Metalloporphyrin Molecular Sieves

Israel Goldberg*[a]

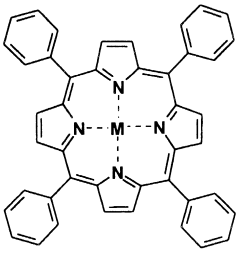
Abstract: Crystal-engineering strategies have been systematically developed for the rational design by self-assembly of diverse metalloporphyrin molecular-sieve materials. Cooperative coordination and hydrogen bonding algorithms of molecular recognition proved particularly useful for this aim. The supramolecular concepts used in the construction of stable nanoporous solids and some unique sieve-type structures obtained thus far are illustrated.

Keywords: crystal engineering · molecular sieves · nanoporous solids · porphynoids · supramolecular chemistry · zeolite analogues

Introduction

The design of molecular solids with structural and functional similarity to inorganic zeolites is an exciting challenge in materials chemistry. Such compounds are an increasingly important class of materials in the areas of separation, sorption, sensing, drug delivery, and catalysis, as evidenced by extensive investigations in recent years of porous organic solids that intercalate, or possess channels and cages all of which are readily accessible, to other molecular components.[1, 2] Supramolecular chemistry and crystal engineering offer an attractive strategy for the formulation of *noncovalent* polymeric architectures with tunable nano-sized cavities (pore dimensions in zeolites normally range from approximately 0.4 to 1.5 nm). These methods involve the generation of higher-order structures with controlled geometries from molecular building blocks (*"tectons"*) by exploring the relatively weak noncovalent interaction motifs that can exist between molecules. These interactions should act in a cooperative and convergent way in order to overcome competing solvation forces and negative entropy effects, and to sustain an open lattice with large void volumes. The supramolecular interaction motifs (*"synthons"*) to be formed therefore require robust tecton units, which are capable of constructing rigid supramolecular networks through suitably designed molecular recognition algorithms. The highly directional and relatively strong binding nature of ligand-to-metal coordination and hydrogen bonding constitute the most promising methodologies for target-oriented solid-state synthesis of crystalline materials.[3] Recent literature manifests the enormous progress that has been made over the past decade in formulations of uniquely structured network and polymeric solids.

The flat, rigid, and thermally stable metalloporphyrin framework has turned out to be an extremely versatile and particularly attractive building block for the designed tailoring of porous solids as well as of other molecular devices.[4] In the former context, earlier reports focused on expansive clathrates and intercalates formed by the *meso*-tetraphenylporphyrin (TPP, **1**) derivative, in which the commonly open architecture of the lipophilic porphyrin lattice was found to be strongly conserved by virtue of $\pi-\pi$ attraction between the aromatic metalloporphyrin cores and molecular shape features.[5] These materials were classified as "porphyrin



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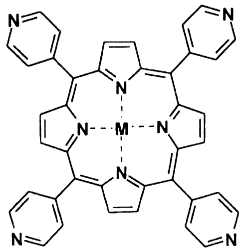

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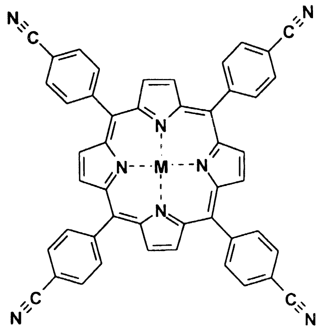

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[a] Prof. I. Goldberg
School of Chemistry, Sackler Faculty of Exact Sciences
Tel Aviv University, Ramat Aviv, 69978 Tel Aviv (Israel)
Fax: (+972)-3-6409293
E-mail: goldberg@post.tau.ac.il

sponges", which readily incorporate guest components of different nature, size, and shape within the lattice pores. Following this lead, we anticipated that the transformation from materials with variable interporphyrin voids to materials with fixed-size tubular cavities ("sieves") can be achieved by utilizing tectons with effective molecular recognition sites. These sites should have capacity for cooperative bonding in order to allow efficient tesselation of the tectonic units into rigid network architectures. The availability of the porphyrin moieties in diverse polyfunctional forms through simple synthetic modifications facilitates such formulations. In a typical system, the active sites for the supramolecular interaction are symmetrically placed at the peripheral positions of the phenyl rings, and serve for lateral "programming" of the supramolecular motif. The metal ion inserted into the porphyrin core provides additional capacity for axial programming.[5c] These features represent two of the most plausible modes of direct self-assembly of multiporphyrin polymers.[6] In addition, metal ions with characteristic coordination preferences can serve as external templates for tesselation of network arrangements with desired geometries.

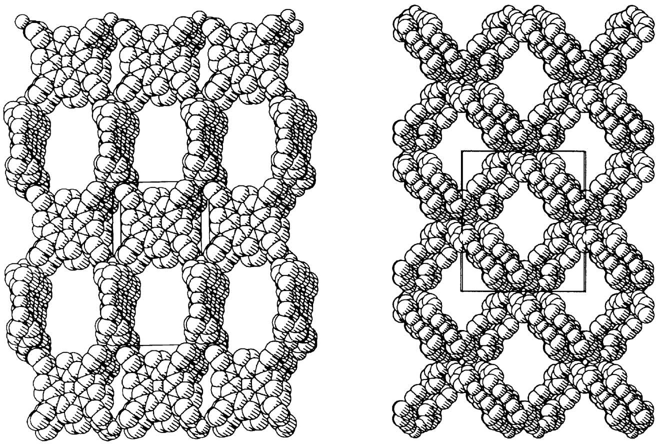


Figure 1. Space-filling illustrations of molecular-sieve materials based on Cu^{II}TPyP (left) and Cu^{II}TCNPP (right) tectons, which are tesselated by external Cu^{I} templates.[8] The latter have a tetrahedral coordination environment. The channel voids in these structures are about 1.0–1.2 nm wide, and accommodate solvent molecules (e.g., nitrobenzene) and counter ions of the Cu^{I} auxiliaries. The frames outline the crystallographic unit cell in the corresponding structures.

Crystal-Engineering Strategies of Metalloporphyrin Sieves

Coordination polymers: Coordinative bonds are most significant among the thermodynamically labile "noncovalent" interactions, and appear to be quite effective in the organization and stabilization of polymeric porphyrin assemblies in solution as well as in the solid state.[7] The pioneering reports relating to the deliberate assembly of porphyrins into network solids with large channels appeared in the literature in 1994. They were based on metallated tetrapyridylporphyrin (TPyP, **2**) and tetracyanophenylporphyrin (TCNPP, **3**) tectons that contain metal-ligating functions (aromatic N: or C≡N:) on the periphery.[8] Robson and co-workers inserted four-coordinate copper ions into the porphyrin core and used external transition metal auxiliaries with tetrahedral coordination geometry (Cu^{I}) to tesselate the Cu^{II}TPyP units into networked coordination polymers. The solid framework structures they obtained reveal very large channels running through the crystal, the cross section of which is larger than 1 nm (Figure 1). The porphyrin lattice in these materials takes up less than half of the crystal volume. The channel space within it is occupied by highly disordered nitrobenzene solvent molecules and by counter ions of the Cu^{I}-ion template. However, it has been reported that these frameworks do not survive solvent removal and that they deteriorate rapidly in the open air at ambient conditions. In order to eliminate the need of using an external metal auxiliary (along with its counter ion), we have used the Zn^{II}TPyP building blocks (as opposed to Cu^{II}, the Zn^{II} ion prefers either five- or six-coordinate environment). This idea was stimulated also by earlier observations by Fleischer and co-workers that Zn^{II}TPyP readily self-assembles in solution into oligomeric and polymeric moieties with the aid of direct coordination between the pyridyl function of one unit to the metal center of a neighboring unit.[7c] Our efforts led to a successful formulation of a uniquely structured and previously unknown three-dimensional coordination polymer, through direct interporphyrin interaction, with the porphyrin metal center acting as a templating agent.[9] Two, out of the four, pyridyl rings of every porphyrin unit are involved in this coordination. The resulting honeycomb architecture has a trigonal symmetry and represents a molecular-sieve material with ~0.6 nm wide channels centered around the threefold rotation axes and accessible to other species (Figure 2). The walls of these channels are lined by the uncoordinated pyridyl groups, with their N-sites exposed to interaction with the adsorbed guest species (e.g., H_2O and MeOH; the small polar solvents incorporated into this lattice can be readily exchanged in a reversible manner by related species). More recent evaluations of identical Co^{II}TPyP and Mn^{II}TPyP architectures have confirmed the high thermal stability (up to 400 °C) of this material, its ability to sorb various small guest molecules (e.g., also EtOH, CH_3COOH, N_2), and its potential utility in shape-selective catalysis.[10] Similar coordination polymers composed of the Zn^{II}TCNPP building blocks yielded much less stable intercalation-type structures with chloroform, nitrobenzene, or anisol guest molecules adsorbed into the lattice.[11]

The TPyP framework itself, with its symetrically disposed ligating sites, is also an excellent building block for the generation of heterogeneous supramolecular networks in combination with other metalloporphyrin units. In this context, we formulated a unique crystalline example of a well-defined two-dimensional coordination polymer that incorporates two different porphyrin entities $[\{Mn^{III}(TPP)\}_2]\cdot(TPyP)\cdot(ClO_4)_2$.[12] These flat polymeric networks stack one on top of the other and dock one onto another in the crystal; their open nature gives rise to the formation of channels that penetrate through the stacked layers (Figure 3). The tubularly shaped voids criss-cross the porphyrin lattice in perpendicular directions, and the smallest cross-section distance between their van der Waals surfaces is about 0.45 nm. They accommodate nitrobenzene solvent molecules, which occupy about

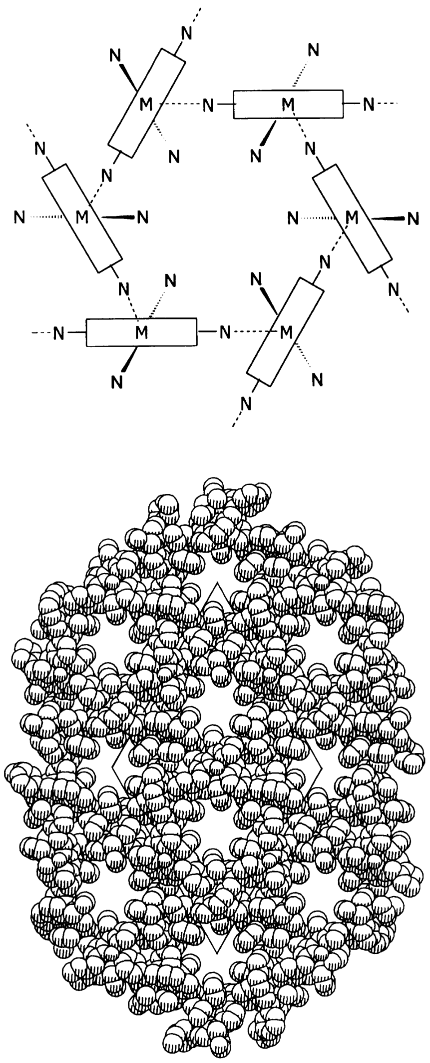


Figure 2. Representation of Zn^{II}TPyP-based honeycomb architecture, which is tesselated by direct coordination between the metalloporphyrin building blocks.[9] Top: The basic hexagonal motif of trigonal symmetry formed by the porphyrin units (represented as rectangles, each with four peripheral N sites and metal ion (M) in the center). This motif extends into a honeycomb pattern in the equatorial plane. The two-dimensional networks thus formed stack one on top of the other, and interpenetrate into one another, along the normal direction to yield a very stable architecture. Bottom: Space-filling model of the entire structure viewed down the threefold axis. The effective van der Waals diameter of the channels which propagate through this solid is about 0.6 nm.

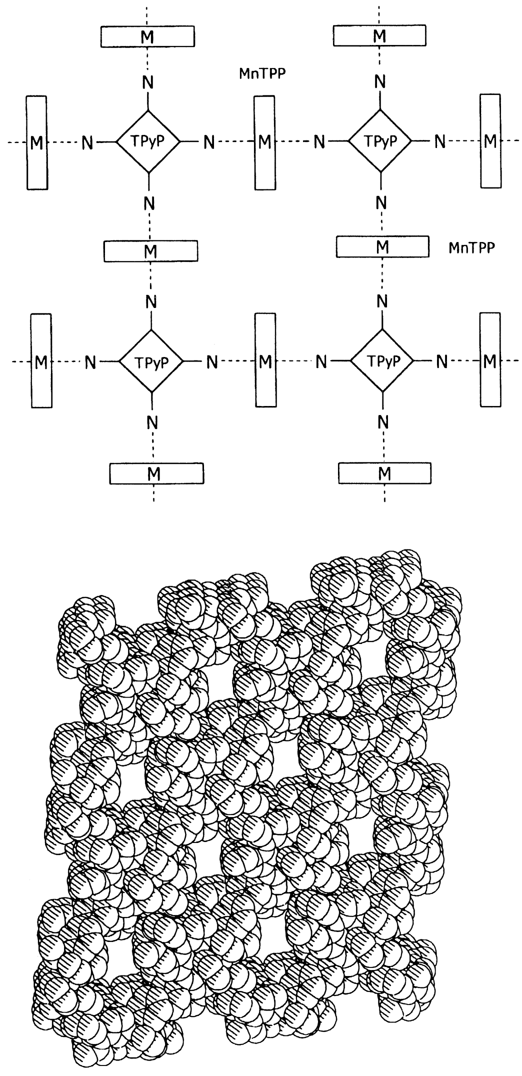
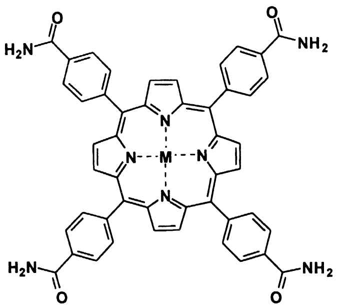


Figure 3. Top: Schematic illustration of the heterogenous coordination polymer constructed from TPyP and Mn^{III}TPP units (the ClO_4^- counter ions are omitted for clarity). Bottom: Space-filling model of the crystalline material, showing 0.45 nm wide (at the narrowest point) channels accessible to other species.[12]

46 % of the crystal volume. It is remarkable that even after most of the solvent is expelled from the crystal by heating, the channeled porphyrin architecture in this material is preserved up to 300 °C.[12]

Generation of additional heterogeneous multiporphyrin arrays on the basis of coordination bonds of the TPyP ligand to external heavy metal auxiliaries (e.g., Cd, Hg, Pb) has been reported more recently.[13] Once the metal-templated TPyP network forms, the porphyrin cores can be further populated to a varying extent by other metal ions. Yet, these multichromophore materials consist of two-dimensional networks, some resembling intercalates, and do not have rigidly defined channels. Inorganic, bimetallic oxide clusters have also been applied in the construction of microporous organic–inorganic hybrid frameworks, with the aid of hydrothermal synthesis.[14] These frameworks represent tesselated TPyP networks in which the monomeric porphyrin units are linked to each other through bimetallic oxide chains into a single-frame three-dimensional structure. They have sizeable pores between the inorganic templates, and can be reversibly sorbed and desorbed by water and alcohols (but not by hydrocarbons) up to about 15 wt %.

Hydrogen-bonding polymers: Parallel efforts have been devoted to the utilization of hydrogen bonds as effective means of structural control in the design of multiporphyrin architectures. Recent findings confirm that cooperative hydrogen bonding alone can provide enough mechanical strength to sustain a large amount of empty space in organic crystals.[15] Porphyrin tectons that contain multiple self-complementary recognition sites on the molecular periphery are particularly attractive here, as they may induce spontaneous self-assembly of supramolecular aggregates which extend in different directions. However, initial efforts with TPP units substituted by the hydroxy sensor groups were not particularly successful in the formation of three-dimensional networks. Our design was based on layered supramolecular patterns with 4-hydroxyphenyl porphyrins,[16] while others constructed columnar motifs with the aid of 3,5-dihydroxyphenyl derivatives.[17] In many of these structures large solvent-filled channels or cavities (often exceeding 50% of the crystal volume) with cross sections of about 0.6–0.7 nm are present. Yet, these arrays were found to assemble in a flexible manner, to yield mostly clathrates and intercalates rather than rigid three-dimensional networks. Other noteworthy investigations involved the tetra(4-amidophenyl)porphyrin (TAPP, **4**), tetra(4-carboxyphenyl)porphyrin (TCPP, **5**), and tetra[4-(3′,5′-diaminotriazino)phenyl]porphyrin (TDTPP, **6**) tecton units. The large size of the central porphyrin core in these molecules, along with the topological constraints associated with optimized intermolecular binding between the self-complementary recognition groups, dictate the formation of porous networks with large void volumes. Their properties can be tuned by the nature of the functional substituents and the shape of a template applied. Gaining further control of the packing of such layers in the normal direction is essential in order to construct a molecular-sieve-type structure, rather than a common clathrate.



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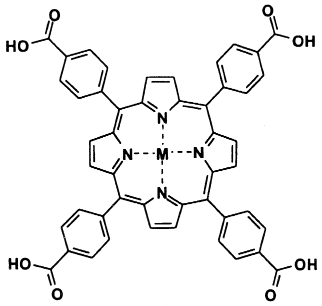

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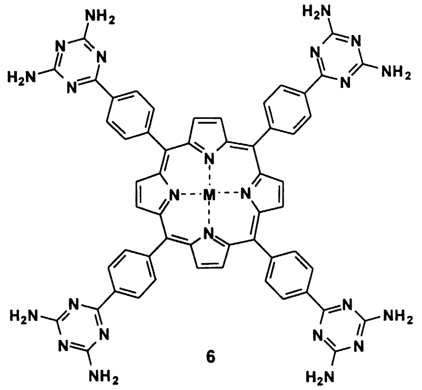

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Formation of open two-dimensional multiporphyrin arrays through cooperative hydrogen bonding between constituent species could be easily achieved. The Zn^{II}TAPP units form networks that do not interpenetrate in the presence of dimethylsulphoxide template, and have interporphyrin cavities of van der Waals dimensions of about 0.6–0.7 × 1.0 nm.[6] The Zn^{II}TCPP entity reveals two different modes of layered polymeric arrangements through self-complementary hydrogen-bonding between the terminal carboxylic functions of adjacent porphyrins.[18] Sodium or potassium 18-crown-6 chlorides were found to be excellent templates for the construction of non-interpenetrating networks with $0.85 \times 1.1\ nm^2$ interporphyrin voids sustained by chain-polymeric self-assembly of the carboxylic functions. Different Zn^{II}TCPP arrays with even larger van der Waals cavities (approximately 1.6 nm wide), directed by cyclic dimeric $(COOH)_2$ modes of self-assembly, could be obtained from other environments.[19] These cavities are already larger than a single monomeric unit of the hydrogen-bonded polymer, and in the absence of a suitable template such networks tend to interlock into one another in order to fill the void space. Consequently, it has become clear that in order to prevent interpenetration it is essential to use sizeable solubilizing and templating agents with a low tendency to interact with the Zn^{II}TCPP lattice. This was realized by using tetra(aminophenyl)porphyrin. This molecule bears four amino groups that on the one hand represent non-complementary binding sites for self-assembly and on the other hand are weaker proton donors than the carboxylic function. It can therefore serve as an excellent templating agent to nucleate the open lattice structure.

The resulting solid consists of very efficiently hydrogen-bonded open networks of Zn^{II}TCPP, which stack in an almost overlapping manner along the normal direction at an average interlayer distance of 4.68 Å (Figure 4).[20] Effective $\pi-\pi$ forces, a fundamental property of the porphyrin–porphyrin interaction in these large aromatic systems,[11, 21] stabilize the stacked organization of the layers. The resulting molecular-sieve structure occupies only 39% of the crystal volume and contains 1.5 nm wide (at the narrowest point) channels propagating through the crystal. In the analysed material, the channels were partly occupied by nitrobenzene. While these crystals deteriorate slowly when left in an open air (loosing the solvent), they are quite stable when covered with a very thin layer of light oil. In fact, as confirmed by diffraction spectra, their structure and morphology remain unchanged (apart from natural thermal expansion or contraction) upon heating and cooling within the range from −160 to +80 °C.[20]

Tesselation of porphyrin-based network motifs with even larger void volumes, has been demonstrated in crystals by incorporation of the diaminotriazine functions to the molecular building blocks. These functions have much higher hydrogen-bonding capacity, spatial flexibility, and more diverse directionality features than the carboxylic group. Indeed, the correspondingly functionalized porphyrin moiety TDTPP (**6**), has been successfully applied to the construction of a uniquely structured solid that consists of flat multi-porphyrin networks with unprecedently large voids, $2.2 \times 2.2\ nm^2$.[22] These assemblies mutually interpenetrate with each other and yield a spectacular concatenated arrangement sustained in three dimensions by cooperative hydrogen bonding (every porphyrin unit takes part in sixteen hydrogen bonds). The resulting architecture is quite stable below 80 °C. It represents a molecular-sieve material, with only 0.6 nm

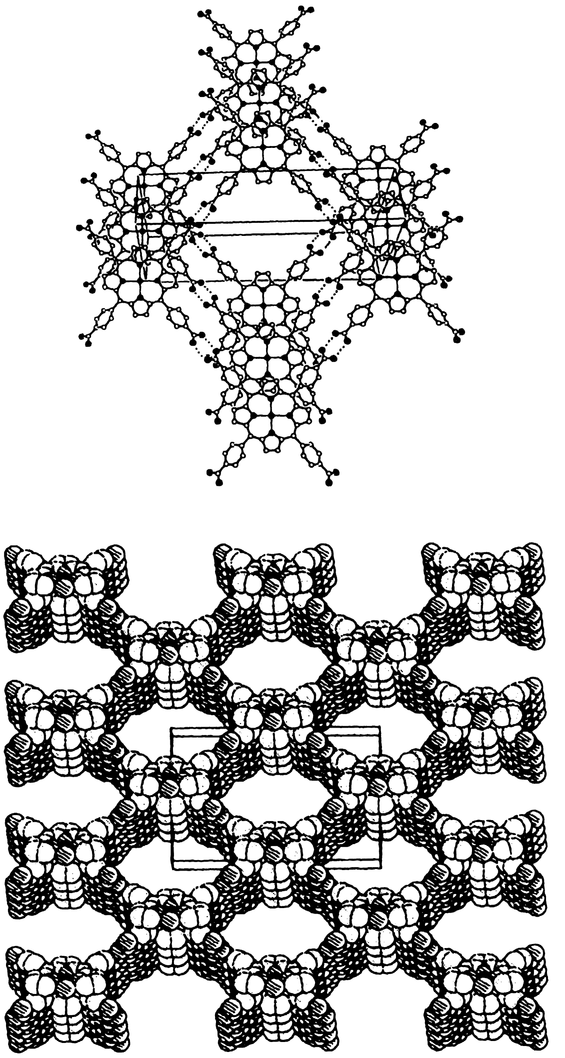


Figure 4. Stable molecular-sieve structure based on Zn^{II}TCPP building blocks.[20] It consists of open, two-dimensional supramolecular arrays sustained by multiple hydrogen bonding (top), which stack very efficiently in an overlapping manner along the normal direction through strong $\pi-\pi$ attractions (bottom). The effective van der Waals width of guest-accessible channels in this material is about 1.5 nm.

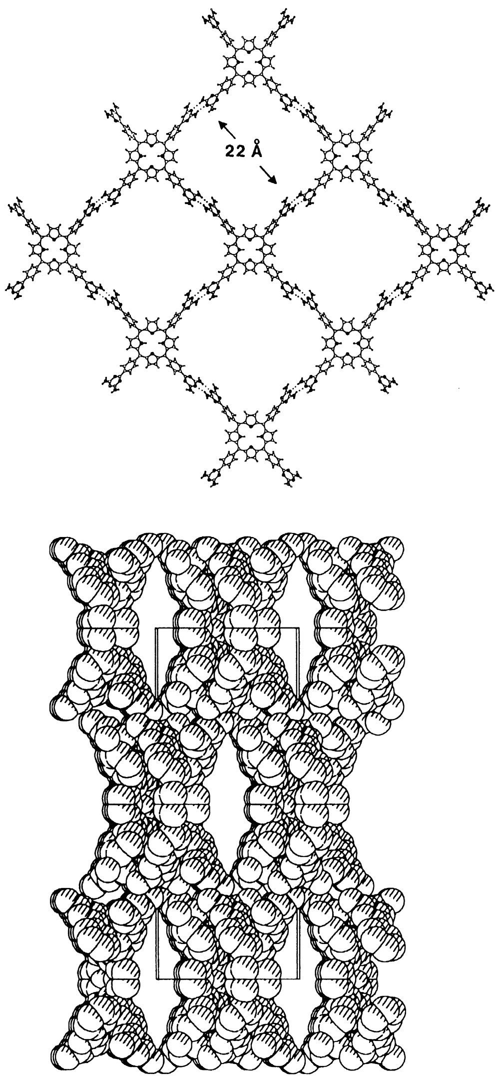
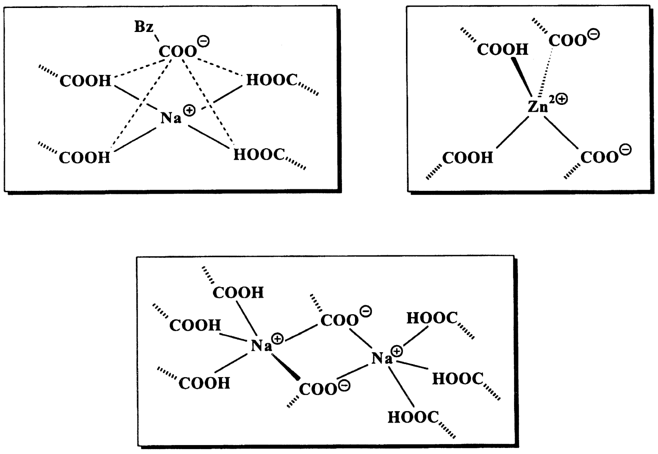


Figure 5. Top: Supramolecular networks of the large Zn^{II}TDTPP building blocks sustained by multiple hydrogen bonds. The distance between opposite van der Waals walls of the interporphyrin void space is about 2.2 nm. Bottom: Space-filling representation of the robust crystal structure, which consists of interwoven hydrogen-bonded networks, and is perforated by 0.6 nm wide channels propagating through the solid.[22]

wide channels that propagate through the crystal between the interweaved networks, and are accessible to other molecules (Figure 5; suitably sized guest molecules such as *N*,*N'*-dimethyl formamide or tetrahydrofuran are incorporated readily within this lattice). A sufficiently large template which may prevent the interpenetration and induce the formation of molecular sieves with ≥ 2 nm wide channels has not been identified as yet.

Porous TCPP-based structures sustained by concerted ion-paired coordination and hydrogen-bonding: Various modes of coordination of carboxylic groups to metal ions have been reported in the literature, and we thought that they could be useful in the design of metalloporphyrin sieves as well. In this context, we have formulated extended networks of the TCPP tecton through multiple coordination of metal ion templates to partly deprotonated carboxylic substituents.[23] Such templates may provide higher enthalpic driving force for the self-assembly process by combining the soft and thermodynamically reversible hydrogen-bonding interactions with stronger ion-pairing attractions between the assembling entities. Tesselation of new supramolecular motifs of TCPP by ion templates has been recently demonstrated in crystals, which characterize a series of mononuclear (Na^+ or Zn^{2+}) and binuclear [$(Na^+)_2$ or $(K^+)_2$] metallo-carboxylic/carboxylate interaction synthons (Scheme 1).[23, 24] The former yield either flat or diamondoid multiporphyrin networks depending on the coordination geometry around the metal ion templates: square-planar (around Na^+) or tetrahedral (around Zn^{2+}).[23] In the solid, the flat arrays are effectively held together in an overlapping manner by stacking $\pi-\pi$ interactions with about 0.6 nm wide channels, which are accessible by guests, propagating through the layers in the normal direction. The robust diamondoid arrays of Zn^{II}TCPP, templated by Zn^{2+} ions, extend in three dimensions, and the only way to pack them in



Scheme 1. Mononuclear (Na^+, Zn^{2+}) and binuclear $[(Na^+)_2]$ metallo-carboxylic/carboxylate interaction synthons. Every carboxylic or carboxylate group shown belongs to a different TCPP building block in the assembled structure.

a condensed crystalline phase must involve interpenetration. This assembly mechanism through ion-pairing is assisted by additional intermolecular hydrogen bonding between the converging Zn^{II}TCPP units. Spacious channels run through the crystal between the interwoven porphyrin arrays in this material (Figure 6). They have an average diameter of 0.75 nm, account for more than 50% of the crystal volume, and are partially filled in a diffused manner by numerous solvent molecules of crystallization (methanol and ethylene glycol), which can be easily exchanged by other species of comparable or smaller size. The geometric rigidity of this architecture imparts to it attractive molecular-sieve features.

The high significance of cooperative hydrogen bonding and coordination forces, acting in concert, for the formulation of Zn^{II}TCPP-based networks with considerable structural integrity is best demonstrated by a successful formulation of a stable metalloporphyrin zeolite analogue (Figure 7).[24] This material constitutes an open, single-framework, three-dimensional polymer in which individual metalloporphyrin units are cross-linked both axially and equatorially by ion-paring interactions, metal–ligand coordination, and hydrogen bonding. This fascinating architecture is a very unique example of a deliberately designed solid that is fully sustained by specific and directional intermolecular interactions and not by virtue of van der Waals forces, as is commonly observed in molecular crystals. Closely packed bilayers of the Zn^{II}TCPP tecton are linked together through the disodium templates and interporphyrin hydrogen bonds. Successively displaced bilayers are interlinked axially by 4,4′-bipyridyl ligands coordinating to the zinc ions. The lattice of this material is perforated by open galleries, which extend between the bipyridyl pillars parallel to the plane of the porphyrin bilayers, and were found to be partly filled by diffused methanol solvent. The cross sections between the van der Waals surfaces of these pillars are 0.8×1.0 and $0.8 \times 1.25\,nm^2$. The framework lattice in this material occupies only 42% of the crystal volume. Yet, it appears to preserve its porous structure and survive expulsion of most of the volatile solvent upon heating of the crystals to about 150 °C. Simple exchange experiments at room temperature indicate that this lattice can absorb reversibly many of the common organic solvents.

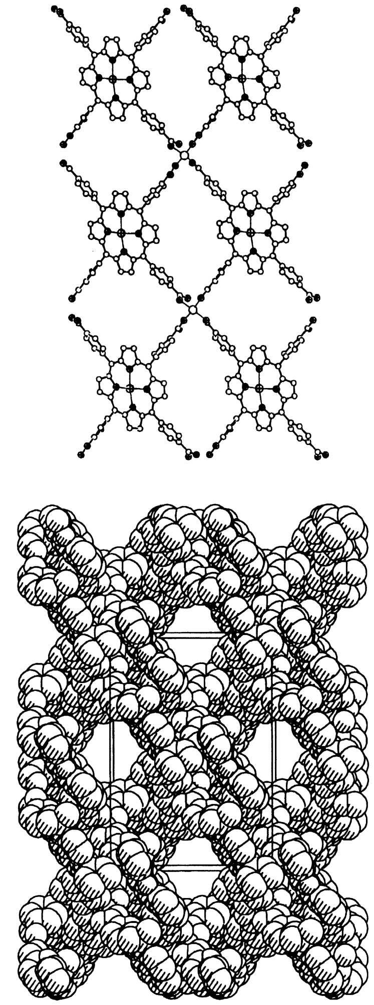


Figure 6. Molecular-sieve structure based on anionic Zn^{II}TCPP networks, tesselated by Zn^{2+} metal ion auxiliaries.[23] Top: The basic aggregation motif of the porphyrin entities around the Zn^{2+} templates (large open circles). Bottom: Space-filling model of the crystal structure. The hexagonally shaped channels, which extend between the interpenetrating diamondoid arrays, have an average van der Waals diameter of about 0.75 nm.

Conclusions

The ability to generate low-density, stable crystalline solids that consist of a single-frame, three-dimensional lattice, in which more than 50% of the crystal volume constitutes open straight channels accessible to other molecules, provides a promising perspective for new robust molecular solids and zeolite mimics with interesting and useful properties. Some of the materials described above represent nanoporous molecular solids with ordered arrays of open channels and unprecedented structural rigidity at high temperatures, which are due to the cooperative effect of the supramolecular interactions engineered into the metalloporphyrin tectons. This stability makes reversible sorption and desorption processes (associated with diffusion of the sorbed molecules through the interporphyrin channels) feasible in these solids,

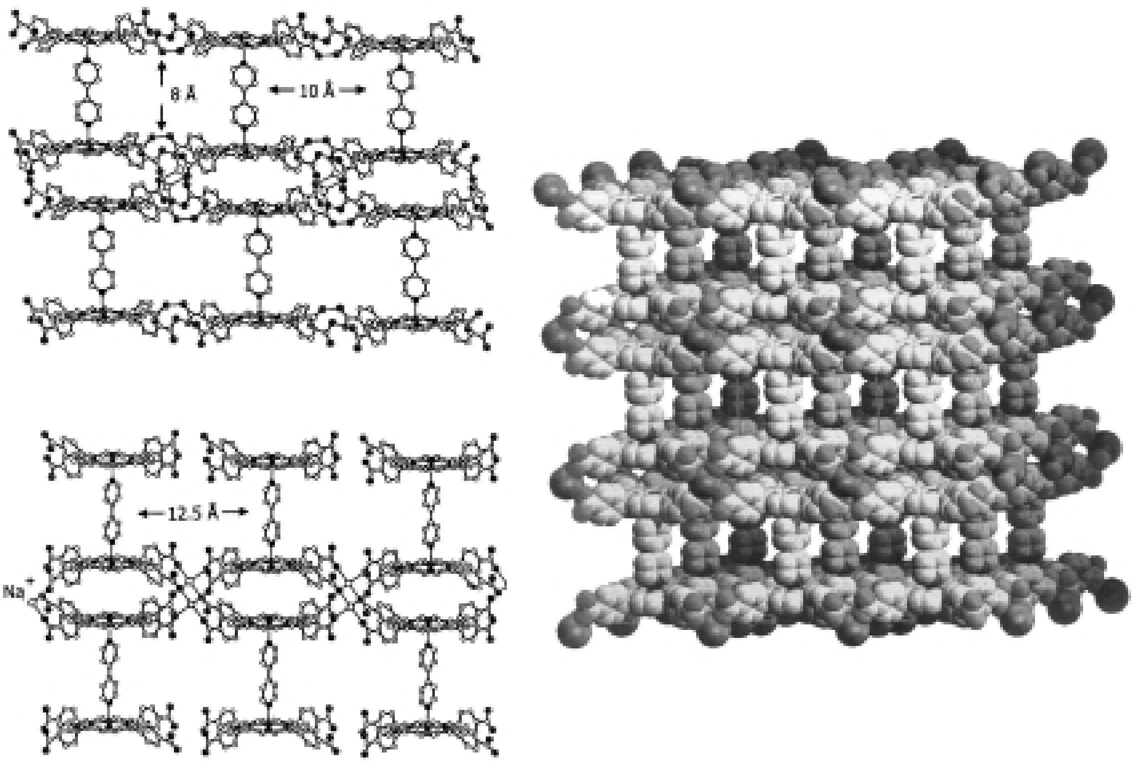


Figure 7. A uniquely structured molecular-sieve material that resembles a zeolite.[24] It is composed of anionic networks (bilayers) of Zn^{II}TCPP, templated by Na^+ ions and cross-linked by 4,4′-bipyridyl bridges. Left: Two perpendicular views of the crystal-engineered assembly, showing the van der Waals dimensions of the open galleries between the bipyridyl pillars which perforate the structure. Right: A perspective space-filling illustration of the nanoporous crystalline architecture.

as in inorganic zeolites. Other solids loose their crystallinity upon expulsion of the intercalated guest, but they can be readily regenerated in a microcrystalline form upon exposure to the vapour of a suitable guest/template component. In view of the continuously growing interest in such materials, there can be little doubt that many new zeolite analogues will be formulated in the near future. These remarkable achievements in nanoscale supramolecular synthesis of molecular-sieve architectures establish a potential for the design and development of a new generation of useful functional materials.

Acknowledgement

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