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A Homochiral Luminescent 2D Porous Coordination Polymer with Collagen-Type Triple Helices Showing Selective Guest Inclusion

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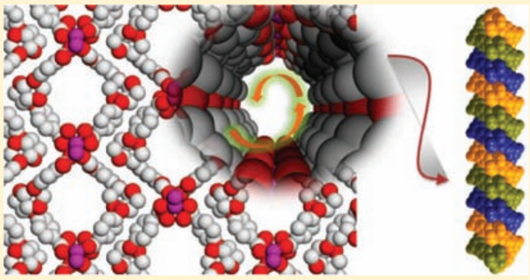
Supporting Information

ABSTRACT: A homochiral luminescent porous coordination polymer, $[Cd(L)(H_2O)]\cdot 3H_2O$, with interconnected collagen like triple-helical chains has been synthesized solvothermally by using cadmium(II) salt and a newly designed D-isosorbide-based, enantiomerically pure chiral ligand. The framework is a 2D porous material and forms a 1D channel along the *a* axis, with the channel dimensions ~6.2 × 4.4 Å^2. The compound has high selectivity in the uptake of water and methanol over other solvents (e.g., tetrahydrofuran, ethanol, benzene, and cyclohexane) inside the channels.



INTRODUCTION

Homochirality and helicity are ubiquitous in nature and are essential to various biological functions. Helices are also the central structural motifs in biological molecules, like α-helical protein, DNA, and collagens are with single-, double-, and triple-helix structures, respectively. All of these helical biopolymers are composed of either the D or L form of basic units and always acquire either left- or right-handedness. Structural studies of helicate compounds with chiral building blocks may help to understand such kinds of unique structural behavior of natural chiral helical biopolymers.[1,2]

Among different types of chiral compounds, in recent years, homochiral coordination polymers or metal–organic frameworks (MOFs)[3] have attracted much attention because of their potential applications in enantioselective catalysis and separation[4−6] and the importance of chirality in biological processes.[2] Because of the lack of chiral porous zeolites, homochiral porous coordination polymers (PCPs) are particularly very attractive materials for industrial applications for the separation of chiral mixtures and as heterogeneous asymmetric catalysts for the economical production of optically active organic compounds. Although numerous examples of porous, achiral PCPs with extremely high surface areas are reported,[7,8] the rational design and synthesis of homochiral porous materials still remains a challenge. Such materials are generally prepared by self-assembly process using three synthetic strategies: (1) spontaneous resolution, (2) chiral induction, and (3) use of enantiopure ligands. In the first method, achiral or racemic ligands form homochiral materials by spontaneous resolution during the self-assembly process, but mostly bulk racemates result with only a few exceptions.[9] In the second method, an auxiliary chiral ligand induces homochirality into the framework without direct involvement in structure formation.[3b,10] These two methods are quite unpredictable because their mechanisms are not yet very clear. The use of enantiopure ligands, on the other hand, is a direct and effective method for the synthesis of homochiral porous materials, where the use of enantiopure ligands leads to generation of a single enantiomeric product.[11] D-Isosorbide is an accessible enantiopure small molecule derived from glucose, and it and its different derivatives have therapeutic uses. Like many other moieties containing hydroxyl groups, modifying the hydroxyl groups of D-isosorbide by organic moieties with proper functional groups can be one of the most effective ways to obtain enantiopure organic ligands. Herein, by attaching a benzoic acid group in a para position with the hydroxyl groups of D-isosorbide, we have synthesized a dicarboxylic acid-based ligand LH_2. We obtained a porous two-dimensional (2D) homochiral compound $[Cd(L)(H_2O)]\cdot 3H_2O$ (**1**) by the self-assembly of LH_2 with cadmium(II) by a solvothermal method. To the best of our knowledge, D-isosorbide-based enantiopure ligands have not been used to synthesize coordination polymers.

EXPERIMENTAL SECTION

Materials and Measurements. All of the reagents and solvents were commercially available and used without further purification. Fourier transform infrared (FTIR) spectra (Figure S8 in the Supporting Information) were recorded on a Nicolet 6700 FTIR spectrophotometer using KBr pellets. Powder X-ray diffraction (PXRD) patterns were measured on a Bruker D8 Advanced X-ray diffractometer at room temperature (RT) using Cu Kα radiation (λ = 1.5406 Å). Thermogravimetric analysis (TGA) was recorded on a Perkin-Elmer STA 6000 TGA analyzer under a N_2 atmosphere with a heating rate of 10 °C/min.

Synthesis of Ligand L′. D-Isosorbide (10 g, 0.0684 mol) and NaH (3.45 g, 0.1436 mol) were mixed in *N*,*N*-dimethylformamide (DMF; 120 mL) solvent under a N_2 atmosphere. Then the reaction mixture was stirred at 75 °C for 10 min. After that, 4-(fluoroethyl)benzoate (23.01 g, 0.1368 mol) was added dropwise. The reaction was continued for 3 h. After cooling to RT, excess NaH was quenched with ice and ethyl acetate. A maximum amount of DMF was removed by

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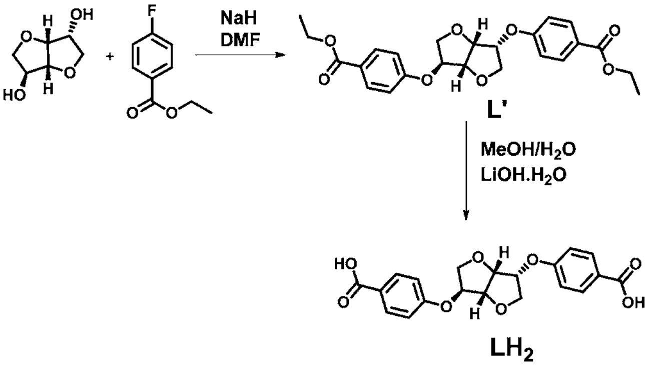
rotary evaporation under reduced pressure, and the mixture was extracted with EtOAc (2 × 250 mL). The combined organic layer was washed with 150 mL of brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to get a crude product, which was purified on silica gel (100 and 200 mesh) column chromatography.

Yield: 15.28 g, 50.52%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39 (dt, J = 1.36 and 7.32 Hz, 6H), 4.06 (d, J = 5.48 Hz, 2H), 4.10 (d, J = 10.52 Hz, 1H), 4.20 (dd, J = 4.12 and 10.56 Hz, 1H), 4.35 (q, J = 7.18 Hz, 4H), 4.67 (d, J = 5.04 Hz, 1H), 4.29−4.87 (m, 2H), 5.04 (t, J = 5.26 Hz, 1H), 6.95−7.01 (m, 4H), 8.00−8.03 (m, 4H). HRMS. Calcd for L′Na ([M + Na]$^+$): 465.46. Found: 465.1525 (Figures S1 and S2 in the Supporting Information).

Scheme 1



Synthesis of Ligand LH_2 (Scheme 1). L′ (15.28 g, 0.035 mol) was dissolved in 250 mL of methanol (MeOH) and 150 mL of water (H_2O). Thereafter, LiOH·H_2O (8.82 g, 0.21 mol) was added at 0 °C. The reaction mixture was stirred overnight. Excess MeOH was removed under reduced pressure and acidified with diluted HCl to get the desired product. The product was filtered, washed with fresh H_2O, and dried under vacuum.

Yield: 9.28 g, 69.8%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.90−3.93 (m, 2H), 4.005 (dd, J = 4.16 and 11 Hz, 2H), 4.58 (d, J = 4.12 Hz, 1H), 5.01−5.05 (m, 3H), 7.04 (d, J = 8.24 Hz, 2H), 7.09 (d, J = 8.68 Hz, 2H), 7.86 (d, J = 8.68 Hz, 2H), 7.91 (d, J = 8.72 Hz, 2H) (Figure S2 in the Supporting Information).

Synthesis of [Cd(L)(H_2O)]·3H_2O (1). Single crystals of **1** were prepared by reacting 0.125 mmol of Cd$(NO_3)_2$·4H_2O, 0.125 mmol of ligand (LH_2), and 0.2 mmol of NaOMe in 3 mL of H_2O and 2 mL of tetrahydrofuran (THF) by a solvothermal technique, in a Teflon-lined autoclave. The autoclave was heated under autogenous pressure at 160 °C for 3 days and then cooled to RT for a 24 h period. Upon cooling to RT, the desired product appeared in ∼45% yield.

X-ray Structural Studies. Single-crystal X-ray data of compound **1** were collected at 200 K on a Bruker Kappa APEX II CCD Duo diffractometer (operated at 1500 W power, 50 kV, 30 mA) using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). The crystal was on nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). Data integration and reduction were processed with *SAINT*[15] software. A multiscan absorption correction was applied to the collected reflections. The structure was solved by direct method using *SHELXTL*[16] and was refined on F^2 by a full-matrix least-squares technique using the *SHELXL-97*[17] program package within the *WINGX*[18] program. All non-H atoms were refined anisotropically. All H atoms were located in successive difference Fourier maps, and they were treated as riding atoms using *SHELXL* default parameters. The structures were examined using the *Adsym* subroutine of *PLATON*[19] to ensure that no additional symmetry could be applied to the models. Tables 1 and 2 contain crystallographic data for compound **1**.

Low-Pressure Gas Sorption Measurements. Low-pressure gas sorption measurements were performed using BelSorpmax (Bel Japan). All of the gases used were of 99.999% purity. An as-synthesized compound was heated at 160 °C under vacuum for 16 h to get guest-free compound **1D**. Prior to adsorption measurement, the guest-free sample **1D** was pretreated at 150 °C under vacuum for 5 h using BelPrepvacII and purged with N_2 upon cooling.

Table 1. Crystal Data and Structure Refinement for Compound 1

identification code	compound **1**
empirical formula	$C_{20}H_{24}CdO_{12}$
fw	568.79
temperature (K)	200(2)
wavelength (Å)	0.71073
cryst syst	orthorhombic
space group	$C222_1$
unit cell dimens	a = 7.3160(5) Å b = 26.4953(19) Å c = 24.2927(17) Å
volume (Å^3)	4708.9(6)
Z	8
density (calcd) (Mg/m^3)	1.605
abs coeff (mm^{-1})	0.988
F(000)	2304
cryst size (mm^3)	0.15 × 0.14 × 0.10
θ range for data collection (deg)	1.75−28.69
index ranges	$-7 \le h \le 9$, $-35 \le k \le 33$, $-25 \le l \le 32$
reflns collected	13528
indep reflns	5550 [R(int) = 0.0658]
completeness to θ = 28.69°	99.9%
abs correction	semiempirical from equivalents
max and min transmn	0.9077 and 0.8660
refinement method	full-matrix least squares on F^2
data/restraints/param	5550/0/294
GOF on F^2	1.125
final R indices [$I > 2\sigma(I)$]	R1 = 0.0659, wR2 = 0.1695
R indices (all data)	R1 = 0.0693, wR2 = 0.1715
absolute structure param	0.00(6)
largest diff peak and hole (e/Å^3)	1.511 and −2.065

■ RESULTS AND DISCUSSION

Compound **1** was synthesized by a solvothermal reaction of LH_2 and Cd$(NO_3)_2$·4H_2O in a THF/H_2O mixture solvent and characterized by a single-crystal X-ray diffraction (SC-XRD) technique. The phase purity of as-synthesized compound **1** was confirmed by PXRD measurement. SC-XRD analysis revealed that compound **1** crystallizes into a chiral orthorhombic crystal system, space group $C222_1$ with a Flack parameter of 0.00(6), indicating enantiomeric purity of the single crystals. Circular dichroism (CD) measurement (Figure S5 in the Supporting Information) and NMR of LH_2, together with NMR of the digested MOF (Figures S3 and S4 in the Supporting Information), show that racemization of the chiral ligand does not occur under solvothermal conditions. The asymmetric unit of **1** consists of one L, two Cd^{II} ions with half-occupancy, and four H_2O molecules (one-coordinated and three-non-coordinated). One cadmium (Cd1) has an octahedral coordination environment with an O6 donor set from two coordinated H_2O molecules and four carboxylate O atoms from four different ligands. The other cadmium (Cd2) also has an octahedral geometry but in distorted shape with an O6 donor set from two monodentate and two bidentate carboxylate groups from four different ligands. Cd−O distances are in the ranges of 2.242−2.276 Å for Cd1 and 2.259−2.427 Å for Cd2.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Compound1[a]

Cd1−O7#2	2.242(5)	Cd2−O2#2	2.259(5)
Cd1−O7#3	2.242(5)	Cd2−O2	2.259(5)
Cd1−O1#4	2.260(7)	Cd2−O8#2	2.315(6)
Cd1−O1	2.260(7)	Cd2−O8	2.315(6)
Cd1−O9#4	2.276(7)	Cd2−O7	2.427(5)
Cd1−O9	2.276(7)	Cd2−O7#2	2.427(5)
		O7−Cd1#6	2.242(5)
		O7−Cd1#6	2.242(5)
O7#2−Cd1−O7#3	90.7(3)	O2#2−Cd2−O2	81.7(3)
O7#2−Cd1−O1#4	98.6(2)	O2#2−Cd2−O8#2	93.1(2)
O7#3−Cd1−O1#4	82.1(2)	O2−Cd2−O8#2	163.8(2)
O7#2−Cd1−O1	82.1(2)	O2#2−Cd2−O8	163.8(2)
O7#3−Cd1−O1	98.6(2)	O2−Cd2−O8	93.1(2)
O1#4−Cd1−O1	178.9(3)	O8#2−Cd2−O8	95.9(3)
O7#2−Cd1−O9#4	172.0(3)	O2#2−Cd2−O7	108.4(2)
O7#3−Cd1−O9#4	89.4(2)	O2−Cd2−O7	89.4(2)
O1#4−Cd1−O9#4	89.2(3)	O8#2−Cd2−O7	106.74(19)
O1−Cd1−O9#4	90.0(3)	O8−Cd2−O7	56.02(19)
O7#2−Cd1−O9	89.4(2)	O2#2−Cd2−O7#2	89.4(2)
O7#3−Cd1−O9	172.0(3)	O2−Cd2−O7#2	108.4(2)
O1#4−Cd1−O9	90.0(3)	O8#2−Cd2−O7#2	56.02(19)
O1−Cd1−O9	89.2(3)	O8−Cd2−O7#2	106.74(19)
O9#4−Cd1−O9	91.7(4)	O7−Cd2−O7#2	156.7(3)
		Cd1#6−O7−Cd2	109.5(2)

[a] Symmetry transformations used to generate equivalent atoms: #1, $x - {}^{3}/_{2}, y - {}^{1}/_{2}, z$; #2, $-x, y, -z + {}^{1}/_{2}$; #3, $x + 1, y, z$; #4, $-x + 1, y, -z + {}^{1}/_{2}$; #5, $x + {}^{3}/_{2}, y + {}^{1}/_{2}, z$; #6, $x - 1, y, z$.

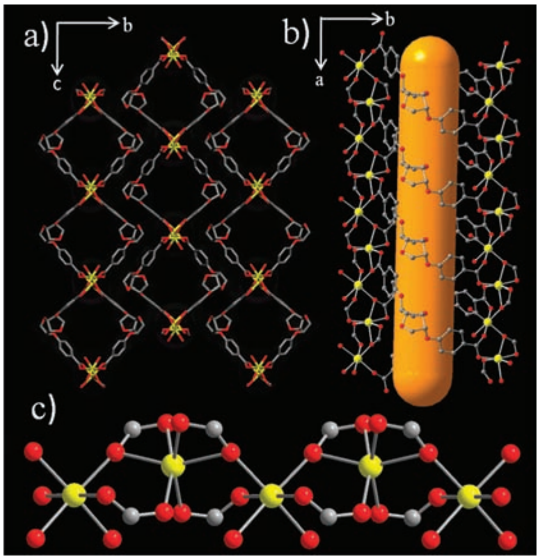


Figure 1. (a) Packing diagram of compound **1** along the *bc* plane. (b) View of the 1D channel running along the *a* axis shown. (c) Coordination environment around the metal centers showing two different types of Cd^{II} in the metal carboxylate chain. (Color code: cadmium, yellow; carbon, gray; oxygen, red. H atoms and free solvents are omitted for clarity).

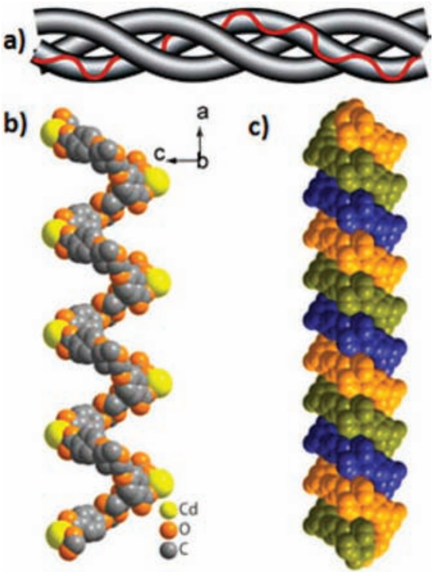


Figure 2. (a) Structure of collagen. (b) Space-filling views of the left-handed single-helical chain and (c) triple-helical chains of compound **1**.

One of the two O atoms of the bidentate carboxylate groups coordinated to Cd2 is bridged with the other cadmium (Cd1) from both sides, thus extending the metal carboxylate chain along the *a* axis. Because of the roof-type arrangement of the D-isosorbide core and the flexibility in the ether moiety, the dicarboxylate ligand could arrange itself into a V shape. This V-shaped ligand coordinated to the cadmium ions at both ends with carboxylate O atoms, and this subsequently resulted in a 2D porous coordination framework (Figures 1 and S6 and S7 in the Supporting Information).

The most interesting feature of the structure is its triple-helical[12] arrangement of the framework, very similar to the triple-helical structure of a group of biologically important protein molecules called collagen. Each V-shaped dicarboxylate-based ligand connected to Cd^{II} at both ends has resulted in a left-handed helical strand with a pitch of 14.632 Å and a width of ca. 13 Å. It is noteworthy that the pitch of this helix is even greater than the pitch of most open protein helices, i.e., polyproline (9.36 Å).[13] Three such identical helical chains are extended along the *a* axis to form a left-handed triple-helical structure (Figure 2). This structure has a very good resemblance to the structures of collagen types II, III, VII, VIII, and X, where three identical α chains (homotrimers) form right-handed triple-helical supramolecular structures.[14] These helices interconnect each other and also by both sides edge sharing at Cd^{II} with two identical triple helices result in the 2D homochiral framework.

The results of solid-state CD spectral measurements in the wavelength range 400−250 nm confirmed the enantiopure nature of the ligand LH_2 and compound **1**. As shown in Figure 3, the ligand and bulk crystals of **1** in powder form show a positive Cotton effect at 297.95 and 291.03 nm, respectively, revealing its homochiral nature. The enantiopure nature of compound **1** also supports the SC-XRD structure with chiral space group $C222_1$ and a Flack parameter value of 0.00(6). These results also indicate that there is no racemization of the ligand during solvothermal synthesis, and the chiral feature transfers from the original chiral ligand to the framework.

The resultant 2D framework is a porous sheetlike architecture and forms a 1D channel along the *a* axis within the 2D sheets, with maximum channel dimensions ~6.2 × 4.4 $Å^2$ (the channel size is measured by considering the van der Waals radii for constituting atoms). The cavities of the framework are occupied by disordered H_2O molecules.

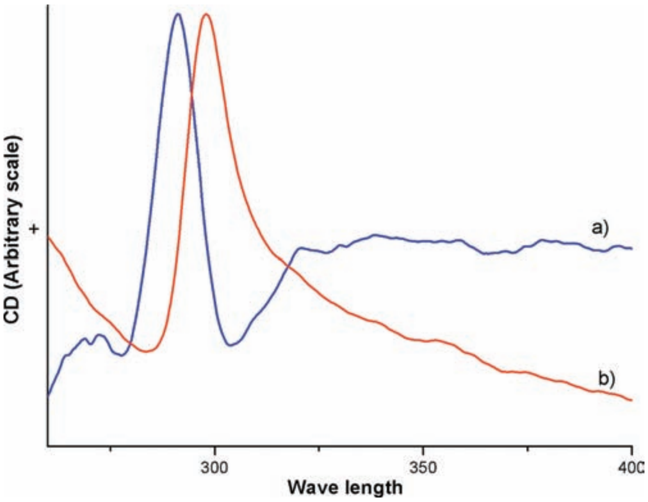


Figure 3. Solid-state CD spectra of (a) compound **1** and (b) ligand LH_2.

PLATON[20] analysis revealed that the 2D porous structure contains voids of 1035.5 Å^3 that represent 22% per unit cell volume.

TGA analysis revealed that the framework is stable up to 400 °C (Figure S9 in the Supporting Information). The desolvated phase (**1D**) was generated by heating the compound for 16 h at 160 °C under reduced pressure. TGA data confirm the removal of guest H_2O molecules. Very similar PXRD data of **1D** with the as-synthesized compound **1** suggest that the framework is quite rigid after removal of coordinated H_2O molecules. A slight flexible behavior of the framework was observed after removal of the guest H_2O molecules, as we can see from slight variations in the PXRD pattern of **1D**. To test the reversibility of the transformation, we exposed **1D** to H_2O vapor for 3 days; the desolvated phase transformed to its original structure, which was confirmed by PXRD data (Figure 4).

To check the porous properties of the 2D chiral framework (**1D**), we carried out gas and solvent sorption measurements. It shows no uptake of N_2 (1.62 cm^3/g) but some uptake for CO_2 (13.54 cm^3/g) (Figure S10 in the Supporting Information). The pore size of the as-synthesized compound is 6.2 × 4.4 Å^2, but the PXRD pattern (Figure 4c) of the desolvated compound is little different from that of the as-synthesized compound. This indicates that the desolvated structure is not exactly the same as the as-synthesized compound, and most probably the pore size is squeezing after removal of the guest molecules. It is well-known in the literature and we also observed recently in one of our compounds that it is not always only the pore size but also host–guest interaction that decides the amount of adsorbate taken by the MOF.[21,22] CO_2 has a smaller kinetic diameter and a larger quadrupole moment value than N_2, so it can interact more strongly with the surface of the pore in the host framework, thus showing little uptake and hysteresis behavior. Interesting phenomena were observed in solvent sorption experiments at 298 K. Selective sorption of H_2O[23−27] and MeOH was observed over many other organic solvents [ethanol (EtOH), THF, benzene, and cyclohexane; Figures 5 and S11 in the Supporting Information]. Very small amounts of other organic solvent sorption compared to H_2O and MeOH are desirable for removal of H_2O and MeOH from organic solvents. After removal of coordinated H_2O molecules, the framework now has open metal sites and also the pore is hydrophilic in nature because of the presence of several O atoms on the pore surface. Although the pore size of the desolvated phase may not be big enough to enter guest molecules into the pore (as we can see from PXRD, the structure changed and most probably squeezed after removal of the coordinated guest molecules present in the pore) but because of the hydrophilic nature of the pore surface and open metal sites, H_2O and MeOH molecules strongly interact with the surface and so enter into the pore, which is also supported by the flexible nature of the ligand. Also, because of the strong interaction of H_2O and MeOH with the pore surface, desorption becomes very difficult and therefore hysteresis sorption profiles are shown.[28]

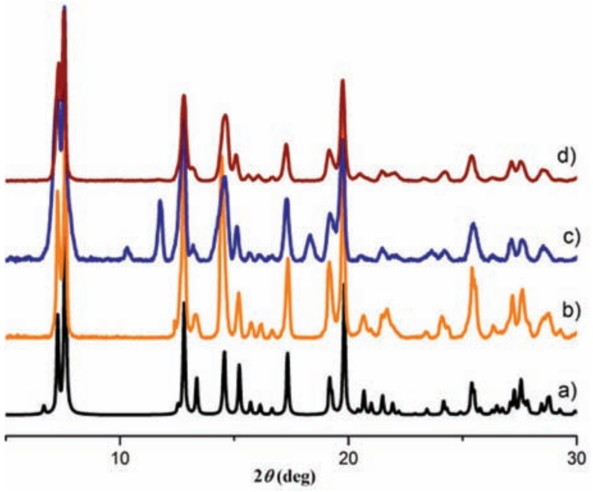


Figure 4. (a) Simulated, (b) as-synthesized, (c) desolvated, and (d) resolvated PXRD patterns of compound **1**.

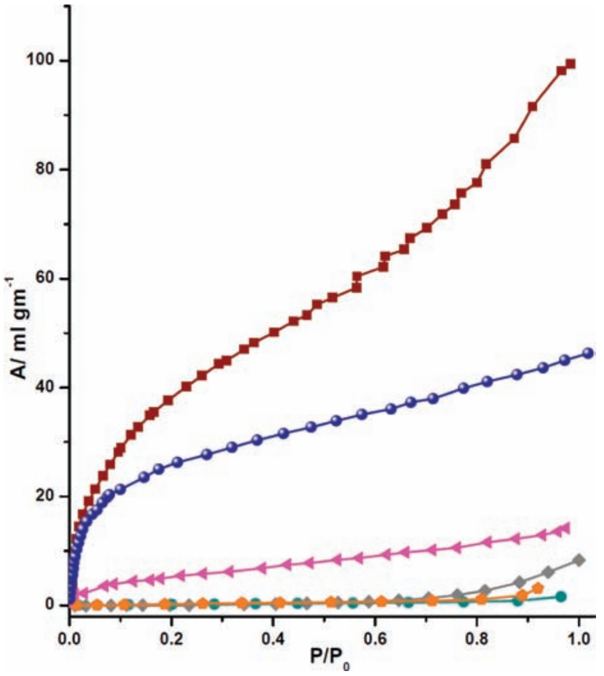


Figure 5. Solvent sorption graphs of compound **1D**. (Color code: H_2O, wine; MeOH, royal blue; EtOH, pink; THF, gray; cyclohexane, dark cyan; benzene, orange).

Luminescent properties of compound **1** (d^{10} metal complex) were examined at RT by solid-state fluorescence spectra (Figure 6). The intense fluorescence spectrum was observed at 363 and 354 nm (upon excitation at 281 nm) for compounds **1** and **1D**, respectively. A luminescent spectrum of LH_2 was also recorded under the same conditions. Ligand LH_2 exhibits a fluorescent band at 402 nm (upon excitation on 291 nm). The shift of the emission spectra from 402 to 363 nm upon complexation is due to the deprotonation and the chelating coordination action of the carboxylate anion. The slight shift of the spectrum for the desolvated compound from the as-synthesized compound may be due to the change in the coordination environment.

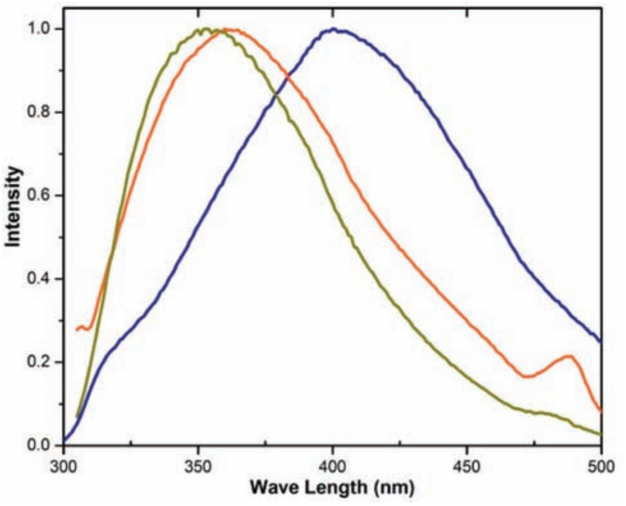


Figure 6. Emission spectra for solid-state compounds at RT. (Color code: ligand, blue; as-synthesized compound, orange and desolvated compound, dark yellow).

In conclusion, we have designed one D-isosorbide-based enantiopure dicarboxylic acid based ligand, and with Cd^{II}, a luminescent homochiral porous framework has been synthesized solvothermally and characterized. The framework consists of interconnected triple-helical chains, very similar to the triple-helical structure of a group of biologically important protein molecules called "collagen". Enantiopurity of the new ligand and its cadmium(II) framework has been checked by CD measurements. The porous framework is very stable even after removal of the guest molecules, which shows size-selective inclusion of H_2O and MeOH over other solvents (e.g., THF, ethanol, benzene, and cyclohexane) inside the channels.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

HRMS, NMR, and FTIR spectra, TGA, sorption isotherms, and X-ray crystallographic data of compound **1** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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