessellated by chloride anions (green spheres) that hydrogen bond to OH-functions (red spheres) of three neighboring species.²³ Hydrogen atoms are omitted for clarity.

4 Assembly of three-dimensional frameworks

The design strategies described above relate to deliberate formulations of flat two-dimensional multi-porphyrin arrays, which self-organize in the bulk solid either by tight π - π stacking of their extended aromatic surfaces (Fig. 2b),^{10,20c} or *via* concatenation of the porphyrin nets.¹⁷ As a natural extension of this study, the construction of single-framework architectures of three-dimensional connectivity poses the next challenge. As expected, this is a rather difficult goal, which requires overcoming highly negative entropy effects. Not surprisingly, the success rate in the design of porous 3D architectures is lower than that with the 2D networks. Crystal engineering of three-dimensional multi-porphyrin frameworks can be approached and achieved in several ways, as exemplified below.

4.1 Coordination diversity of metal linkers

One of the possible options is tessellation of the peripherally functionalized TPPs or M-TPPs by metal ion bridges of tetrahedral or octahedral coordination directionality, as described below by three representative examples. Focusing on the TCPP platform, we used the Zn^{II} linker, which exhibits as exo-cyclic bridging entity a tetrahedral coordination environment when reacted *e.g.*, with Zn-TCPP, Pd-TCPP or Pt-TCPP.²⁴ The products in this case consist of open three-dimensional diamondoid type arrays (Fig. 9a). In order to fill space the creation of a thermodynamically stable condensed crystalline phase would be most often associated with

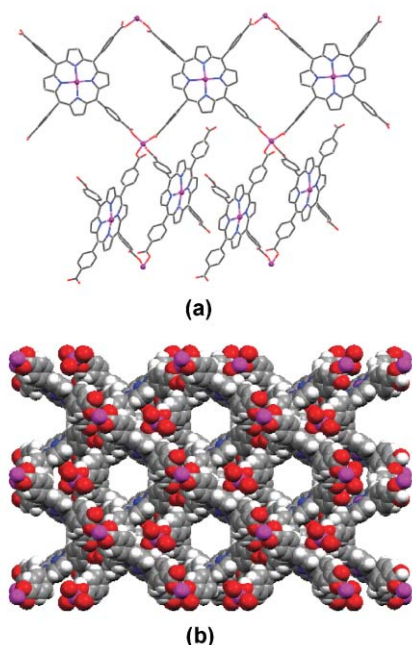


Fig. 9 (a) Diamondoid networking mode of Zn-TCPP through external tetrahedral zinc ion linkers (pink spheres). Hydrogen atoms are omitted for clarity. (b) Space filling illustration of the three-dimensional architecture formed by the interwoven networks, depicting the 0.75 nm wide channel voids that propagate through the crystals. Note the pink Zn-connectors surrounded by carboxylate O-atoms of the neighboring porphyrin units.^{11a,24}

interweaving of the diamondoid nets into one another. Still, as observed in the zinc-bridged Zn-TCPP case, the interconnected framework occupies only 40% of the crystal volume and contains continuous channels of approximate 0.75 nm van der Waals diameter, which penetrate the crystal between the interlocked polymeric arrays (Fig. 9b). We found that other metal ions as external linkers (*e.g.*, sodium) can also effect formation of single framework three-dimensional architectures when reacted with TCPP.^{20a,b}

With the widely used TPyP platform, another example is provided by the open three-dimensional architecture (perforated by channels of nanometric dimensions) obtained by reacting Cu-TPyP units with Cu^I tetrahedral connectors.⁸ Again the porphyrin framework accounts for less the 50% of the crystal volume, the large intra-framework spaces being partly filled by the anions and partly by solvent molecules. The octahedral case is represented by the self-assembly of Fe-TPyP chromophores into a rigid organic-inorganic hybrid framework mediated by the Fe(Mo₆O₁₉)₂ oxide cluster.^{9d} In this case, the external iron linker coordinates to pyridyl groups of six different converging porphyrins, thus creating a robust three-dimensional connectivity. The Mo₆O₁₉ anionic clusters accommodate the large voids generated in this lattice.

Another way of achieving connectivity in three dimensions is associated with the use of metal ion clusters (rather than single ions) as inter-porphyrin linkers and/or of significantly bent (rather than planar) porphyrin building blocks. Building on the above-described concept of networking TCPPs with metal linkers, this has been elegantly demonstrated by reacting TCPP with metal ions under solvothermal conditions (which promote formation of metal ion clusters) in a basic environment. We formulated successfully porous TCPP-based framework solids stabilized by polynuclear sodium and potassium clusters.²⁰ Additional 3D coordination polymers have been synthesized by others by reacting solvothermally TCPP with cobalt and Zn₄O ions. The former yielded a particularly interesting material. During the solvothermal reaction of the TCPP unit the cobalt reagents, metalation of the porphyrin core by the small Co ions (which is associated with marked distortion of the macrocycle from planarity), as well as inter-coordination of the metalloporphyrin species by clusters of the cobalt ions occurred simultaneously. This led to the formation of a single-framework three-dimensionally inter-coordinated zeolite-like architecture, which consists of bent metalloporphyrin entities tessellated to each other by trimeric clusters of the cobalt ions (Fig. 10a). The resulting material is perforated by ~1 nm wide tri-directional channels (Fig. 10b), revealing uniquely selective (by size, shape and functional-group) molecular sieving features.^{12a}

4.2 Formulations assisted by organic ligand auxiliaries

From the crystal-engineering point of view we anticipated at the outset that other mechanisms of expanded framework formation could be accessible, those involving organic ligands as potential axial bridges between the metal centers of adjacent chromophores (*e.g.*, bidentate amines of the bipyridyl type) being particularly attractive.^{14,25} Ideally, suitably designed metalloporphyrin building blocks may act as octahedral nodes

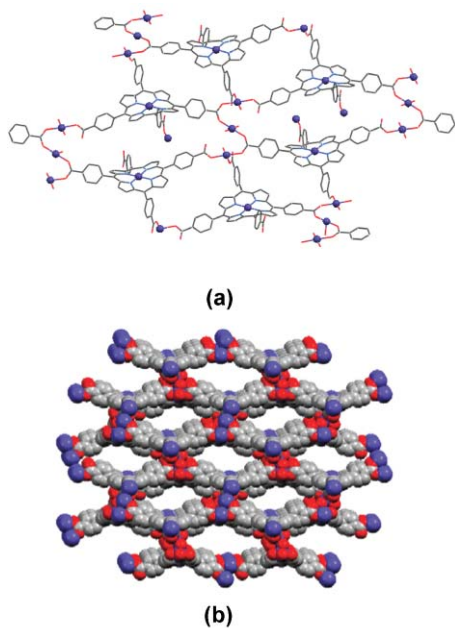


Fig. 10 (a) Connectivity scheme of bent Co-TCPP units, exhibiting the three-nuclear cobalt-ion clusters (dark blue spheres), which serve as inter-porphyrin connectors in orthogonal directions. The peripheral carboxyphenyl fragments represent connections to further Co-TCPPs. (b) The zeolite-type architecture (space-filling illustration) viewed down the ~ 1 nm wide voids that can be used for molecular sieving.^{12a} (H-atoms are omitted). Similarly open channels perforate the framework structure along the other two axes.

of the polymeric framework by adopting one of the following scenarios: (a) intermolecular hydrogen-bonding in the equatorial directions to four neighboring porphyrins (see above—Section 3.1) combined with axial coordination to two other porphyrin moieties from above and below through a bridging organic ligand; (b) peripheral coordination of the porphyrins through metal ion linkers (see Section 3.2), along with axial inter-coordination through a bridging ligand; (c) concerted association in the lateral as well as axial directions through organic ligand auxiliaries. These syntheses require six-coordinate metalloporphyrin scaffolds with favorable lateral multiple hydrogen bonding (*e.g.*, M-TOHPP or M-TCPP) or coordination (*e.g.*, M-TPyP or M-TCPP) capacities. Moreover, they are oftentimes very slow reactions, as formation of the periodic structures has to be “synchronized” with optimization of the cooperative directional interactions between the porphyrin units in three dimensions. The above molecular recognition patterns have been successfully expressed in a series of new polymeric materials that we made. Thus, in compounds obtained by reacting Zn-TOHPP with different bipyridyl ligands, a combined mechanism of axial coordination to the zinc ions of neighboring porphyrins and lateral multiple hydrogen bonding provides the organizing force for the three-dimensional supramolecular assembly (Fig. 11a).²⁶ The hydrogen-bonding linkage may take place either directly between the porphyrin entities, or through the bipyridyl bridges with their N-sites acting as proton acceptors, or both. The relatively weak nature and lability of these interactions allows for spontaneous interpenetration of the

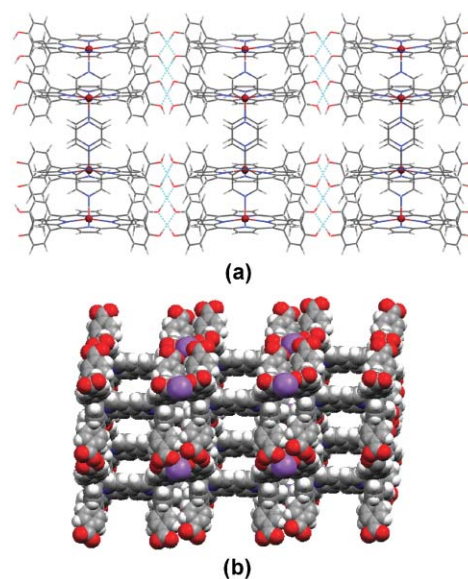


Fig. 11 (a) Interpenetrating networks of Zn-TOHPP inter-linked by hydrogen bonds in the lateral directions, and inter-coordinated *via* 4,4'-bipyridyl ligands in the axial direction.²⁶ (b) Space filling perspective of a single-framework three-dimensional TCPP-based architecture. It is composed Zn-TCPP bilayers inter-coordinated by external sodium ions (violet spheres), which are then linked together through axial bipyridyl bridges.^{11b} This organic zeolite analog is characterized by orthogonal open (~ 1 nm wide) galleries that propagate in the crystal parallel to the porphyrin bilayers.

open polymeric arrays into one another, and full utilization of the self-complementary molecular recognition elements during the crystal growth. These architectures still contain wide intralattice voids accessible to guest moieties from the crystallization solvent. They represent, however, “soft” materials that collapse readily upon expulsion of the included solvent.

Formulations of more robust molecular solids require incorporation of charge-assisted interactions, *e.g.*, by employing ionic bridging auxiliaries along axial and/or equatorial directions. In this context, we synthesized successfully a framework material by using the dicationic bipyridinium [2]pseudorotaxane bridging ligand: 1,2-bis(4,4'-bipyridinium)-ethane-dibenzo-24-crown-8.^{20b} Here a large crown ether ring is threaded on the molecular axle of the ditopic bipyridinium ligand, imparting bulkiness and geometric rigidity to the system. When using M-TCPP as the porphyrin scaffold in this case, deprotonation of two of the carboxylic groups accounts for the charge balance in the system. The resulting solid exhibits a fascinating three-dimensional architecture with roughly octahedral binding pattern around each porphyrin node. In the axial directions the metalloporphyrin cores connect on both sides by coordination to the [2]pseudorotaxane dication, which then coordinate to subsequent porphyrins from above and below in a linear polymeric fashion. Simultaneously, the porphyrin units associate in the equatorial plane into continuous open networks through cooperative charge-assisted strong hydrogen bonding between the carboxylic and carboxylate groups, where every unit in the layer is linked to four neighboring molecules at the corners of a pseudo-square array. Due to the large ligand-long spacing

between successive porphyrin layers, thus formed frameworks interweave into one another.^{20b} The ‘axial’ linear [–porphyrin–ligand–porphyrin–] coordination polymers of one framework interpenetrate through the hydrogen-bonded porphyrin layers of another framework, and the [2]pseudorotaxane ligands that are embedded within a given layer link to porphyrin units of neighboring layers located above and below. This framework structure is not porous due to the bulky shape (another parameter of controlling the porosity feature) of the ligand species.

Our carefully designed and uniquely attractive example of an orthogonal single-framework assembly of inter-coordinated porphyrin units is illustrated in Fig. 11b. It involves metal–ligand coordination in all three dimensions. It was obtained by reacting Zn-TCPP with the 4,4'-bipyridyl ligand (as axial bridging auxiliary), and in the presence of sodium ions (as equatorial linkers to the carboxylic/carboxylate functions).^{11b} The assembled open multiporphyrin architecture represents another “organic zeolite”. It consists of porphyrin bilayers held together by ion-pairing forces through the sodium ions. The latter coordinate to the carboxylate groups of several porphyrin units, providing a robust interaction scheme in the equatorial plane. Successively displaced bilayers are then cross-linked in the axial directions from both sides by the bipyridyl ligands that coordinate to the metalated porphyrin cores. The lattice created is perforated by nearly 1 nm wide-open galleries that extend between the bipyridyl pillars in different directions parallel to the plane of the porphyrin bilayers. This single framework coordination polymer occupies less the 40% of the crystal volume, and the channel voids that propagate through the crystal can accommodate a wide range of other suitably sized molecules. It exhibits a remarkable thermal stability up to about 150 °C on expulsion of the accommodated solvent guest (nitrobenzene being one of the best templates in crystallizations of open porphyrin architectures), reflecting on robustness of the cooperative interaction scheme applied in this case.^{11b}

4.3 Building porphyrin frameworks without external linkers

The structural and functional versatility of the basic TPP platform allows for further diversification of the framework design. This involves simultaneous incorporation of complementary core-metal ions and metal-ligating sites, as well as diverging hydrogen bonding functions into these building blocks, in order to afford effective self-assembly of the porphyrin units without resorting to external reagents. A straightforward approach to this end, based on the known interaction types, is to employ a metalloporphyrin platform bearing both 4-carboxylic and 4-pyridyl groups (in 2 : 2 or 3 : 1 combinations, which preserve a balanced number of the interacting functions). The pyridyls of one unit can coordinate axially to the porphyrin core of another porphyrin, while the self-complementary carboxylic groups of adjacent molecules may associate at the same time in the equatorial plane (carboxyl-to-pyridyl hydrogen bonding is also possible). In general, there are several options for self-assembly, oftentimes of complex connectivity, which can be realized, depending on the particular pattern of functionalization. A preliminary

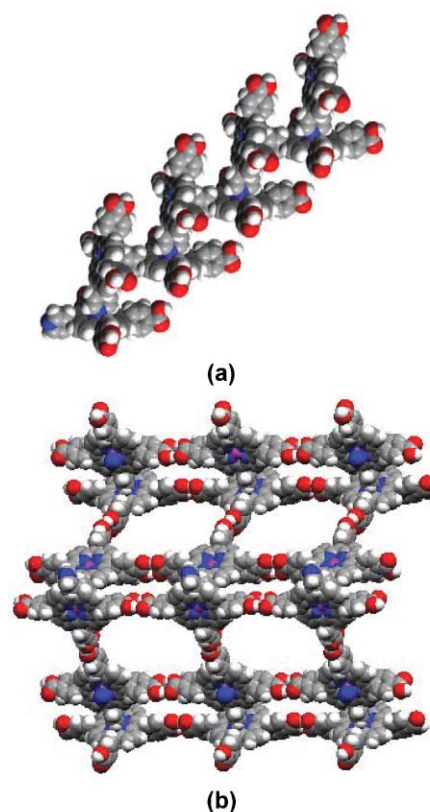


Fig. 12 Sections of the three-dimensional polymeric organization of mono(4-pyridyl)-tris(4-carboxyphenyl) zinc-porphyrin. (a) Staircase like coordination between the pyridyl site of one porphyrin to the porphyrin core of an adjacent unit. (b) A wavy layered organization wherein each molecule is connected laterally to three neighboring units by the (COOH)₂ H-bonded dimer, and to the center of the fourth one by coordination through its pyridyl site. In the obtained structure, every porphyrin core of this layer axially coordinates further to other units as in (a), yielding a complex, porous yet robust architecture.²⁷

example of this approach is provided by the networking of mono(pyridyl)–tris(carboxyphenyl)–substituted zinc–porphyrin into a spatially extended coordination and hydrogen-bonding polymer (Fig. 12).²⁷ Axial ligation of the pyridyl group of one porphyrin to the zinc center of another creates a zig-zag coordination polymer. Each such polymeric aggregate is then hydrogen bonded to neighboring polymers along three different directions parallel to the porphyrin plane, *via* the cyclic dimeric (COOH)₂ units, yielding a complex three-dimensional architecture illustrated in Fig. 12.

5 Epilog

Our systematic efforts to formulate porous porphyrin-based framework solids, initiated more than a decade ago, have led to interesting results. We have shown that effective crystal engineering of such materials with desired connectivity by solid-state supramolecular synthesis, which combines molecular and solid-state chemistry in a modular fashion, is a feasible task not only for inorganic salts and small organic molecules,²⁸ but also for larger building blocks of more than 1 nm in diameter. The condensed solid phase provides a

favorable medium for stabilizing ordered supramolecular domains (which might be only *meta*-stable in solution), by amplifying through cooperativity and periodicity the enthalpic contributions of the individually weak non-covalent intermolecular interaction. This survey presents some useful designs of the porphyrin building block (by simple chemical modification), and discusses the crystal engineering toolbox that has been successfully employed in our constructions of extended multi-porphyrin domains. It relates also to key molecular recognition elements that affect the topology of the framework architectures, and which can be used to tune their nano-cavities. Of particular importance in the above context is our discovery of the extremely versatile TCPP building block and its related derivatives to this end. The robustness, large size, and square-planar functionality (either perfect or slightly modified) of the porphyrin scaffold on one hand side, along with its rich supramolecular chemistry on the other hand side, promote the formation of open arrays. It affords framework solids with an easy to tailor grid size that resemble molecular sieve and zeolite materials. In the latter context, however, only a small number of the porous solids have shown adequate long-term stability at ambient conditions to become technologically useful. The application of asymmetric porphyrin building blocks in such supramolecular synthesis is less predictable, but it has great potential for formulations of polar materials and needs to be explored further. The available results lay a solid ground for further development of porous porphyrin-based solids. Although the difficulties involved in the rational crystal synthesis of adequately robust and practical materials are formidable (which considerably slows down the progress made both in basic research and technological applications), there is a strong stimulation for further comprehensive investigations of the non-covalent supramolecular chemistry of porphyrins and related macrocyclic molecules, in order to better understand the process of self-assembly and provide effective “bottom-up” methodologies for the design of new functional molecular materials by crystal engineering.

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