

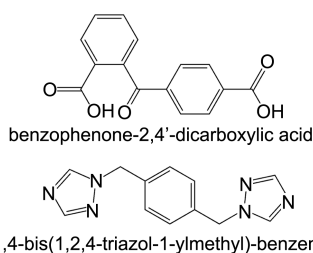
A CdSO₄-like 3D Framework Constructed from Benzophenone-2,4'-dicarboxylic Acid and 1,4-Bis(1,2,4-triazol-1-ylmethyl)-benzene: Synthesis, Structure and Physical Properties

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Investigations into coordination polymers remain intensely active not only because of their diverse topology and intriguing structures but also because of their potential applications in many fields, such as ion-exchange, heterogeneous catalysts, optical devices, magnets, and gas storage.¹⁻⁶ It is well known that the structure of the coordination polymer is mainly influenced by some factors such as temperature, the neutral ligands, the organic anions, the metal atoms, and so on.^{7,8} Among these factors, the organic ligand is the key factor that influences the construction of coordination polymer. Up to now, a number of symmetrical V-shaped aromatic polycarboxylic derivatives, such as 4,4'-oxybis(benzoic acid), 4,4'-sulfonyldibenzoic acid, benzophenone-4,4'-dicarboxylic acid, 2,2-Bis(4-carboxyphenyl)hexafluoropropane, and so on, have been extensively used to prepare coordination polymers.⁹⁻¹² However, benzophenone-2,4'-dicarboxylic acid (H₂BPDC) as an asymmetrical V-shaped aromatic polycarboxylic derivatives have received less attention in the construction of coordination polymers (Scheme 1).¹³ On the other hand, as a flexible derivative of triazole, the 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene (BTX) possesses the merits of triazole which can coordinate with the metal ions in various modes (Scheme 1). In addition, the phenylene ring and triazole ring can freely rotate to meet the requirements of the coordination geometries of metal atoms on the basis of its -CH₂- spacer.¹⁴ Taking these into consideration, we explored the self-assembly of a Cd(II) ion, H₂BPDC, and BTX under hydrothermal conditions, and obtained a novel 3D coordination polymer: {[Cd(BTX)-(BPDC)]H₂O}_n. Herein, we report the synthesis, crystal structure, and physical properties.



Scheme 1. Structural formula of BTX and H₂BPDC.

Experimental Section

Materials and Physical Measurements. The 1,4-bis(triazol-1-ylmethyl)-benzene (BTX) ligand was synthesized according to the literature method.¹⁵ All other reagents and solvents were commercially available and used without further purification. Infrared spectrum was obtained within the 4000-400 cm⁻¹ as KBr disks on a VECTOR 22 spectrometer. Elemental analysis was performed on a Perkin Elmer 240C elemental analyzer. Powder X-ray diffraction (PXRD) patterns were obtained on a Shimadzu XRD-6000 X-ray diffractometer with Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation at room temperature. Fluorescent spectrum was recorded on a Fluoro Max-P spectrophotometer. Thermal gravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris 1 TGA analyzer from room temperature to 950 °C with a heating rate of 20 °C min⁻¹ under nitrogen.

Synthesis of {[Cd(BTX)(BPDC)]H₂O}_n (1). A mixture of Cd(NO₃)₂·6H₂O (0.0346 g, 0.100 mmol), H₂BPDC (0.0270 g, 0.100 mmol), BTX (0.0240 g, 0.100 mmol) and KOH (0.00560 g, 0.100 mmol) in H₂O (10 mL) was sealed in a 16 mL Teflon-lined stainless steel container and heated at 150 °C for 72 h. After cooling to room temperature, colorless block crystals were collected by filtration and washed by water and ethanol several times (yield 23.3%, based on BTX). Elemental analysis for C₂₇H₂₂CdN₆O₆ (Mr = 638.92): C 50.76, H 3.47, N 13.15%; found: C 50.90, H 3.48, N 13.17%. IR (KBr, cm⁻¹): 3549 (m), 3462 (m), 3139 (m), 1655 (m), 1619 (s), 1597 (s), 1557 (w), 1371 (s), 1279 (s), 1133 (m), 999 (s), 927 (s), 842 (s), 770 (s), 730 (s), 672 (s), 471 (w).

Structural Determination and Refinement. Crystallographic diffraction data for complex **1** was recorded on a Siemens (Bruker) SMART CCD diffractometer using monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 291 K. Absorption correction was applied using multi-scan technique. The structure was solved by direct method using the program SHELXL-97 and refined by full-matrix least-squares technique on F^2 with SHELXL-97.¹⁶ All non-hydrogen atoms were located in difference Fourier maps and refined with anisotropic temperature parameters. All H atoms were refined isotropically, with the isotropic vibration parameters

Table 1. Crystal and experimental data of **1**

Empirical formula	C ₂₇ H ₂₂ CdN ₆ O ₆	
Formula weight	638.92	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
<i>a</i> / Å	9.576(2)	
<i>b</i> / Å	14.123(4)	
<i>c</i> / Å	18.793(5)	
β / °	91.437(3)	
<i>V</i> / Å ³	2540.8(11)	
<i>D</i> _{calc} / g·m ⁻³	1.670	
<i>F</i> (000)	1288	
Limits of data collection / °	1.80 ≤ θ ≤ 26.00	
Reflections collected	18638	
Independent reflections (<i>R</i> _{int})	4990 (0.0643)	
Goodness of fit	1.070	
<i>R</i> indices (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> ₁ = 0.0443, <i>wR</i> ₂ = 0.1055	
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0564, <i>wR</i> ₂ = 0.1117	

$$R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \omega R_2 = \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}^{1/2}$$

Table 2. Selected bond distances (Å) and angles (°) for **1**

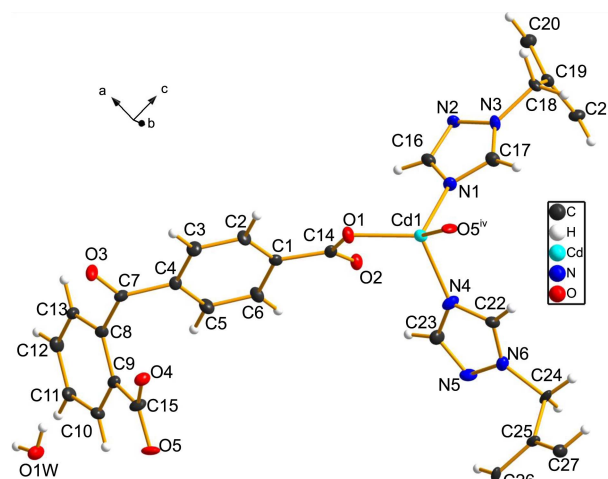
Cd(1)-N(1)	2.010(3)	Cd(1)-N(4)	2.022(3)
Cd(1)-O(1)	1.958(3)	Cd(1)-O(5) ⁱ	1.994(3)
O(1)-Cd(1)-N(1)	111.53(13)	O(1)-Cd(1)-N(4)	113.57(14)
O(1)-Cd(1)-O(5) ⁱ	114.62(12)	O(5) ⁱ -Cd(1)-N(1)	109.50(13)
O(5) ^{iv} -Cd(1)-N(4)	97.03(12)	N(1)-Cd(1)-N(4)	109.70(14)

Symmetry transformations used to generate equivalent atoms: ⁱ*x*, -*y*+1/2, *z*+1/2.

related to the non-H atom to which they are bonded. A summary of the structural determination and refinement for the title complex is listed in Table 1 and the selected bond distances and angles are shown in Table 2.

Results and Discussions

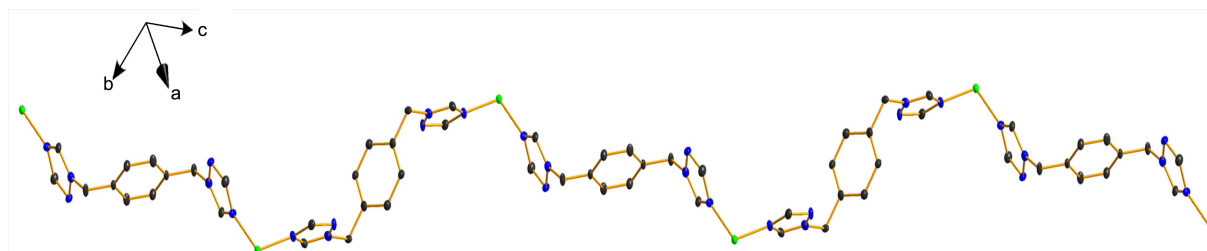
As shown in Figure 1, complex **1** crystallizes in the centrosymmetric monoclinic space group *P*2₁/*c* with an asymmetric unit consisting of a divalent cadmium ion, one fully deprotonated BPDC ligand, two crystallographically independent halves of BTX ligands (btx-A, N1-N3; btx-B, N4-N6) and one lattice water molecule. Each Cd(II) center possesses a {CdO₂N₂} coordination environment, with two

**Figure 1.** An ORTEP drawing of **1** showing 30% ellipsoid probability. Symmetry codes: *iv* *x*, -*y*+1/2, *z*+1/2.

triazole nitrogen donor atoms from two different BTX ligands and two oxygen donor atoms from monodentate carboxylate groups belonging to two different BPDC²⁻ ligands (Cd1-O1 = 1.958(3), Cd1-O5^{iv} = 1.994(3), Cd1-N1 = 2.010(3), Cd1-N4 = 2.022(3)) [symmetry codes: (*iv*) *x*, -*y*+0.5, *z*+0.5] (Figure 1). The distortion of the tetrahedron can be indicated by the calculated value of the τ_4 parameter, which is 0.93 for Cd1 (for a perfect square planar geometry, τ_4 equals 0; a perfect tetrahedral geometry is described when τ_4 equals 1), showing the tetrahedral geometry is not perfect but distorted.¹⁷ Cd1 atoms are connected into zig-zag [Cd(BTX)]_n chains by BTX-A and BTX-B ligands (Figure 2). The Cd...Cd contact distances through the crystallographically distinct BTX ligands are 14.9055(30) and 14.6580(23) Å. These differences are provided by conformational variances within the distinct BTX ligands. In complex **1**, BTX-A and BTX-B ligands lying on an inversion centre adopt *trans* conformations, and two triazole rings are parallel to each other in the same ligand. In BTX-A, the dihedral angle between the planes of triazole and benzene rings is 86.0(1)°, the related dihedral angle in BTX-B is 102.9(8)°.

Adjacent [Cd(BTX)]_n chains are conjoined into a 3D [Cd(BTX)(BPDC)]_n coordination polymer (Figure 3) by bridging BPDC²⁻ ligands that bridge pairs of Cd atoms with a Cd...Cd contact distance of 9.4259(25) Å.

A further insight into the nature of this intricate frame-

**Figure 2.** View of zig-zag [Cd(BTX)]_n chain.

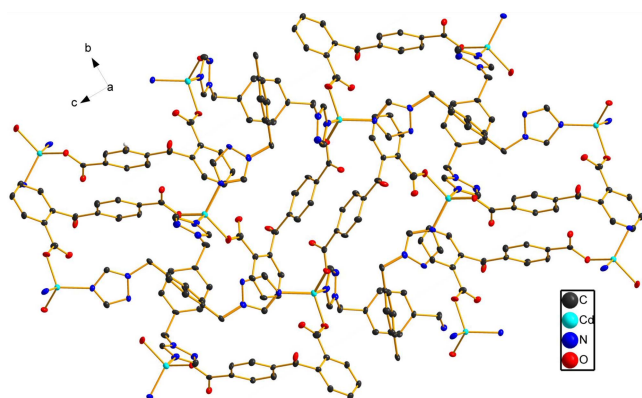


Figure 3. View of 3D structure of complex 1.

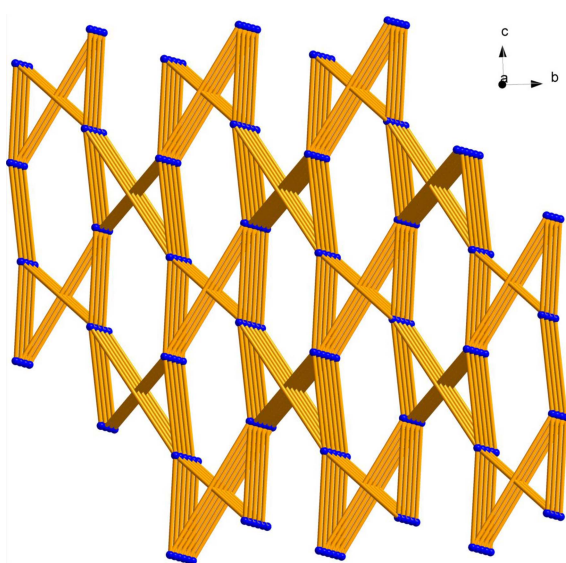


Figure 4. Network perspective of the 4-connected 3D ($6^5 \cdot 8$) point symbol in complex 1. The blue spheres represent the Cd atom nodes.

work can be acquired by using topological analysis. A topological analysis of this net was performed with TOPOS software.¹⁸ From the topological point of view, if the CdII ions are considered as 4-connected nodes, the BPDC and BTX ligands are reduced to linkers, the whole framework can be simplified as a 4-connected net with the ($6^5 \cdot 8$) topology. Comparing the topology of complex 1 with those of known minerals, 1 possesses the distorted CdSO_4 topology, as shown in Figure 4. The unligated water molecules occupy a solvent-accessible incipient space comprising 5.3% of the unit cell volume, according to PLATON.¹⁹

The phase purity of the as-synthesized complex 1 was testified by X-ray powder diffraction (XRPD) experiment. The peak positions of the experimental and simulated XRPD patterns are in good agreement with each other, which demonstrates that complex 1 has been obtained successfully as a pure crystalline phase (Figure 5). The differences in intensity may be owing to the preferred orientation of the powder samples.

Thermogravimetric analysis of 1 (Figure 6) demonstrates

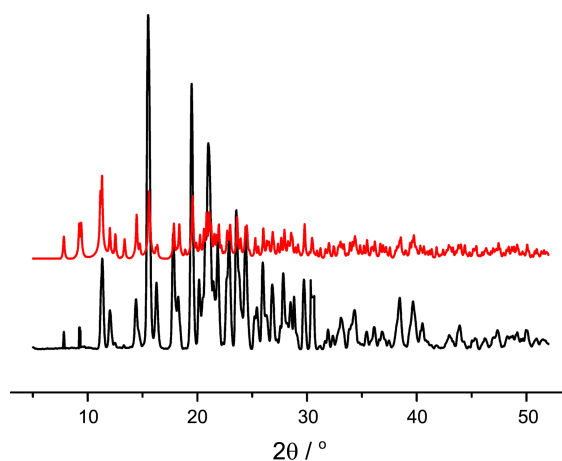


Figure 5. The simulated (Black) and experimental (Red) PXRD of complex 1.

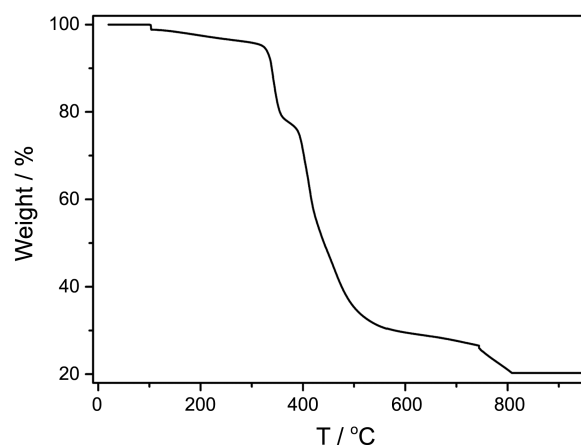


Figure 6. Thermogravimetric curve of complex 1.

that a weight loss of 2.71% in 25–105 °C corresponds to the release of one lattice water molecules (calculated 2.82%) for complex 1. The organic ligands began to decompose at 320 °C, with the 20.24% mass remnant at 810 °C consistent with production of CdO (20.10% calcd).

The photoluminescent property of complex 1 has been studied in the solid state at room temperature. The free ligands show the emission maximum at 462 nm for BTX (excitation at 395 nm) and at 394 nm for H_2BPDC (excitation at 350 nm), which may be caused by the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transition.²⁰ Irradiation of complex 1 with ultraviolet light ($\lambda_{\text{ex}} = 340$ nm) in the solid state resulted in a relatively emission band centered on ~ 415 nm (Figure 7), which is blue-shifted by 47 nm with respect to the free BTX. According to a recent review of d^{10} metal coordination polymer luminescence, the Cd(II) ions are difficult to oxidize and reduce. As a result, the emissive behavior of 1 can be attributed to ligand-centered electronic transitions.²¹

In conclusion, we have successfully synthesized a new cadmium(II) coordination polymer based on benzophenone-2,4'-dicarboxylic acid and 1,4-bis(1,2,4-triazol-1-ylmethyl)-benzene, which is characterized by IR, elemental analysis, thermal analysis and single-crystal X-ray diffraction. The

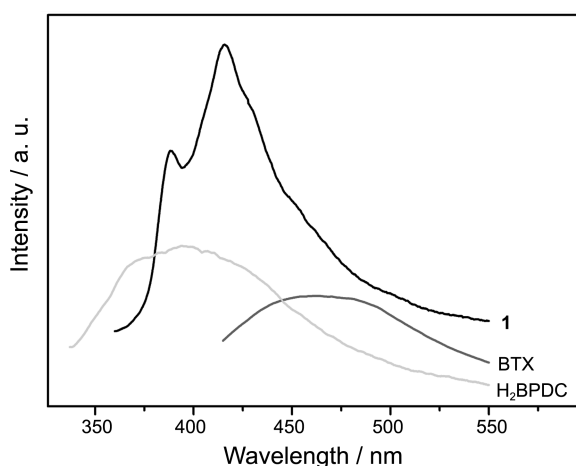


Figure 7. The solid-state emission spectrum of complex **1** recorded at room temperature.

crystal structure of complex **1** shows a novel three-dimensional framework with 4-connected 3D CdSO₄ topology. In addition, complex **1** exhibits strong fluorescent emissions in the solid state at room temperature.

Supplementary Material. CCDC-911506 (**1**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Telephone: (44) 01223 762910; Facsimile: (44) 01223 336033; E-mail: deposit@ccdc.cam.ac.uk].

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