

A Novel 3-D Self-Penetrating Topological Network Assembled by Mixed Bridging Ligands

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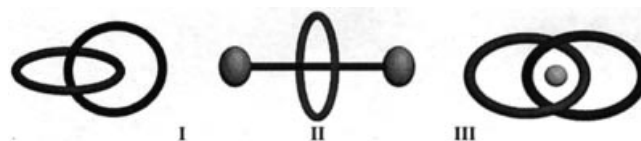
The assembly of 5-sulfoisophthalic acid (H_3sipa) and 4,4'-bipyridine (bpy) with Cd^{2+} ions gave rise to a new polymeric complex $\{[\text{Cd}_3(\text{sipa})_2(\text{bpy})_4(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}\}_n$ (**1**). X-ray diffraction analysis reveals that complex **1** has a 3-D self-penetrating network formed by the interlocking and interweaving of two types of one-dimensional chains comprising two kinds of

$\text{Cd}_4(\text{sipa})_4$ and $\text{Cd}_4(\text{bpy})_4$ units, respectively. The sipa^{3-} ligand serves as the connector and the Cd^{2+} ion as the node. Thermogravimetric analysis (TGA) and the luminescence property of **1** are discussed.

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The analyses and studies of diverse topological networks have recently received much attention.^[1] In these reports a variety of fascinating types of entanglements of individual motifs observed are of special interest due to their important role in natural organic entities.^[2] In the past decades, a number of new types of entanglements that are often described as interpenetrating networks,^[3] have been constructed from organic building units. Among these entangled polymeric systems, some representative species such as catenanes(**I**), rotaxanes(**II**) or pseudocatenate/rotaxanes(**III**), have been reported (Scheme 1).^[4–8] Based on studies on catenane and rotaxane molecules, the introduction of metal ions into polymeric frameworks greatly intrigued many chemists. Aside from unique topological features, these entangled metal-containing species are attractive for use in new functional materials, as well as for the development of molecular devices and studies on bionics.^[9–11] The formation of different entanglements or interpenetrations may result from the presence of large free voids in a single network.^[3b,7a] It has been shown that long bridging ligands can produce large voids, which may generate interpenetrating structures or large open cavities. For example, 1,3,5-benzenetricarboxylate (btc) which serves as a three-part connector that affords the (6,3) graphite-like sheet and terephthalate and 4,4'-bipyridine that generate the (4,4) sheet, were widely used to design and synthesize directed compounds with interpenetrating or large open cavity structures.^[12] Our synthetic approach starts by focusing on the construction of new topological frameworks using different kinds of bridging ligands. Two long bridging ligands, 4,4'-

bipyridine (bpy) and 5-sulfoisophthalic acid (H_3sipa), were used, together with Cd^{2+} ions. We hoped each of them could form independent structural units with large voids, and the interlocking or interpenetrating of the two kinds of units with each other could generate an entangled structure. In this communication, we report on a 3-D self-penetrating coordination polymer, $\{[\text{Cd}_3(\text{sipa})_2(\text{bpy})_4(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}\}_n$ (**1**), constructed by the interlocking and interconnecting of two types of metal-ligand rings $\text{Cd}_4(\text{sipa})_4$ and $\text{Cd}_4(\text{bpy})_4$.



Scheme 1

The hydrothermal reaction of NaH_2sipa , $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 4,4'-bipyridine and water at 160 °C for 3 days resulted in the formation of light-yellow crystals of **1**. The element analysis and IR spectrum confirm the formula of **1**. Single-crystal X-ray diffraction reveals complex **1** has a 3-D self-penetrating framework constructed from Cd^{2+} ions, and the ligands sipa^{3-} and bpy. There are two types of coordination environments around the Cd^{2+} ions in the crystal structure: Cd(1), which is at the center of a distorted octahedral geometry, is coordinated by two oxygen atoms from two $-\text{SO}_3$ groups of different sipa^{3-} ligands and four nitrogen atoms from four bpy ligands; Cd(2) is coordinated by two nitrogen atoms from two bpy ligands, four oxygen atoms from a water molecule and two carboxylate groups, in a highly distorted octahedral geometry. Here, two coordination oxygen atoms from two $-\text{SO}_3$ groups on Cd(1) and two coordination nitrogen atoms from two bpy on Cd(2) are located in *cis*-positions with bond angles of 86.00 and

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97.48° for O–Cd(1)–O and N–Cd(2)–N, respectively. Such *cis* positions that are sterically hindered have rarely been observed in reported studies,^[13] and may induce the formation of the ring structures Cd₄(sipa)₄ and Cd₄(bpy)₄. The formation of open cavities or channels may be favored by the *trans* locations of the ligands.

In **1**, four cadmium ions and four bpy ligands form a Cd₄(bpy)₄ unit with a side length of 11.46 × 11.79 Å and diagonal measurement of 15.55 × 17.28 Å based on the metal–metal distances. Different metal–metal distances in the tetragonal sheet arise as a result of the different torsions and curves of the bpy ligands linking Cd(1) and Cd(2), respectively. The fully deprotonated sipa^{3−} ligand acts as a tridentate ligand linking three cadmium ions by its monodentate sulfonic, monodentate carboxylate and chelating carboxylate groups. Four sipa^{3−} ligands and four cadmium ions form a 32-membered ring unit, Cd₄(sipa)₄. The two kinds of units, Cd₄(sipa)₄ and Cd₄(bpy)₄, interlock and interconnect with each other to produce a self-penetrating structural unit (Figure 1),^[2c,14] in which the sipa^{3−} ligand penetrates through the Cd₄(bpy)₄ ring and strong face to face π–π stacking interactions involving the aromatic rings from the closest neighboring sipa^{3−} and bpy ligands (with an average distance of about 3.50 Å) is observed. Each Cd₄(bpy)₄ unit interlocks two Cd₄(sipa)₄ units and each Cd₄(sipa)₄ unit interlocks two Cd₄(bpy)₄ units through cadmium ion nodes, yielding an interwoven structure that is extended in different directions forming a three-dimensional self-penetrating topological network.

In the Cd₄(bpy)₄ unit, four cadmium ions are coplanar, and two such adjacent planes have a dihedral angle of 57°. Therefore, through the sharing of the vertex cadmium ion knots, the Cd₄(bpy)₄ units are further extended into a one-dimensional twisted 8-like chain (see a in Figure 2). Through the sharing of the sipa^{3−} sides, the Cd₄(sipa)₄ units propagate a one-dimensional ladder-like chain (see b in Figure 2), in which all the cadmium ions are coplanar and the sipa^{3−} ligands are situated in the zygomorphic sites of the plane. The two types of one-dimensional chains interlock and interweave together to form a two-dimensional framework through the sharing of cadmium ions in the *ab* plane (see c in Figure 2). The 1-D ladder-like chains comprising Cd₄(sipa)₄ units possess an AB array (left, direction up; right, direction down) along the *a* axis and AA array along the *c* axis, while the 1-D twisted 8-like chains formed by the Cd₄(bpy)₄ units have an AA illustration down the *b* axis and ABC display along the *c* axis. The two-dimensional structure extend in different directions generating a 3-D packing network with micro channels that can accommodate free water molecules (Figure 3). It is worth noting that the structure of **1** reveals a new topological net: Cd1 acts as a “6-connected” center, Schläfli symbol (4²; 6⁴; 8⁹); Cd2 as a “4-connected” center, Schläfli symbol (4; 6⁴; 8); and sipa^{3−} as a “3-connected” center, Schläfli symbol (6²; 8). Considering the stoichiometry, the overall topology is (Cd1)(Cd2)₂(sipa)₂, Schläfli symbol (4²; 6⁴; 8⁹)(4; 6⁴; 8)₂ (6²; 8)₂.

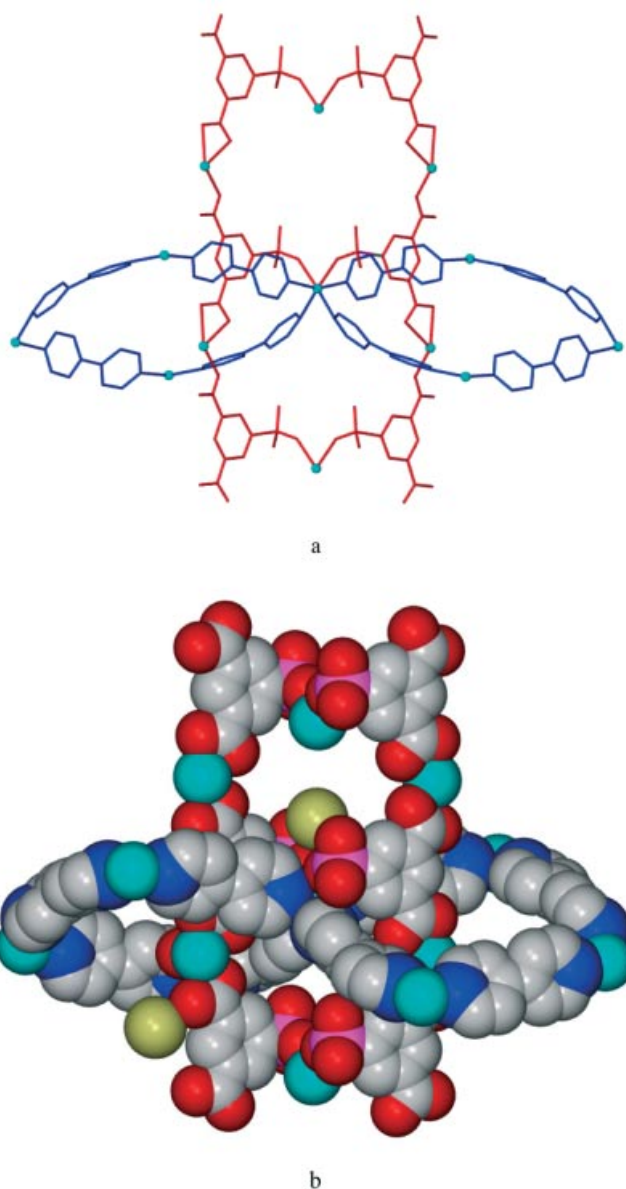


Figure 1. (a) The interlocking self-penetrating unit formed by Cd₄(sipa)₄ (red) and Cd₄(bpy)₄ (blue) units through sharing node Cd²⁺ ions; (b) space-filling diagram: turquoise sphere representing Cd²⁺ ion, brown-yellow: free water, scarlet red: oxygen, gray: carbon, blue: nitrogen, pink: sulfur

The thermogravimetric analysis (TGA) study shows that the first weight loss of 5.75% (calcd: 5.86%) observed from 63 to 144 °C corresponds to the loss of three free water and coordinated water molecules per formula unit (5H₂O/{[Cd₃(sipa)₂(bpy)₄(H₂O)₂]}·3H₂O}), and the structural framework begins to collapse at 340 °C. Heating-cooling and dehydrate-hydrate experiments were carried out according to the TGA results, and monitored by X-ray powder diffraction. The crystalline sample of complex **1** is heated to 145 °C under autogenous pressure for 4 hours, the guest water molecules are lost from the sample and some characteristic XRPD peaks become weaker or disappear. However, when the resulting dehydrated products are immersed

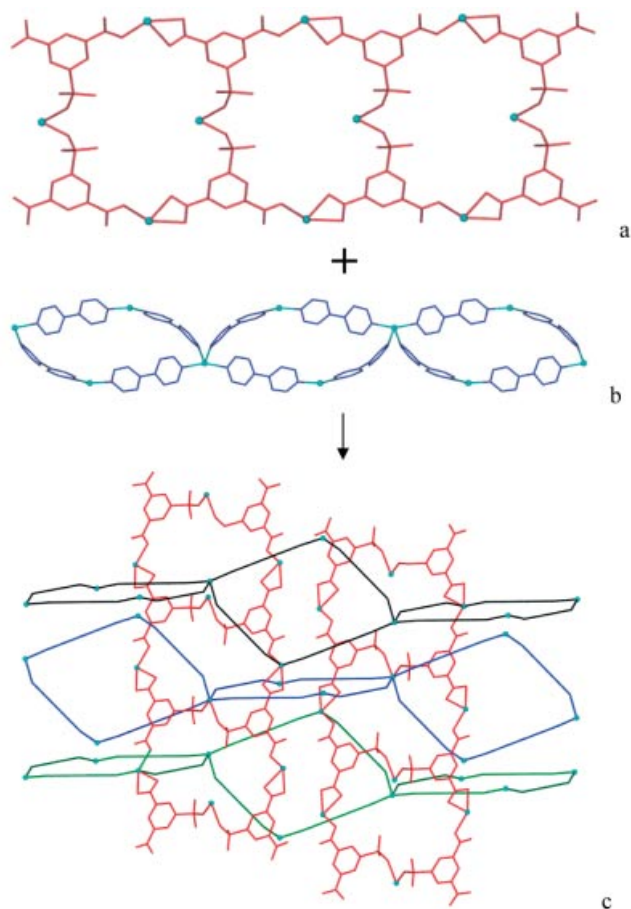


Figure 2. (a) 1-D ladder-like chains formed by $\text{Cd}_4(\text{sipa})_4$ units (red); (b) 1-D twisted 8-like chains formed by $\text{Cd}_4(\text{bpy})_4$ units (blue); (c) schematic presentation of 2-D framework in the ab plane

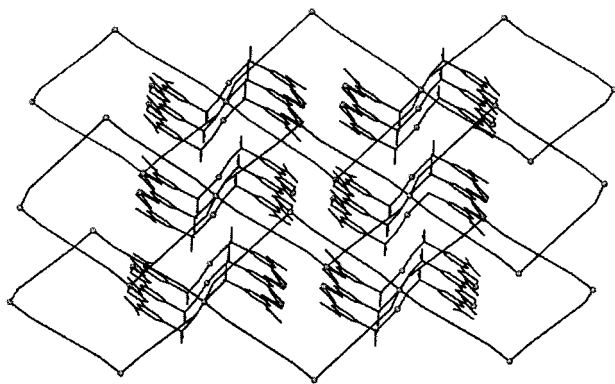


Figure 3. 3-D packing structure for **1** along the b axis, guest water molecules are omitted for clarity

in water for 12 hours, the XRPD pattern and infrared spectrum for the rehydrated sample are almost the same as those of the original sample, illustrating that the framework of **1** is retained on the removal of guest water molecules. The details of the XRPD analyses for **1** are provided as Supporting Information. The luminescence spectrum of **1** in the solid state at ambient temperature exhibits an intense

broadband fluorescent emission at 453 nm on photo-excitation at 354 nm, suggesting that **1** may be suitable as a candidate for a stable and solvent-resistant blue fluorescent material due to its stability in air and insolubility in common solvents.^[15]

In summary, a novel three-dimensional self-penetrating network constructed from two mixed bridging ligands has successfully been prepared; although many entangled structures have been reported, those constructed by mixed bridging ligands are rather few. The present work shows that a novel structure can be designed and assembled through the combination of the topology of organic ligand and the coordination geometry of metal ion. Further studies on this subject are still underway.

Experimental Section

Synthesis of 1: A mixture of NaH_2sipa (0.266 g, 1.0 mmol), $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.231 g, 0.75 mmol), 4,4'-bipyridine dihydrate (0.192 g, 1.0 mmol) and water (10 mL) was placed in a 25 mL Teflon[®]-lined stainless autoclave under autogenous pressure at 160 °C for 3 days after which it was cooled slowly to room temperature over a 24 hour period. The light yellow block-like crystals of **1** were separated from the reaction mixture in about a 23% yield (0.35 g). $\text{C}_{56}\text{H}_{48}\text{Cd}_3\text{N}_8\text{O}_{19}\text{S}_2$: calcd. C 43.72, H 3.14, N 7.28; found C 43.60, H 2.94, N 7.31%. IR (KBr (cm^{-1})): 1605 (vs), 1556 (s), 1491 (w), 1416 (m), 1363 (s), 1230 (s), 1198 (s), 1105 (w), 1043 (m), 806 (m), 719 (w), 629 (m), 582 (m), 492 (w), 432 (w).

X-ray Crystallography: $\text{C}_{56}\text{H}_{48}\text{Cd}_3\text{N}_8\text{O}_{19}\text{S}_2$, **1**, $M_r = 1538.34$, $0.28 \times 0.22 \times 0.18 \text{ mm}^3$, monoclinic, space group $C2/c$, $a = 35.578(4)$, $b = 10.232(1)$, $c = 16.211(1) \text{ Å}$, $\beta = 108.913(2)^\circ$, $V = 5583.5(1) \text{ Å}^3$, $Z = 4$, $D_c = 1.830 \text{ Mg/m}^3$, $F_{000} = 3072$, $\mu = 1.293 \text{ mm}^{-1}$, $T = 298(2) \text{ K}$, $2\theta_{\text{max}} = 50.1^\circ$, 8252 reflections collected, 4836 unique ($R_{\text{int}} = 0.0437$). Final GooF = 1.077, $R_1 = 0.0469$, $wR_2 = 0.0833$ with $I > 2\sigma(I)$.

Data collection for **1** was performed on a Siemens SMART-CCD diffractometer equipped with a graphite-monochromated Mo- K_α radiation ($\lambda = 0.71073 \text{ Å}$) at 293 K. All absorption corrections were applied using the SADABS program. The structures were solved by direct methods, the metal atoms were located from the E-maps, and other non-hydrogen atoms were derived from the successive difference Fourier syntheses. The hydrogen atoms were located from the difference map and refined isotropically. The structure was refined on F^2 by full-matrix least-squares using the SHELXTL-97 program package.

CCDC-221212 (for **1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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