

Nanoporous Crystals of Calixarene/Porphyrin Supramolecular Complex Functionalized by Diffusion and Coordination of Metal Ions

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The high concentration and high degree of order provided by the crystalline state potentially imply high activity of reactions associated with high stereocontrol. However, among the forms of matter, the solid state is the least reactive, as reactions in the bulk are generally difficult to promote because of the close packing. For this reason, microporous frameworks having voids and channels of various aperture sizes and shapes are important for a wide range of technological applications, such as selective guest storage and molecular sieving as well as use as nanoreactors.¹ Natural and artificial zeolites and metal phosphates are an important class of robust, rigid nanoporous materials whose frameworks are based on the strength and directionality of the covalent nature of bonds.² These properties are also present in the class of completely artificial metal–organic polyhedra that can be rationally designed and functionalized through their constituents.³ Crystalline open frameworks based on supramolecular complexes held together by generally weak interactions represent a relatively new kind of microporous materials. These artificial materials, which are obtained by self-assembly, are attracting interest because they can simultaneously combine specific catalytic and stereochemical properties with plasticity. Among the noncovalent frameworks, several hydrogen-bonded open networks have been designed and realized, exploiting the directional property of the hydrogen bond.⁴ Noncovalent design and synthesis, which are based on nondirectional interactions, are less accessible because of the inherent difficulty of avoiding a close-packed solid by controlling only these weak interactions. Among the molecular building blocks, porphyrins are especially useful for the design and synthesis of such supramolecular solids.^{5,6} These assemblies can also have interesting applications as artificial antennas for light-harvesting by mimicking the natural systems.⁷ The use of hydrogen bonding or metal ion coordination has produced a wide range of porphyrin-based frameworks.^{5,8} Cavitand molecules, which have application as molecular sensors, are another important building block for the supramolecular assembly of porous solids.⁹ These molecules with a preorganized cavity are very flexible with respect to functionalization and are capable of forming very specific host–guest interactions.¹⁰ Notably, some cavitands can easily self-assemble around the tetracationic porphyrin *meso*-tetrakis(4-*N*-methylpyridyl)porphyrin (H₂TMPyP), forming star-shaped supramolecular complexes (Figure 1a).^{11–13} These supramolecular species are stabilized by synergistic noncovalent interactions, namely, electrostatic, stacking, and CH⋯π interactions. These highly symmetric star-branched complexes can be used to design new porous bicomponent materials that simultaneously have the chemical properties of both building blocks.

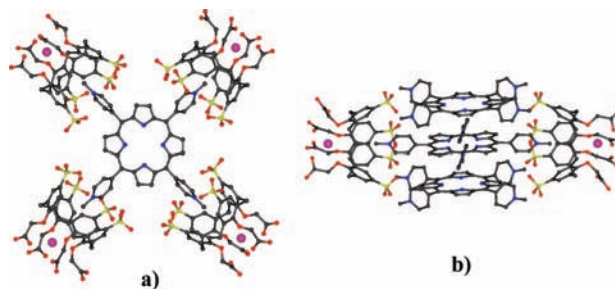


Figure 1. Supramolecular 3:4 porphyrin/calixarene. (a) Host–guest interaction formed by a central tetracationic porphyrin and four multianionic calixarenes. Each calixarene hosts a sodium ion (violet circles) in the lower rim. The two porphyrins stacked with the central porphyrin above and below the figure plane have been omitted for clarity. (b) Side view of the supramolecular 3:4 porphyrin/calixarene complex at pH 2. The two calixarenes interacting with the central porphyrin above and below the figure plane have been omitted for clarity.

By the templating action of H₂TMPyP toward the polyanionic calixarene 5,11,17,23-tetrasulfonato-25,26,27,28-tetrakis(hydroxyl-carbonylmethoxy)calix[4]arene (C4TsTeⁿ⁻) in the cone conformation (with the negative charge *n*– depending on pH), we have recently obtained crystals of calixarene/porphyrin with a stoichiometry tuned by pH.^{11,12} With a central 1:4 porphyrin/calixarene species (Figure 1a) as the starting material, it has been shown^{11,12} that it is possible to stack above and below the central porphyrin up to six metallated or nonmetallated porphyrins to form a final 7:4 species. In particular, crystallization at pH 2 results in a structure made up of neutral 3:4 porphyrin/calixarene units (Figure 1b). These units were found to pack in such a way as to form one-dimensional channels (11 × 13 Å). However, crystallization at pH 6 causes self-assembly of a tetraanionic 5:4 unit with two additional porphyrins, one stacked above and one below the supramolecular complex. In these crystals, additional tetracationic H₂TMPyP units balance the charge of the 5:4 units, forming a relatively closed packing. X-ray analysis of crystals of the complex, obtained from a solution buffered at pH 8.2, showed that the supramolecular 3:4 units can stack in polymeric chains.¹²

We report here the X-ray analysis of the new highly porous crystal form of a calixarene/porphyrin supramolecular complex, **1**, which was obtained by increasing the pH to 9.5 (ammonia buffer). These zeolite-like single crystals, consisting of a three-dimensional multicomponent supramolecular framework that accounts for only 39% of the crystal volume, can easily be functionalized by diffusion of metal ions in aqueous solution. In particular, we describe the crystal-to-crystal conversion of **1** to crystal structures **2** and **3**, which were obtained by addition of ZnCl₂ and NiCl₂, respectively, to the mother solution.

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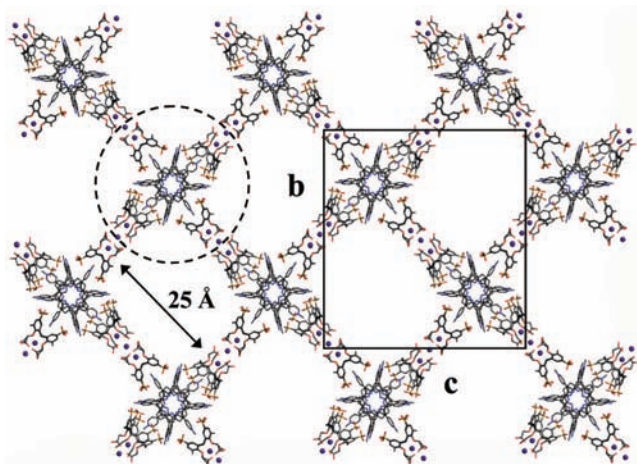


Figure 2. Two-dimensional network of 3:4 porphyrin/calixarene units. The square-grid network is slightly distorted into a diamond shape with 92 and 88° angles. The dashed line highlights a 3:4 unit.

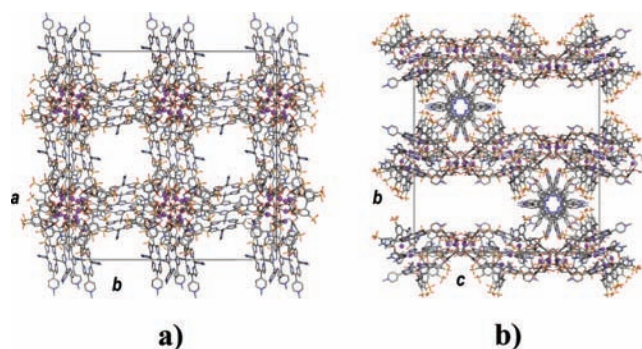


Figure 3. Projections of the structure along (a) the z axis and (b) the x axis. The view along the y axis is referred to that in (b) by a translation of the origin by $1/4$ along the two axes.

In tetragonal crystals of **1**, the anionic 3:4 porphyrin/calixarene units (Figure 1) are held together in a different fashion than the previously reported structures.^{11,12} The four carboxylate rims of the 3:4 units are bridged by Na^+ ions to the carboxylate rims of the adjacent 3:4 units, forming an approximately two-dimensional square network (Figure 2). The Na^+ ions bridging the calixarene carboxylate rims of the adjacent 3:4 units are octacoordinated (in a square-antiprism arrangement) by the carboxylate oxygen atoms. These oxygen atoms also coordinate in a square-antiprism arrangement the sodium ions hosted in the calixarenes (Figure S1 in the Supporting Information). The electron density maps of the structure of **1** also show the presence of one $\text{OH}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_2\text{CH}_2\text{OH}$ molecule (from PEG 300 used for crystallization) per asymmetric unit, located close to the calixarene surface (Figure S1).

The two-dimensional networks of Figure 2, which have exceptionally large openings of $23 \times 27 \text{ \AA}$, are parallel to the crystallographic yz plane and stacked at $x = 1/4$ and $3/4$. These planes interpenetrate with identical two-dimensional networks (Figure S2 in the Supporting Information) parallel to the xz plane and stacked at $y = 0$ and $1/2$, as shown in Figure 3.

The resulting three-dimensional network has large interconnected channels that are occupied by sodium ions and PEG and solvent molecules. In particular, a series of parallel channels of minimum dimensions $6 \times 6 \text{ \AA}$ are formed along the tetragonal z axis (Figure 3a). These channels are interconnected with two other series of channels of dimensions $6 \times 24 \text{ \AA}$ running along the x and y axes, respectively. The projection along the x axis is shown in Figure

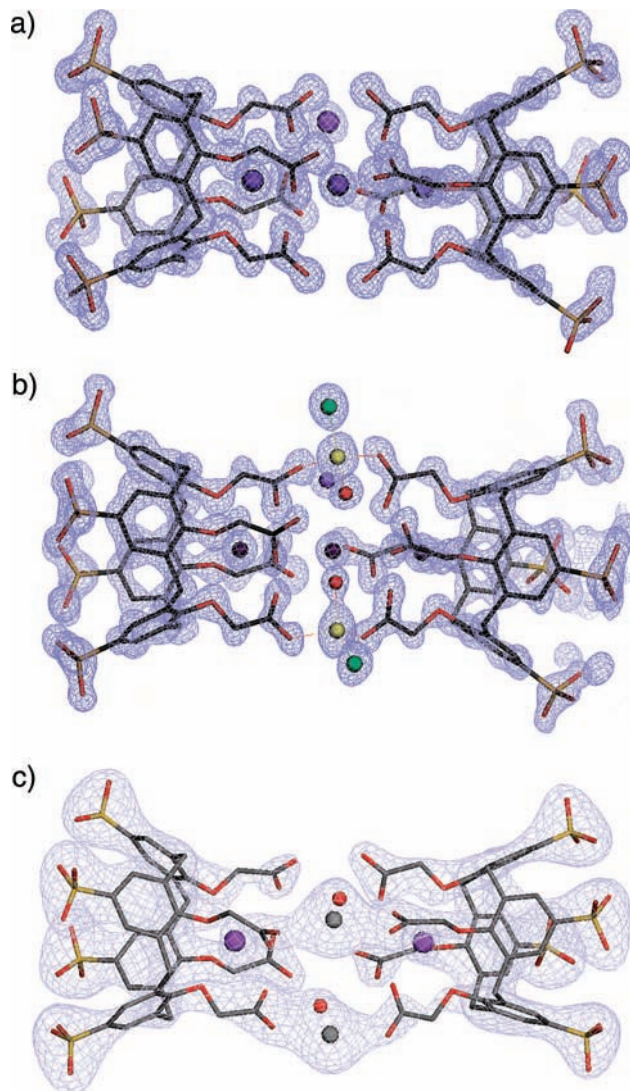


Figure 4. Electron density maps [contour levels: 2σ for (a) and (b), 1.5σ for (c)] in the calixarene bridging regions of the crystal structures of (a) **1**, (b) **2**, and (c) **3**. (a) In **1**, the sodium ions (purple) bridging the calixarene carboxylate rims of the adjacent 3:4 units are octacoordinated in a square-antiprism arrangement by the carboxylate oxygen atoms. (b) In **2**, two zinc ions (yellow) coordinate the carboxylates of two adjacent calixarenes. A chloride ion (green) and a water molecule (red) complete the distorted tetrahedral coordination around each zinc ion. The central sodium ion assumes a distorted snub disphenoid coordination. (c) In **3**, two nickel ions (gray), which are related by a twofold axis, coordinate axially to carboxylates of two symmetry-related calixarenes, while the bridging Na^+ ion is displaced outside the calixarene–calixarene interface. A further ligand, tentatively assigned as water molecule (red), was detected as part of the incomplete coordination sphere of each nickel ion.

3b. It should be emphasized that the pore volume in **1** is exceptionally large (61%) for a framework held only by weak nondirectional interactions. The sodium ions as well as the PEG molecules located in the channels are very close to the walls, determining a decrease in the opening of the channels.

Inspection of the crystal structure of **1** suggested the possibility of easy diffusion of metal ions through the channels formed by the negatively charged framework and perhaps metalation of the external porphyrins of the 3:4 units. Porphyrins are generally metallated by Zn^{2+} , but since a crucial intermediate with two zinc ions above and below the porphyrin plane is required in the proposed mechanism,¹⁴ the Zn metalation of the stacked porphyrins in the crystal should be hampered. In fact, addition of an excess of

ZnCl₂ to the red-colored solution containing crystals of **1** resulted in a change of the solution color to green-yellow while the crystals maintained their red color (Figure S3 in the Supporting Information). However, some crystals deformed and broke. A fragment of a broken crystal suitable for X-ray analysis confirmed the absence of metalation of the porphyrins. Nevertheless, significant changes with respect to **1** (Figure 4a) appear in the cavities of the new species **2**, due to the coordination of two zinc ions to the carboxylates of two adjacent calixarenes (Figure 4b). The electron density maps reveal that a chloride anion and a water molecule complete the distorted tetrahedral arrangement of the zinc anions (Figure 4b).

Addition of NiCl₂ to the solution containing crystals of **1** resulted, as for ZnCl₂, in a change of the solution color and a deformation of the crystals. The poor-quality diffraction pattern did not allow a complete structural determination of this new derivative **3**. However, we were able to collect a data set at 1.9 Å resolution, analysis of which revealed an increase in the crystal symmetry (space group *I4₁/amd*) with respect to **1** (space group *I4₁/a*). This solid-state/solid-state transition implies a severe reorganization of the molecules (Figure S4 in the Supporting Information), with a reduction in the crystallinity of the solid. The structure solution allowed us to establish that the bridging Na⁺ ion is displaced outside the two calixarenes whereas two Ni²⁺ ions are located in positions close to those of Zn²⁺ ions (Figure 4c).

The central sodium ion, which in **1** is coordinated in an almost regular square antiprism by the eight carboxylate groups (Figure S5 in the Supporting Information), assumes a distorted snub disphenoid geometry in **2**, replacing in the coordination process two carboxylate ligands with two Zn–Na-bridging water molecules (Figure S6 in the Supporting Information). These bridging water molecules are located on one side of the calixarenes (H₂O–H₂O distance 3.67 Å), thereby removing completely the axial symmetry of the cavitands. While the two zinc ions in **2** are coordinated by the opposite carboxylate groups in positions 1 and 3 of the calixarenes, the two nickel ions in **3** coordinate axially to two adjacent carboxylates (Figure S7 in the Supporting Information). The introduction of the bivalent ions changes significantly the mutual position of the two calixarenes. In particular, the distances between the internal sodium ions are lengthened from 6.68 Å in **1** to 7.41 Å in **2** and 7.7 Å in **3**. The mean planes passing through the methylene groups of two adjacent calixarenes make an angles of 16.1° in **2** and 17.5° in **3**, which should be compared with the corresponding value of 2.5° in **1**. The bivalent ions substitute for some of the Na⁺ counterions located close to the sulfonic groups (Figure S8 in the Supporting Information).

In conclusion, a highly flexible nanoporous material has been obtained by synergistic noncovalent interactions of calixarene and porphyrin building blocks. This supramolecular zeolite-like structure was easily functionalized by diffusion and coordination of metal ions. This new bifunctionalized porous material containing a porphyrinic pigment together with a potential catalytic metal center represents a further step toward an artificial system having the two functions needed to mimic the steps of the oxidative processes of photosynthetic pathways.¹⁵

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Supporting Information Available: Crystallization procedures, X-ray diffraction data, CIF files, and further descriptions of the structures for **1**, **2**, and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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