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Cadmium−Porphyrin Coordination Networks: Rich Coordination Modes and Three-Dimensional Four-Connected $CdSO_4$ and (3,5)-Connected hms Nets

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ABSTRACT: Functionalized tetraarylporphyrin molecules have been widely used as ligands for the design of supramolecular coordination arrays. Even though a large number of porphyrin coordination compounds have been synthesized, three-dimensional networks are still less common. Here we report the hydrothermal synthesis and structure characterizations of four cadmium−porphyrin compounds based on *meso*-tetra(4-pyridyl)porphyrin (H_2TPyP). In these structures, both cadmium and porphyrin exhibit rich coordination chemistry. The porphyrin molecule displays four types of coordination modes in which each porphyrin molecule bonds to one, two, four, and five cadmium sites. The Cd^{2+} site shows equally diverse coordination modes and exists in five different coordination environments. The porphyrin molecules are connected through Cd^{2+} cations or $Cd_3(SC_2H_2OH)_2^{4+}$ clusters into molecular (Cd−TPyP-1), two-dimensional (Cd−TPyP-4), and three-dimensional networks (Cd−H_2TPyP-2 and Cd−TPyP-3). Three-dimensional frameworks are of particular interest because they adopt interesting and rare framework topologies (cds and hms types).

Introduction

In recent years, supramolecular chemistry based on porphyrin has attracted increasing interest. Because of their interesting properties such as electron and energy transfer, redox, and dynamic photophysical properties, porphyrin-based structures are potentially useful for a wide range of applications including molecular sensing, organic magnets, biomimetic models of photosynthetic systems, and redox catalysts.[1,2] Furthermore, the diverse structural features of porphyrin molecules allow them to function as versatile building blocks for the construction of supramolecular arrays that may function as zeolite-like porous materials that have already been demonstrated in a variety of metal−organic framework materials.[3,4]

Porphyrin macrocycles can be regarded as rather rigid square planar building blocks. Chemical *meso* substitution on the porphyrin periphery allows the introduction of coordinating ligands that provide a facile route for either hydrogen bonding or coordination bonds. Through such interactions, porphyrin molecules can be assembled into different supramolecular arrays.[5–7] The thermal and chemical stability of porphyrins allows them to be used as starting materials even at relatively high temperatures, making it feasible to prepare their compounds under hydrothermal conditions.

Using *meso*-tetraarylporphyrin such as *meso*-tetra(4-pyridyl)porphyrin (H_2TPyP) and *meso*-tetra(4-carboxyphenyl)porphyrin ligands, researchers have synthesized a number of porphyrin coordination polymers. Some of them possess very interesting three-dimensional (3D) framework structures.[8–11] A typical structural feature in these structures is that porphyrin molecules are connected by individual metal cations into extended structures.

A large family of unique nanosized supertetrahedral clusters exist such as $Cd_{32}S_{14}(SPh)_{36}\cdot 4DMF$,[12] $[Cd_{17}S_4(SCH_2CH_2OH)_{26}]$,[13] and $(NMe_4)_4[Cd_{10}S_4(SPh)_{16}]$.[14] Using organic multifunctional ligands to organize these semiconducting clusters into 3D supperlattices is particularly interesting since the materials synthesized by this method are expected to exhibit synergetic effects (e.g., optical properties) from both inorganic and organic components.[15]

This work is part of our systematic study investigating the reaction chemistry and crystallization process of Cd−S clusters with bi- or polydentate organic ligands.[16] We have shown that by using simple bipyridine ligands, it is possible to assembly metal sulfide clusters into zero-, one-, or two-dimensional arrays. In particular, a 3D framework structure has been made from in situ formed tetradentate ligands and $[Cd_8(SPh)_{12}(SO_4)]^{2+}$ cubic clusters. The important physical properties of porphyrin molecules motivate us to incorporate them into this organic–inorganic hybrid system.

Here, we report hydrothermal synthesis and structural characterization of four porphyrin compounds assembled from either free-base (H_2TPyP) or metalated *meso*-tetra(4-pyridyl)porphyrin molecules. The porphyrin molecules are connected through single metal cations or small Cd−S building units into molecular (Cd−TPyP-1), 2D framework (Cd−TPyP-4), or 3D (Cd−H_2TPyP-2 and Cd−TPyP-3) structures. Both the ligand (*meso*-tetra(4-pyridyl)porphyrin) and the metal cation (Cd^{2+}) exhibit rich coordination chemistry. Each porphyrin molecule can coordinate from one to five metal cations, while the metal cation Cd^{2+} displays five different coordination environments. Of particular interest are two 3D framework structures (Cd−H_2TPyP-2 and Cd−TPyP-3) that possess an interesting four-connected $CdSO_4$-type net and a rare (3,5)-connected hms-type net.

Experimental Section

Synthesis. The chemicals in this work were used as received. Two salts, $[N(CH_3)_4]_4[Cd_{10}S_4(SPh)_{16}]$ (**1**) and $Cd_{10}(SCH_2CH_2OH)_{16}\cdot[ClO_4]_4$ (**2**), were prepared by literature procedures.[14,17] A light yellow intermediate (**3**) with the composition $Cd_{10}S_4(SPh)_{12}$ was obtained by heating **1** at 250 °C for 3 h.[18] These three compounds (**1**, **2**, and **3**) were then used for the synthesis of the following compounds.

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Table 1. A Summary of Crystallographic Data in This Study

name	Cd−TPyP1	Cd−H$_2$TPyP2	Cd−TPyP3	Cd−TPyP4
composition[a]	Cd(TPyP)·Py	Cd(H$_2$TPyP)(SH)$_2$	Cd$_2$(TPyP)I$_2$	Cd$_3$(TPP)$_2$(SCH$_2$CH$_2$OH)$_2$(DMF)$_2$
space group	*C*2/c	*Pnna*	*C*2/c	*C*2
a, Å	13.615(2)	12.852(7)	20.490(3)	16.221(2)
b, Å	18.578(3)	15.668(7)	25.064(4)	19.434(3)
c, Å	14.846(3)	20.390(10)	16.563(3)	14.943(2)
β, deg	103.143(3)	90	90.683(3)	114.198(2)
R1 ($I > 2\sigma$)	0.0758	0.0639	0.0591	0.0424
$2\theta_{\max}$	56.6	56.0	56.6	56.6

[a] H$_2$TPyP = *meso*-tetra(4-pyridyl)porphyrin, C$_{40}$H$_{26}$N$_8$; TPyP = deprotonated *meso*-tetra(4-pyridyl)porphyrin, C$_{40}$H$_{24}$N$_8$; Py = pyridine, C$_5$H$_5$N; DMF = *N*,*N*′-dimethylformamide, C$_3$H$_7$NO.

Cd−TPyP-1 {Cd(TPyP)·C$_6$H$_5$N}. A mixture containing 0.101 g of the light yellow precursor (**3**), 0.049 g of H$_2$TPyP, 0.0673 g of Na$_2$SO$_4$, 5.076 g of acetonitrile, and 2.072 g of pyridine were prepared and stirred in a 23 mL Teflon-lined stainless steel autoclave and stirred for 20 min The vessel was then sealed and heated at 190 °C for 9 days. After the mixture was cooled to room temperature, Cd−TPyP-1 could be recovered in the form of purple prismatic crystals with the yield of ~50%.

Cd−H$_2$TPyP-2 {Cd(H$_2$TPyP)(SH)$_2$}. Compound **1** (0.3300 g), 0.0520 g of I$_2$, 0.0248 g of Na$_2$SO$_4$, 0.0582 g of H$_2$TpyP, and 2.0653 g of ethanol/H$_2$O (1:1 volume) were mixed in a 23 mL Teflon-lined stainless steel autoclave, and the mixture was stirred for 20 min The vessel was then sealed and heated at 190 °C for 4 days. After the mixture was cooled to room temperature, purple crystals of Cd−H$_2$TPyP-2 could be obtained in the yield of ~17%.

Cd−TPyP-3 {Cd(TPyP)·CdI$_2$}. Compound **1** (0.3291 g), 0.0496 g of I$_2$, 0.0252 g of Na$_2$SO$_4$, 0.0565 g of H$_2$TpyP, and 2.1125 g of ethanol were mixed in a 23 mL Teflon-lined stainless steel autoclave, and the mixture was stirred for 20 min. The vessel was then sealed and heated at 190 °C for 3 days. After the mixture was cooled to room temperature, purple crystals of Cd−TPyP-3 could be obtained in the yield of ~83%.

Cd−TPyP-4 {Cd$_3$(TPyP)$_2$(SCH$_2$CH$_2$OH)$_2$·2DMF}. A mixture of 0.2913 g of compound (**2**), 0.0928 g of H$_2$TpyP, and 5.0368 g of dimethylformamide was prepared in a 23 mL Teflon-lined stainless steel autoclave and stirred for 20 min. Then the vessel was sealed and heated at 140 °C for 4 days. After the mixture was cooled to room temperature, large dark red crystals of Cd−TPyP-4 could be obtained in the yield of ~75%.

Structure Determination. From each sample, a crystal suitable for X-ray diffraction was selected and glued to a thin glass fiber with 5 min epoxy and mounted on a SMART CCD diffractometer with a Mo Kα X-ray source operating at 50 kV and 30 mA. The empirical absorption corrections were based on the equivalent reflections, and other possible effects such as the absorption of glass fiber were also corrected. The structures were solved by direct methods and refined using SHELXTL 5.1.[19] The final full-matrix refinements were against F^2. A summary of crystallographic data is given in Table 1.

Results and Discussion

Compositional, Structural, and Topological Description. With bipyridal ligands, it has been convincingly demonstrated that Cd−S clusters can be organized into one- or two-dimensional superlattices.[16] One objective of this work was to examine the chemistry of Cd−S clusters in the presence of functionalized porphyrin molecules such as H$_2$TPyP employed here. In this work, Cd−S clusters were employed as the starting materials for the synthesis. In the synthesis of Cd−TPyP-1, the Cd−S cluster was activated at four corners through thermal removal of four corner coordinating ligands. The results of the synthesis, however, show that these clusters are not retained in the final crystallization product, which indicates that the reaction chemistry between H$_2$TPyP and Cd−S clusters differs from that between bipyridal ligands and Cd−S clusters. In particular, the chelating ability of the porphyrin molecule seems to play a major role in destabilizing Cd−S clusters by chelating individual Cd^{2+} ions.

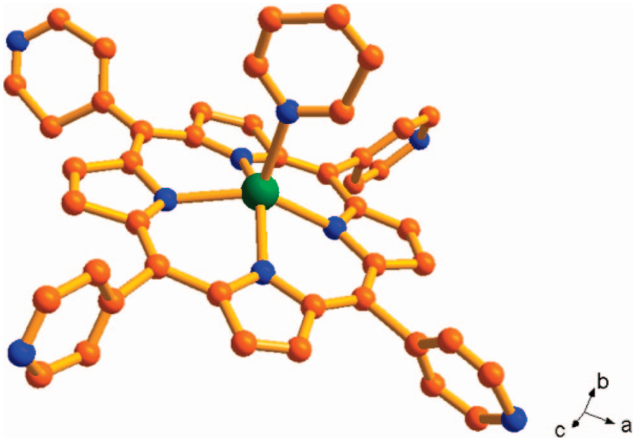

Figure 1. The molecular structure of Cd−TPyP-1: green, Cd; blue, N; orange, C. Hydrogen atoms are omitted for clarity.

Cd−TPyP-1. Cd−TPyP-1 possesses a simple molecular structure as shown in Figure 1. The Cd^{2+} cation is charge-balanced by the dianionic porphyrin molecule (TPyP^{2-}). The metal site is located near the center of the porphyrin ring with coordination geometry of the distorted square pyramid. The Cd^{2+} site is slightly above the porphyrin plane (by ~0.66 Å) toward the axially attached pyridine molecule. It is worth noting that four pyridyl groups on the periphery are not used for coordination so that neighboring porphyrin molecules are not bridged together.

Cd−H$_2$TPyP-2. Cd−H$_2$TPyP-2 has a 3D architecture with two interpenetrating but identical lattices (Figure 2). The nonmetalated porphyrin molecule exists as a neutral ligand and the Cd^{2+} cation is charge-balanced by two −SH groups. Each H$_2$TPyP functions as a tetradentate ligand to connect four different Cd(SH)$_2$ units together through its four peripheral pyridyl groups. Each Cd center adopts octahedral coordination in which two axial positions are occupied by charge-balancing −SH groups, while four equatorial positions are coordinated to pyridyl groups from four different H$_2$TPyP neutral molecules.

In this particular compound, both cadmium sites and centers of porphyrin molecules can be considered as four-connected nodes with square-planar geometry. Although the structure resulting from nodes with only the square-planar connectivity is often two-dimensional, Cd−H$_2$TPyP-2 has an infinite 3D network. This is because porphyrin molecules adopt two mutually perpendicular orientations, thus extending the connectivity into the 3D space. Because of the lattice interpenetration, only 27% of the crystal volume of Cd−H$_2$TPyP-2 is empty as calculated by the program PLATON.[20] The framework topology can be represented as the CdSO$_4$-type four-connected net (denoted the cds net) (Figure 2).[21−23] The cds net (vertex symbol $6\cdot6\cdot6\cdot6\cdot6_2\cdot*$) is among a few 3D nets that are constructed from square-planar centers. A closely related net is the NbO net (vertex symbol $6_2\cdot6_2\cdot6_2\cdot6_2\cdot8_2\cdot8_2$).[24]

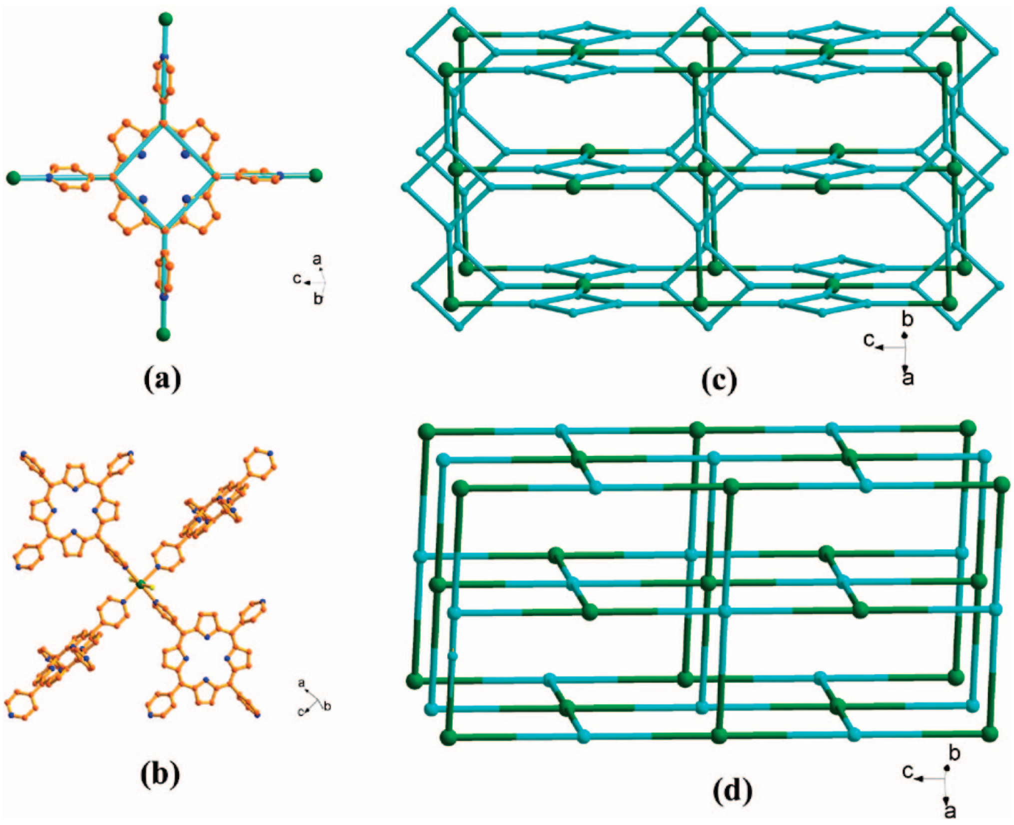

Figure 2. The structure of Cd−H_2TPyP-2. (a) Each H_2TPyP molecule functions like a four-connected square unit to link four Cd atoms: green, Cd; blue, N; orange, C. (b) Each Cd cation is coordinated by four H_2TPyP molecules and two −SH groups. (c) Topological representation of the 3D framework of Cd−H_2TPyP-2. Only one sublattice is shown for clarity. (d) The $CdSO_4$-type net in Cd−H_2TPyP-2, in which each porphyrin molecule is replaced by a four-connected node.

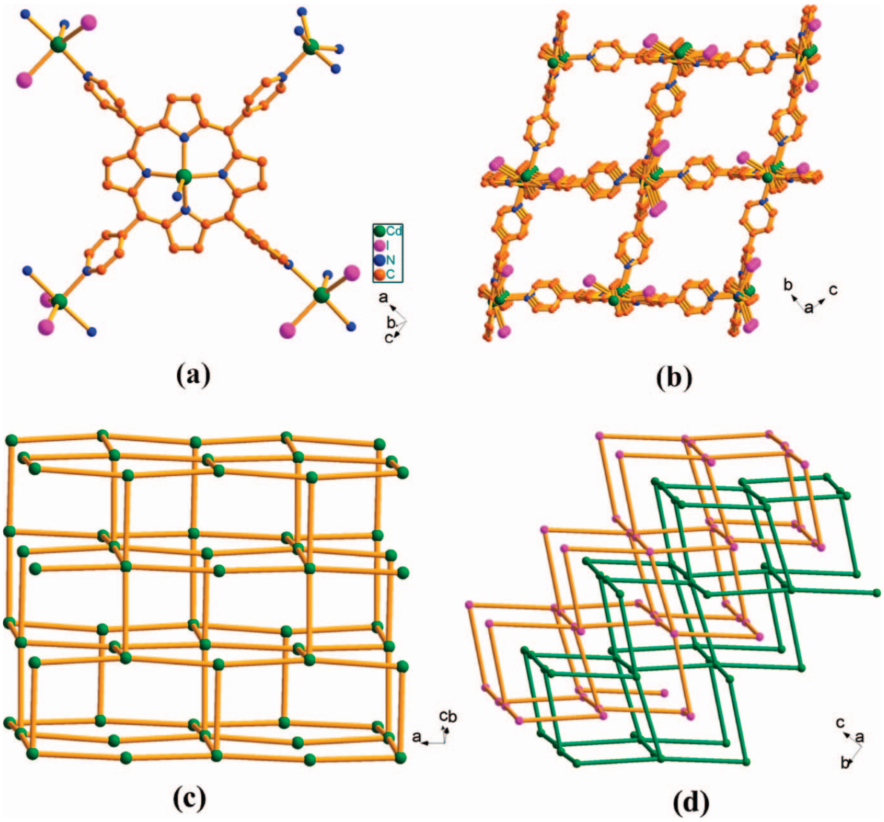

Figure 3. (a) Two coordination modes of Cd cations are present in Cd−TPyP-3. (b) Three-dimensional framework structure of Cd−TPyP-3. Only one sublattice is shown for clarity: green, Cd; blue, N; orange, C; purple, I. (c) Topological representation of the (3,5)-connected hms net in Cd−TPyP-3. (d) The 2-fold interpenetrating net.

Cd−TPyP-3. Cd−TPyP-3 consists of two interpenetrating 3D lattices. There is only one crystallographically unique porphyrin molecule. Each porphyrin is coordinated to five Cd ions, one at the core and four through pyridyl groups. Because the ratio between Cd^{2+} and dianionic porphyrin is two, the extra positive charge is balanced by two I^- ions. Two types of Cd sites (in an equal ratio) are present. One is located at the porphyrin core with geometry of distorted square pyramid. As shown in Figure 3, this Cd^{2+} site is also above the porphyrin plane (by 0.61 Å) toward the axially coordinated pyridyl moieties (Cd−N 2.307 Å) from the adjacent $TPyP^{2-}$ molecules. The other Cd^{2+} site adopts geometry of distorted trigonal bipyramid with coordination to two I^- ions and three pyridyl groups. This Cd site is three-connected because of two terminal I^- ions.

The topology of each sublattice in Cd−TPyP-3 is quite open. However, due to the interpenetration, only 23% of the crystal volume of Cd−TPyP-3 is empty as calculated by the program PLATON. Cd−TPyP-3 exhibits an interesting and rather rare framework topology. As shown in Figure 3, the Cd^{2+} site at the porphyrin core acts as the five-connected node, while the other Cd^{2+} site acts as the three-connected node. The whole framework can therefore be topologically represented as a (3,5)-connected net. In such a net, the three- and five-connected nodes are not alternating because there are direct connections between adjacent five-connected nodes. This also explains that these two types of nodes are in a 1:1 ratio. The vertex symbol for the five-connected Cd node is $6\cdot6\cdot6\cdot6_2\cdot6_2\cdot6_2\cdot6_2\cdot6_2\cdot6_2\cdot*$, while the vertex symbol for the three-connected Cd node is $6_3\cdot6_3\cdot6_3$. The net can be viewed as stacked hexagonal layers and is denoted as the hms net.[25] Another feature of this net is that it is a self-dual net,[26] so it is easy to form a 2-fold interpenetrating framework. To our knowledge, this is the first metal−organic framework that adopts the hms-type net.

Cd−TPyP-4. Cd−TPyP-4 has a layered structure with solvent DMF molecules sandwiched between adjacent layers. Surprisingly, only one of four pyridyl groups in each $TPyP^{2-}$ molecule is used for coordination. In each layer, $TPyP^{2-}$ molecules are connected into the extended two-dimensional framework through the $Cd_3(SC_2H_2OH)_2^{4+}$ units that contain the Cd−S−Cd−S−Cd chain shown in Figure 4. Two outer Cd^{2+} sites are located at the core of two separate porphyrin molecules and have the geometry of the distorted square pyramid, which is similar to that in Cd−TPyP-1 and Cd−TPyP-3. The central Cd^{2+} site has a coordination number of 6 with two coordinated to S sites (Cd−S 2.541 Å), two to OH sites (Cd−O 2.517 Å), and two to N sites of two pyridyl groups (Cd−N 2.465 Å). The S and OH atoms are from two $SCH_2CH_2OH^-$ ligands, while the two N atoms are from two separate $TPyP^{2-}$ molecules.

In terms of the framework connectivity, the center Cd^{2+} site within the Cd−S−Cd−S−Cd represents the four-connected node with connectivity to four other crystallographically identical Cd^{2+} sites. The Cd^{2+} site at the porphyrin core is two-connected between two four-connected Cd^{2+} sites and can therefore be omitted in the net analysis (Figure 4). Thus, the two-dimensional structure of Cd−TPyP-4 can be described as a four-connected distorted square-grid-type net (Figure 4).

Porphyrin Coordination Chemistry. For each H_2TPyP molecule, the core is constructed from four pyrrole rings while its periphery is modified by four pendent pyridyl arms. Both the core and the four pyridyl moieties possess the coordination ability to bind metal cations, which allows the $TPyP^{2-}$ ligand to bind metal cations ranging in number from one to five. This provides an opportunity to construct the porphyrin coordination polymers in a variety of ways.

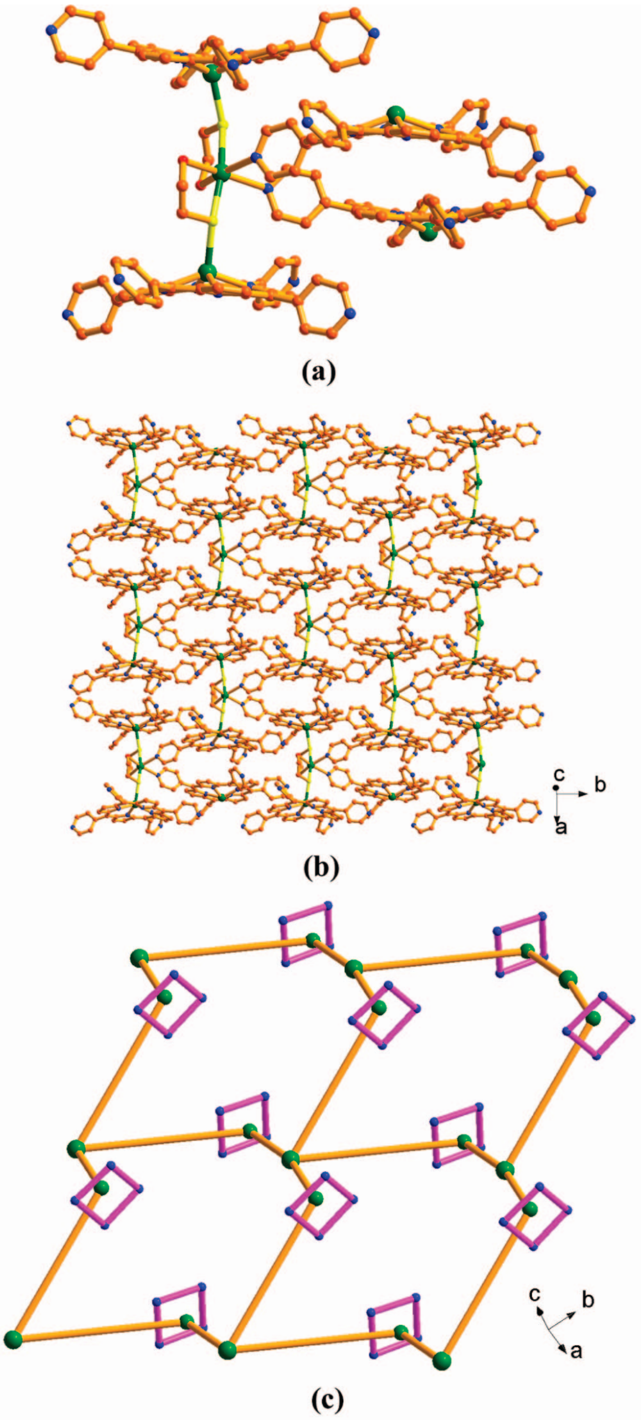

Figure 4. (a) The local coordination geometry in Cd−TPyP-4. (b) $Cd_3(SCH_2CH_2OH)_2$ units connect porphyrin molecules into two-dimensional sheets: green, Cd; blue, N; orange, C; yellow, S; red, O. (c) Topological representation of the distorted square-grid-type net. The porphyrin molecules are illustrated as purple squares.

In structures reported here, the porphyrin molecule displays four types of coordination modes in which each porphyrin molecule bonds to one, two, four, and five cadmium sites (Figure 5). In the molecular complex Cd−TPyP-1, the porphyrin binds only one metal cation at the core so that no extended framework structure could form. In Cd−H_2TPyP-2, even though each porphyrin molecule is in the neutral form, its four pyridyl groups are all used for coordination. Therefore, each porphyrin functions

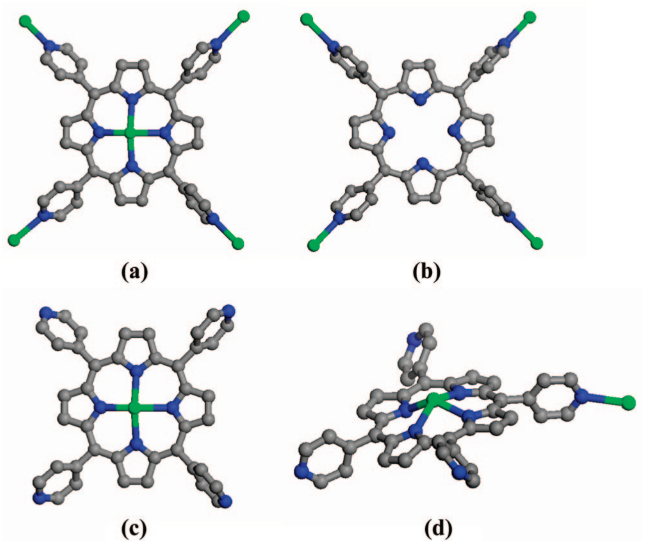

Figure 5. Different coordination modes of the porphyrin molecule: green, Cd; blue, N; gray, C; all hydrogen atoms are omitted for clarity. (a) Each porphyrin bonds to five Cd^{2+} sites in Cd−TPyP-3. (b) Each porphyrin bonds to four Cd^{2+} sites in Cd−H_2TPyP-2. (c) Each porphyrin bonds to only one Cd^{2+} site in Cd−TPyP-1. (d) Each porphyrin bonds to two Cd^{2+} sites in Cd−TPyP-4.

as a tetradentate ligand. In Cd−TPyP-3, each porphyrin ligand binds to five metal sites by using its core and four pyridyl groups.

Interestingly, only two coordination sites of the porphyrin molecule are used for the construction of the layer structure in Cd−TPyP-4. The synthetic conditions apparently play an important role in determining the coordination mode of the porphyrin ligand. For example, Cd−H_2TPyP-2 and Cd−TPyP-3 were synthesized under similar conditions except for the difference in the solvent (ethanol/water for Cd−H_2TPyP-2 and ethanol for Cd−TPyP-3). The absence of water seems to promote the formation of the Cd−I bond because of the possibility for hydrolysis of the Cd−I bond under hydrothermal conditions.

Coordination Chemistry of Cd^{2+} Sites. Similar to the porphyrin molecule, the Cd^{2+} cation shows equally diverse coordination modes with three types of coordination geometries in five chemical environments (Figure 6). The most common geometry is the square pyramid when the Cd^{2+} is at the center of the porphyrin ring. Such geometry occurs in Cd−TPyP-1, Cd−TPyP-3, and Cd−TPyP-4. Because of the large size of the Cd^{2+} ion, it is actually located above the porphyrin plane (by 0.61 to 0.77 Å) toward the axial ligands that can be the pyridyl moiety or the −SH group here. Such deviation from the plane of the porphyrin ring makes it unlikely for the Cd^{2+} to adopt the octahedral geometry, which is common for smaller metal cations such as Mg^{2+} and Fe^{2+}.

When not trapped by the porphyrin ring, the Cd^{2+} can have a coordination number of either 5 or 6 in structures reported here. The distorted octahedral geometry is found in Cd−H_2TPyP-2 and Cd−TPyP-4, while the distorted trigonal bipyramid occurs in Cd−TPyP-3. Compared with the octahedral and square pyramidal geometry, the trigonal bipyramid is less common and has not yet been found in known metal−porphyrin coordination polymers. Several other metal coordination modes including tetrahedral,[9] T-shaped,[27] and linear geometries have also been observed for metal centers in porphyrin coordination polymers.[28] The rich chemistry of the porphyrin ligand and the diverse coordination modes of metal cations provide a variety of ways for constructing 3D frameworks based on H_2TPyP (or $TPyP^{2-}$).

Charge Balance and Extraframework Volume. It has been shown that it is generally easier to produce permanent porosity in a neutral framework because in the absence of the charge balancing species within the pore space, the host–guest interaction is usually weak and the guest molecules may be more readily removed. All structures in this study were neutral

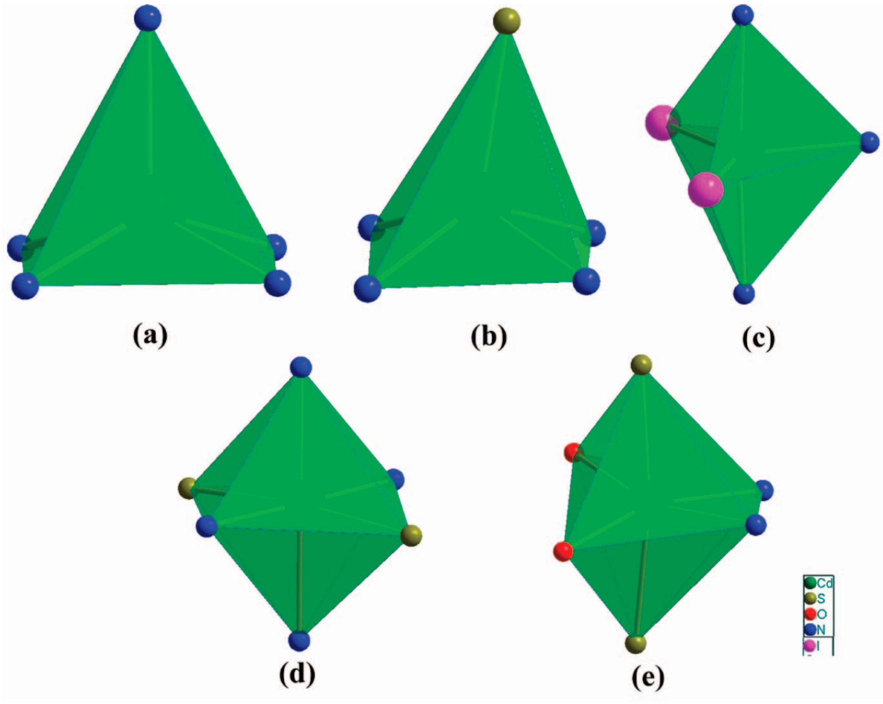

Figure 6. Five different coordination environments of Cd cations: (a) square pyramidal geometry in Cd−TPyP-1 and Cd−TPyP-3; (b) square pyramidal geometry in Cd−TPyP-4; (c) trigonal bipyramidal geometry in Cd−TPyP-3; (d) octahedral geometry in Cd−H_2TPyP-2; (e) octahedral geometry in Cd−TPyP-4; green, Cd; blue, N; yellow, S; red, O; purple, I.

frameworks or molecules. The Cd^{2+} charge is balanced locally by the coordinating anions: dianionic porphyrin, SH$^-$, I$^-$, and HOCH$_2$CH$_2$S$^-$. However, no significant void space is present. In Cd−H$_2$TPyP-2 and Cd−TPyP-3, the 2-fold interpenetration is responsible for the reduced void space even though the coordination chemistry permits the assembly of the highly open 3D topology. Without the interpenetration, Cd−H$_2$TPyP2 and Cd−TPyP-3 could have void space as high as 63% and 61%, respectively. Therefore, the method for the elimination of interpenetration is essential for the design of porous materials. One strategy used by Yaghi and co-workers was to carry out the reactions under more dilute conditions.[29] In addition, the selection of reaction temperature and solvent might also be important to prevent the interpenetration. Additional research is needed to explore the possibility of generating porosity in the system studied here.

Conclusions

A series of molecular and framework structures based on *meso*-tetra(4-pyridyl)porphrin have been synthesized and characterized. In addition to a molecular complex and a two-dimensional square-grid-type coordination poloymer, two 3D coordination polymers with interesting and rare topological features (CdSO$_4$-type and hms-type) have been found. Cd−TPyP-3 is the first coordination polymer that exhibits the rare hms-type net that contains the combination of three- and five-connected nodes. In these structures, *meso*-tetra(4-pyridyl)porphyrin exhibits rich coordination chemistry and bonds to one, two, four and five cadmium sites in different structures. The metal Cd^{2+} ion shows equally rich coordination modes in five different environments with three coordination geometries. This rich chemistry involving both porphyrin and metal cations may be exploited further to develop a larger number of novel framework structures based on porphyrin molecules.

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Supporting Information Available: Crystallographic data including positional parameters, thermal parameters, and bond distances and angles (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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