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# Highly Stable Chiral Cadmium 1,2,4-Benzenetricarboxylate: Synthesis, Structure, and NLO and Fluorescence Properties

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Employing an unsymmetrical 1,2,4-benzenetricarboxylate as a bridging ligand, a new 3-D chiral cadmium coordination polymer [Cd$_2$(OH)(1,2,4-BTC)] (1,2,4-BTC = 1,2,4-benzenetricarboxylate) has been prepared under hydrothermal conditions and characterized by single crystal X-ray diffraction. This compound crystallizes in the orthorhombic space group $P2_12_12_1$, with cell parameters $a = 6.900(2)$ Å, $b = 7.404(3)$ Å, $c = 19.116(5)$ Å, $V = 976.5(5)$ Å$^3$, and $Z = 4$. Its structure contains 2-D Cd–O–Cd connectivity, which is further linked by the 1,2,4-BTC ligand into a 3-D supramolecular framework. The 1,2,4-BTC ligand shows a novel and unprecedented coordination mode: nine bonds to eight metals with each carboxylate as a tridentate group. The compound exhibits intense photoluminescence at room temperature and shows distinct NLO properties. On the basis of the results of TG/DTA analyses, the structure is thermally stable up to ∼ 380 °C.

## Introduction

The construction of metal−organic frameworks (MOFs) based on metal−ligand coordinative covalent bonding is of great interest, mostly motivated by their intriguing structural features and enormous range of applications in catalysis and adsorbent and molecular recognition.[1] Yaghi and co-workers have demonstrated that MOFs can be designed and constructed to generate cavities or channels of various sizes and shapes through control of the architecture and functionalization of organic linkers.[2] However, to date, the precise prediction of a MOF with a chiral framework employed in heterogeneous asymmetric catalysis and enantioselective separations is still a daunting task because the formation of such a framework is governed by many factors, such as possible noncovalent intermolecular forces, the solvent, the reaction composition, the type of templates used, et cetera.[3] The control of framework chirality is particularly difficult because the reaction mechanisms have not been understood so far.[4]

Most chiral frameworks reported to date were synthesized from simple achiral components under a spontaneous condition without any chiral sources, such as $[In_2(OH)_2(BTC)_2]_n\cdot 2nHpy$, $Zn_2(BTC)(NO_3)\cdot H_2O\cdot 5C_2H_5OH$, et cetera.[5] A more straightforward approach is the use of chiral organic linkers or chiral metal complexes as structure-directing agents.[6] Recent work performed by Lin et al. has demonstrated that chiral MOFs can be synthesized by combining unsymmetrical bridging ligands and metal centers with well-defined coor-

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dination geometries.[7−9] Accordingly, a series of chiral MOFs based on metal pyridinecarboxylates have been obtained, such as [Zn(isonicotinato)$_2$],[7b] [Zn(nicotinato)$_2$],[7c] and M{4-[2-(4-pyridyl)ethenyl]benzoate}$_2$ (M = Zn, Cd), et cetera.[7d] It seems that the asymmetry of the organic ligands can be transferred to certain building units of those compounds, which can further connect to each other by organic ligands to form chiral topologies and maintain the original asymmetry. To explore the synthetic strategy of chiral MOFs, Chen et al. reported the use of a new synthetic technique that employed in situ generation of unsymmetrical organic ligands under hydrothermal conditions to prepare chiral compounds.[10]

Keeping in mind the aforementioned points, we believe that the structures of unsymmetric bridging ligands have a significant effect on the recognition and crystallization of metal centers into chiral solids; therefore, we extended our research into the metal/unsymmetric bridging carboxylate system to obtain new chiral compounds. As a result, in this article, we report an exceptionally stable chiral coordination polymer [Cd$_2$(OH)(1,2,4-BTC)] **1** (1,2,4-BTC = 1,2,4-benzenetricarboxylate), which is generated from unsymmetrical 1,2,4-benzenetricarboxylate and shows distinct NLO and fluorescence properties.

## Experimental Section

**General Methods.** All chemicals used in these syntheses were of reagent grade and used as purchased without further purification. Infrared (IR) spectra were recorded from KBr pellets in the range of 400−4000 cm$^{-1}$ on a Nicolet Impact 410 FTIR spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 element analyzer. Thermogravimetric analyses (TGA) and differential thermal analyses (DTA) were carried out on a Perkin-Elmer TGA 7 thermogravimetric analyzer and a Perkin-Elmer DTA 1700 differential thermal analyzer in air with a heating rate of 5 °C min$^{-1}$.

**Synthesis of [Cd$_2$(OH)(1,2,4-BTC)] (1).** Compound **1** was hydrothermally prepared from a reaction mixture of $CdCl_2 \cdot 2.5H_2O$ (0.219 g, 1 mmol), 1,2,4-BTC (0.420 g, 2 mmol), NaOH (0.240 g, 6 mmol), and distilled water (10 mL) in a molar ratio of 1:2:6:555. The mixture was stirred for 20 min at room temperature and then crystallized in a Teflon-lined stainless steel autoclave with a 23 mL capacity at 220 °C for 120 h. After cooling, colorless crystals for single crystal X-ray diffraction were obtained with a yield of 68% based on Cd. Anal. Calcd for $C_9H_4O_7Cd_2$: C, 24.06; H, 0.89. Found: C, 23.92; H, 0.78. IR (KBr pellet, 4000−400 cm$^{-1}$): 3607 (vs), 3411 (s), 2923 (w), 1561 (s), 1518 (s), 1484 (s), 1357 (vs), 1246 (w), 1135 (w), 1067 (m), 939 (w), 871 (w), 829 (s), 786 (s), 727 (s), 599 (w), 548 (w), 488 (w), 454 (m).

**Table 1.** Crystal Data and Structure Refinement Parameters for **1**

| | |
|---|---|
| empirical formula | $C_9H_4O_7Cd_2$ |
| fw | 448.92 |
| space group | $P2_12_12_1$ (no. 19) |
| $a$, Å | 6.900(2) |
| $b$, Å | 7.404(3) |
| $c$, Å | 19.116(5) |
| $V$, Å$^3$ | 976.5(5) |
| $Z$ | 4 |
| $T$, K | 293(2) |
| $\lambda$(Mo K$\alpha$), Å | 0.71073 |
| $\rho_{calc}$ g cm$^{-3}$ | 3.053 |
| $\mu$(Mo K$\alpha$), mm$^{-1}$ | 4.380 |
| $R_1{}^a[I > 2\sigma(I)]$ | 0.0339 |
| $wR_2{}^b[I > 2\sigma(I)]$ | 0.0776 |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)]^2\}^{1/2}$.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for **1**[a]

| | | | |
|---|---|---|---|
| Cd(1)−O(6)#1 | 2.244(7) | Cd(2)−O(7) | 2.221(6) |
| Cd(1)−O(1)#2 | 2.258(8) | Cd(2)−O(4) | 2.274(7) |
| Cd(1)−O(7)#3 | 2.263(7) | Cd(2)−O(3)#5 | 2.328(7) |
| Cd(1)−O(7) | 2.307(7) | Cd(2)−O(2)#6 | 2.342(7) |
| Cd(1)−O(5)#4 | 2.332(7) | Cd(2)−O(5)#7 | 2.365(7) |
| Cd(1)−O(3) | 2.420(7) | Cd(2)−O(2)#5 | 2.421(7) |
| O(6)#1−Cd(1)−O(1)#2 | 129.0(3) | O(7)−Cd(2)−O(4) | 102.2(3) |
| O(6)#1−Cd(1)−O(7)#3 | 83.7(3) | O(7)−Cd(2)−O(3)#5 | 105.3(2) |
| O(1)#2−Cd(1)−O(7)#3 | 88.2(3) | O(4)−Cd(2)−O(3)#5 | 152.1(3) |
| O(6)#1−Cd(1)−O(7) | 97.0(3) | O(7)−Cd(2)−O(2)#6 | 97.4(3) |
| O(1)#2−Cd(1)−O(7) | 79.8(3) | O(4)−Cd(2)-O(2)#6 | 90.1(3) |
| O(7)#3−Cd(1)−O(7) | 165.04(17) | O(3)#5−Cd(2)−O(2)#6 | 81.5(2) |
| O(6)#1−Cd(1)−O(5)#4 | 146.2(3) | O(7)−Cd(2)−O(5)#7 | 175.8(3) |
| O(1)#2−Cd(1)−O(5)#4 | 82.7(3) | O(4)−Cd(2)−O(5)#7 | 79.1(3) |
| O(7)#3−Cd(1)−O(5)#4 | 86.6(3) | O(3)#5−Cd(2)−O(5)#7 | 73.8(2) |
| O(7)−Cd(1)−O(5)#4 | 100.5(2) | O(2)#6−Cd(2)−O(5)#7 | 86.5(3) |
| O(6)#1−Cd(1)−O(3) | 81.8(3) | O(7)−Cd(2)−O(2)#5 | 83.9(2) |
| O(1)#2−Cd(1)−O(3) | 145.3(3) | O(4)−Cd(2)−O(2)#5 | 116.1(3) |
| O(7)#3−Cd(1)−O(3) | 113.7(2) | O(3)#5−Cd(2)−O(2)#5 | 72.2(2) |
| O(7)−Cd(1)−O(3) | 81.1(2) | O(2)#6−Cd(2)−O(2)#5 | 153.0(2) |
| O(5)#4−Cd(1)−O(3) | 72.7(2) | O(5)#7−Cd(2)−O(2)#5 | 91.9(3) |

[a] Symmetry transformations used to generate equivalent atoms: #1: $x - 1/2, -y + 1/2, -z + 1$; #2: $-x, y - 1/2, -z + 1/2$; #3: $-x, y + 1/2, -z + 1/2$; #4: $-x + 1/2, -y + 1, z - 1/2$; #5: $-x + 1, y - 1/2, -z + 1/2$; #6: $x, y - 1, z$; and #7: $x + 1/2, -y + 1/2, -z + 1$.

**Crystallographic Studies.** A suitable colorless single crystal with dimensions of 0.15 × 0.08 × 0.05 mm$^3$ was glued to a thin glass fiber and mounted on a Siemens Smart CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (graphite-monochromatic Mo *K*α radiation ($\lambda$ = 0.71073 Å)) operating at 50 kV and 40 mA. Intensity data were collected at room temperature. Data processing was performed using the SAINT processing program.[11] The total numbers of measured reflections and observed unique reflections were 2363 and 1436, respectively. The structure was solved in the space group $P2_12_12_1$ by direct methods and refined on $F^2$ by full-matrix least-squares methods using SHELXTL97.[12] All non-hydrogen atoms were easily found from the different Fourier maps and refined anisotropically. The hydrogen atoms on the ligand were placed geometrically. The crystallographic data and details on refinements for **1** are summarized in Table 1. Selected bond distances and angles are listed in Table 2.

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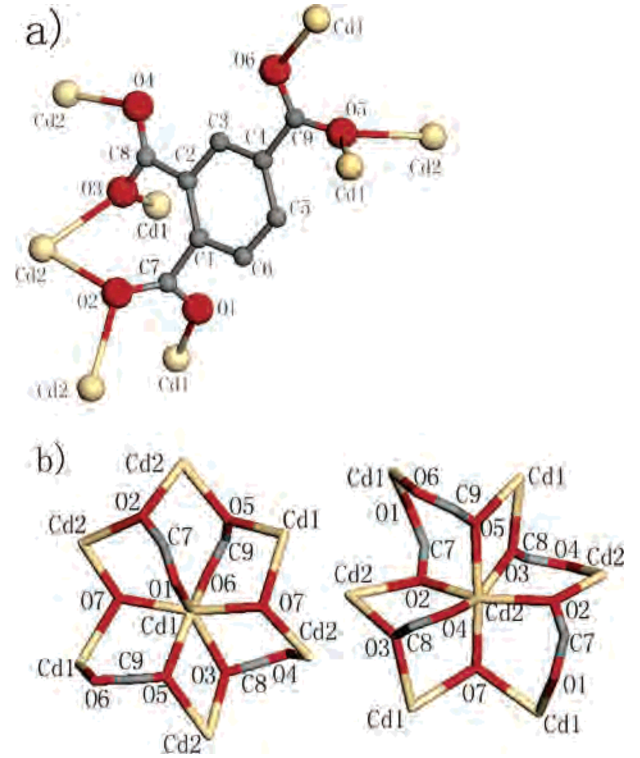

**Figure 1.** (a) Novel coordination mode of the 1,2,4-BTC ligand in compound **1**. (b) Details of the coordination environments of Cd1 and Cd2.

## Results and Discussion

The hydrothermal reaction of 1,2,4-BTC with Cd(II) yields crystals of a product that was formulated as [$Cd_2(OH)$(1,2,4-BTC)] by elemental analyses and a single crystal X-ray diffraction study. The reaction temperature of 200 °C is crucial for the crystallization of the compound. We tried to synthesize the compound at a temperature lower than 200 °C but failed. Colorless crystals of this compound are stable in air and insoluble in water and common organic solvents such as alcohol, toluene, THF, DMF, and DMSO. The absence of the expected characteristic bands at 1730−1690 $cm^{-1}$ (IR) attributed to protonated carboxylate groups indicates the complete deprotonation of 1,2,4-BTC in reactions with Cd(II) ions.

A single crystal X-ray diffraction study performed on **1** revealed an extended 3-D coordination framework that crystallizes in the chiral space group $P2_12_12_1$. The asymmetric unit of **1** consists of two Cd centers, one 1,2,4-BTC anion, and one hydroxyl ion. The 1,2,4-BTC ligand shows a novel and unprecedented coordination mode (Figure 1a): nine bonds to eight metals with each carboxylate as a tridentate group, which has not been seen in other metal 1,2,4-BTC compounds.[13] The number of coordination sites of the 1,2,4-BTC unit here is much higher in metal carboxylates[14−16] and several compounds with 12 bonds to 10 metals, and 10 bonds to 8 metals were found in the 1,2,4,5-benzenetetracarboxylate system.[17] The hydroxyl ion bridges the Cd centers in a slightly unsymmetrical fashion with Cd1−O7 distances of 2.263(7) and 2.307(7) Å and a Cd2−O7 distance of 2.221(6) Å. Both Cd1 and Cd2 atoms adopt highly distorted octahedral coordination geometries. The Cd1 center (Figure 1b) coordinates to four bridging carboxylate oxygen atoms of four separated 1,2,4-BTC ligands and two bridging $\mu_3$-OH oxygen atoms with Cd−O bond distances in the range of 2.244(7)−2.420(7) Å (av (Cd−O) = 2.304 Å), whereas the Cd2 center coordinates to five bridging carboxylate oxygen atoms of four separated 1,2,4-BTC ligands and one $\mu_3$-OH oxygen atom with Cd−O bond distances in the range of 2.221(6)−2.421(7) Å (av (Cd−O) = 2.325 Å). The O−Cd−O angles are in the range of 72.7(2)−165.04(17)° for Cd1 and 72.2(2)−175.8(3)° for Cd2. More data on selected bond distances and angles are presented in Table 2.

Interestingly, in contrast to previously reported metal carboxylates, such as $Zn_3(BDC)_3 \cdot 6CH_3OH$,[18a] $Tb_2(BDC)_3 \cdot (H_2O)_4$,[18b] and $[Cu_3(TMA)_2(H_2O)_2]_3$,[18c] the connectivity of the metal center here is much more complex. Four types of metal-center connectivity have been found in **1**, as shown in Figure 1b: cadmium centers (i) bridged by two carboxylates; (ii) bridged by a carboxylate and a $\mu_3$-OH oxygen atom; (iii) bridged by two carboxylate oxygen atoms; and (iv) bridged by a carboxylate and a carboxylate oxygen atom. This is quite unusual. The dihedral angles between the benzene rings (C1/C2/C3) and the three different carboxylate moieties are 64.6 (C7/O1/O2), 11.1 (C8/O3/O4), and 14.2° (C9/O5/O6), showing that all bonding carboxylate groups strongly deviate from the aromatic ring plane.

The most interesting feature of the structure of **1** is its 2-D inorganic cadmium−oxygen layer along the *c* axis (Figure 2a), which consists of edge-sharing $CdO_6$ octahedra and the 3 and 4 rings of $CdO_6$ octahedra in a 1:1 ratio. This inorganic layer has a two-fold screw axis along the *b* axis. The chains of the Cd1$O_6$ octahedra link the chains of the Cd2$O_6$ octahedra, building up a sandwich, as shown in Figure 2b. Thus, the chiral structure can be viewed as a

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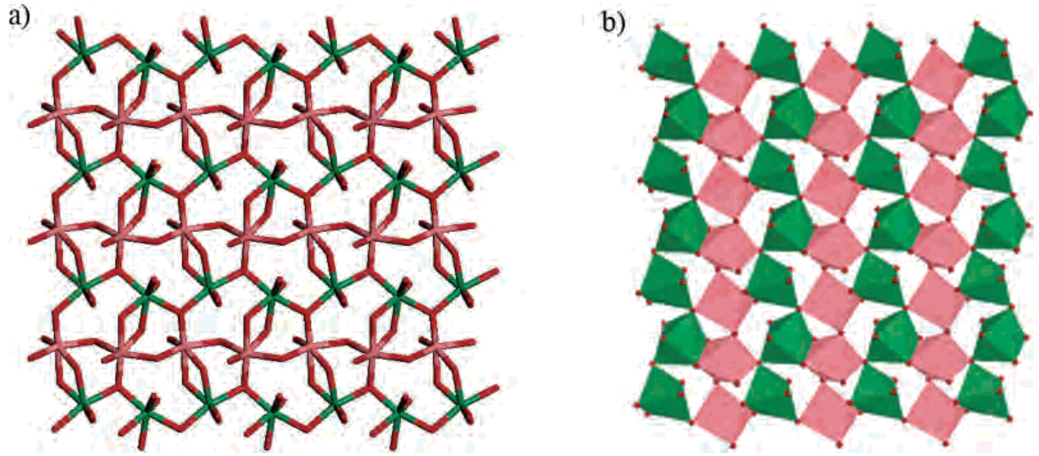

**Figure 2.** (a) Infinite chiral Cd−O−Cd sheets along the *c* axis. (b) Octahedra of the inorganic cadmium−oxygen layer viewed like a sandwich. (Bottle green represents the Cd1O$_6$ octahedra, and pink represents the Cd2O$_6$ octahedra.)

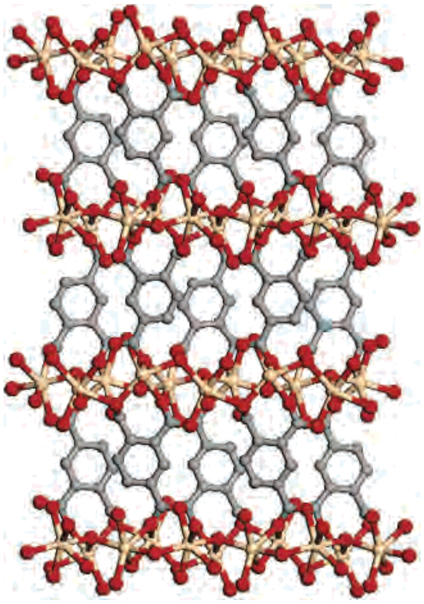

**Figure 3.** View of the 3-D chiral framework along the *b* axis. Color code: Cd, yellow; C, gray; N, blue; and O, red.

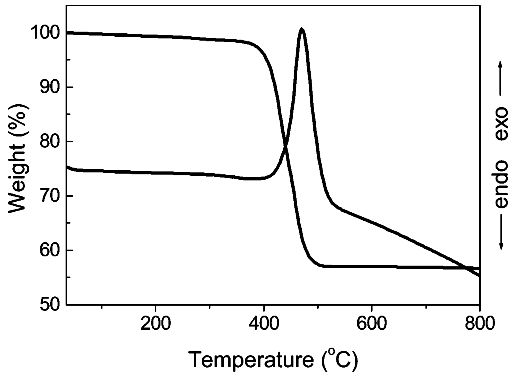

**Figure 4.** DTA−TGA curves for **1** in air.

construction of 1,2,4-BTC linkers connecting the chiral cadmium−oxygen layers and producing a 3-D framework (Figure 3). It is well shown that multidimensional M−O−M frameworks offer advantages in several respects compared to MOFs with isolated metal atoms or clusters. For instance, In$_2$(OH)$_3$(BDC)$_{1.5}$ with 2-D In−O−In sheets was used as a reductant of nitroaromatic substrates and as an oxidant of organic sulfides;[19] however, Co$_2$(OH)$_2$BDC with 2-D Co−O−Co sheets has an unusual metamagnetism.[20] To our knowledge, this is the first instance where such 2-D M−O−M connectivity has been observed in a chiral metal carboxylate.

To understand the thermal stability, we performed the differential thermal analysis (DTA) and thermogravimetric analysis (TGA) in air. Figure 4 shows the DTA−TGA curves for **1**. No weight loss was found before 380 °C, and above this temperature, the structure collapsed because the organic ligand was removed. The surprising thermal stability of **1** is mainly due to the structure, which is reinforced by the presence of strong metal coordination bonds with 1,2,4-BTC units and the existence of infinite inorganic layers. The curve showed an obvious weight loss at 400−530 °C, which is characteristic for the combustion of the organic moiety (weight loss expt, 43.30 wt %: calcd, 42.86 wt %).

Second-order nonlinear optical effects for the powder sample of **1** have been investigated by optical second-harmonic generation (SHG) at room temperature. The intensity of the green light (frequency-doubled output: $\lambda = 532$ nm) produced by the powder sample of the compound is about 0.3 times that produced by a KDP powder, indicating that the compound has a SHG effect that is weaker than that of KDP.[21]

The photoluminescence spectrum of **1** was measured in the solid state at room temperature (Figure 5). Upon excitation at 236 nm, the emission spectrum for the com-

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(19) Gomez-Lor, B.; Gutierrez-Puebla, E.; Iglesias, M.; Monge, M. A.; Ruiz-Valero, C.; Snejko, N. *Inorg. Chem.* **2002**, *41*, 2429.

(20) Kurmoo, M.; Kumagai, H.; Green, M. A.; Lovett, B. W.; Blundell, S. J.; Ardavan, A.; Singleton, J. *J. Solid State Chem.* **2001**, *159*, 343.

(21) The powder second-harmonic generation test was carried out on the sample by the Kurtz and Perry method.[22] Second-harmonic generation intensity data were obtained by placing a powder sample in an intense fundamental beam from a Q-switched Nd:YAG laser of wavelength 1064 nm. The output ($\lambda = 532$ nm) was filtered first to remove the multiplier and was then displayed on an oscilloscope. This procedure was then repeated using a standard NLO material (microcrystalline KDP), and the ratio of the second-harmonic intensity outputs was calculated.

(22) Kurtz, S. W.; Perry, T. T. *J. Appl. Phys.* **1968**, *39*, l3798.

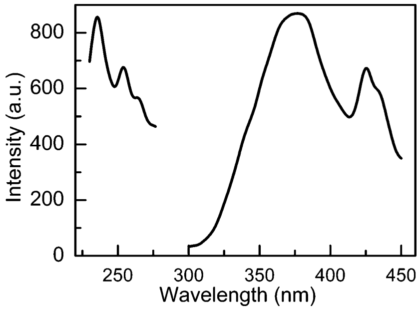

**Figure 5.** Solid-state fluorescence spectra of **1** at room temperature.

pound shows a main peak at 376 nm and a shoulder at about 422 nm. The emission band at 422 nm is attributable to the $\pi^* \rightarrow$ n transitions of the organic ligand because a similar emission band at about 425 nm has also been observed upon excitation at 280 nm for the 1,2,4-BTC ligand. The strong emission at 376 nm can be assigned to ligand−metal charge transfer. The strong fluorescence emission of **1** makes it a potentially useful photoactive material because it is thermally stable and insoluble in common polar and nonpolar solvents.

We attempted to measure the CD spectrum of the sample to understand the L and D percentage distribution of the chiral crystals and observed a complex spectrum with several unsigned up−down absorptions, which apparently needs further study.

## Conclusions

The new 3-D chiral cadmium coordination polymer bridged by unsymmetrical 1,2,4-BTC [$Cd_2(OH)(1,2,4\text{-}BTC)$] has been prepared and characterized. Its structure contains 2-D inorganic cadmium−oxygen layers, which are further linked by a 1,2,4-BTC ligand into a 3-D supramolecular framework. The 1,2,4-BTC ligand shows a novel and unprecedented coordination mode: nine bonds to eight metals with each carboxylate as a tridentate group. The compound exhibits intense photoluminescence at room temperature and shows distinct NLO properties. It remains stable when desolvated and heated to 380 °C. Recent work performed by Lin, Chen, and us shows that the structures of unsymmetric bridging ligands have a significant effect on the recognition and crystallization of metal centers into chiral solids. Further research on this system may focus on the replacement of cadmium and 1,2,4-BTC with other transition metals and unsymmetrical carboxylate ligands to prepare novel polymeric compounds with chiral or noncentrosymmetric structures and explore their valuable properties.

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**Supporting Information Available:** Crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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