

A Novel Coordination Polymer Based on 4,4'-(Hexauroisopropylidene)diphthalic Acid: Synthesis, Structure and Physical Properties

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The design and synthesis of coordination polymers is an attractive area of research, not only owing to their diverse topology and intriguing structures but also due to their potential applications in many fields, such as ion-exchange, catalysis, luminescence, magnets, and gas storage.¹⁻⁶ The mainstream method of constructing such coordination polymers is to utilize organic ligands with aromatic polycarboxylate groups, because of their excellent coordination capability and flexible coordination patterns. Among them, aromatic polycarboxylic derivatives, such as 1,2,4,5-benzenetetra-carboxylic acid, 4,4'-oxydiphthalic acid, 4,4'-(hexauroisopropylidene)diphthalic acid (H₄FA), and so on, have been extensively used to prepare coordination polymers.⁷⁻⁹ Meanwhile, the flexible 1,4-bis(1,2,4-triazol-1-ylmethyl)-benzene (BTX) as an excellent derivative of triazole not only possesses the merits of triazole, but also can adopt different conformations compared with the corresponding 1,2,4-triazole ligand on the basis of the relative orientations of its CH₂ groups.¹⁰ Taking these into consideration, we explored the self-assembly of Cd(II) ion, H₄FA, and BTX under hydrothermal conditions, and obtained a novel 3D coordination polymer: [Cd₃(BTX)₂(HFA)₂·2H₂O]_n. Herein, we report the synthesis, crystal structure, and physical properties.

Experimental Section

Materials and Physical Measurements. The 1,4-bis(triazol-1-ylmethyl)-benzene (BTX) ligand was synthesized according to the literature method.¹¹ All other reagents and solvents were commercial 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. Fluorescent spectrum was recorded on a Fluoro Max-P spectrophotometer. Thermal gravimetric analysis (TGA) was collected on a Perkin-Elmer Pyris 1 TGA analyzer from room temperature to 850 °C with a heating rate of 20 °C min⁻¹ under nitrogen.

Synthesis of [Cd₃(BTX)₂(HFA)₂·2H₂O]_n (1). A mixture of Cd(NO₃)₂·6H₂O (0.0345 g, 0.100 mmol), H₄FA (0.0481 g, 0.100 mmol), BTX (0.0480 g, 0.200 mmol), KOH (0.0336 g, 0.600 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, white block crystals were collected by filtration and washed by water and ethanol several times (yield 12.3%, based on BTX). Elemental analysis for C₆₂H₄₂Cd₃F₁₂N₁₂O₁₈ (*M_w* = 1808.31): C, 41.18; H, 2.34; N, 9.30%; found: C, 41.31; H, 2.36; N 9.33%. IR (KBr, cm⁻¹): 3539 (m), 3199 (m), 3119 (m), 2356 (w), 1680 (m), 1577 (s), 1526 (s), 1420 (s), 1379 (s), 1259 (s), 1171 (s), 1142 (m), 987 (s), 855 (s), 722 (s), 476 (w).

Structural Determination and Refinement. The crystal structure was determined on a Siemens (Bruker) SMART CCD diffractometer using monochromated Mo-K α radiation (λ = 0.71073 Å) at 296 K. Absorption correction was performed by using the SADABS program.¹² 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-C97.¹³ All non-hydrogen atoms were located in difference Fourier maps and refined anisotropically. All H atoms were refined isotropically, with the isotropic vibration parameters 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

Table 1. Crystal and experimental data of 1

Empirical formula	C ₆₂ H ₄₂ Cd ₃ F ₁₂ N ₁₂ O ₁₈
Formula weight	1808.31
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> / Å	9.5035(11)
<i>b</i> / Å	26.955(3)
<i>c</i> / Å	12.6529(14)
β / °	98.8220(10)
<i>V</i> / Å ³	3202.9(6)
<i>D</i> _{calc} / g·cm ⁻³	1.875
<i>F</i> (000)	1788
Limits of data collection ^o	1.51 ≤ θ ≤ 25.50
Reflections collected	23357
Independent reflections (<i>R</i> _{int})	5980 (0.0452)
Goodness of fit	1.063
<i>R</i> indices (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0330, <i>wR</i> ₂ = 0.0796
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0488, <i>wR</i> ₂ = 0.0940

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

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

Cd(1)-N(1)	2.260(3)	Cd(1)-O(1)	2.280(2)
Cd(1)-O(4) ⁱⁱⁱ	2.628(3)	Cd(1)-O(5) ⁱⁱ	2.599(2)
Cd(1)-O(6) ⁱⁱ	2.272(3)	Cd(1)-O(8) ⁱ	2.228(3)
Cd(2)-N(6) ^{iv}	2.269(3)	Cd(2)-N(6) ^v	2.269(3)
Cd(2)-O(5)	2.396(2)	Cd(2)-O(5) ⁱⁱ	2.396(2)
Cd(2)-O(9)	2.276(3)	Cd(2)-O(9) ⁱⁱ	2.276(3)
N(1)-Cd(1)-O(1)	123.56(10)	N(1)-Cd(1)-O(4) ⁱⁱⁱ	82.44(10)
N(1)-Cd(1)-O(5) ⁱⁱ	140.18(10)	N(1)-Cd(1)-O(6) ⁱⁱ	92.14(10)
O(1)-Cd(1)-O(4) ⁱⁱⁱ	80.95(10)	O(1)-Cd(1)-O(5) ⁱⁱ	83.09(9)
O(6) ⁱⁱ -Cd(1)-O(1)	135.22(9)	O(8) ⁱ -Cd(1)-N(1)	117.20(11)
O(8) ⁱ -Cd(1)-O(1)	83.94(10)	N(6) ^{iv} -Cd(2)-O(5)	82.78(10)
N(6) ^{iv} -Cd(2)-O(9)	86.10(11)	N(6) ^{iv} -Cd(2)-O(9) ⁱⁱ	93.90(11)
N(6) ^v -Cd(2)-O(5)	97.22(10)	N(6) ^v -Cd(2)-O(9)	93.90(11)
O(9)-Cd(2)-O(5)	95.66(9)	O(9)-Cd(2)-O(5) ⁱⁱ	84.34(9)

Symmetry transformations used to generate equivalent atoms: ⁱx+1, y, z; ⁱⁱ-x+1, -y+1, -z+2; ⁱⁱⁱ-x+1, -y+1, -z+1; ^{iv}x-1, -y+1/2, z+1/2; ^v-x+2, y+1/2, -z+3/2.

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 $P2_1/c$ with an asymmetric unit consisting of two crystallographically distinct divalent cadmium ions, one of which Cd2 is located on a crystallographic inversion center, one singly protonated HFA trianion, one BTX ligand and an aqua ligand. At Cd1, the coordination environment is a distorted octahedrally $\{CdO_5N\}$ coordination environment, defined by one nitrogen atom from one BTX ligand, and five oxygen atoms from four separate HFA³⁻ ligands. On the other hand, Cd2 is the octahedral coordination in a $\{CdN_2O_4\}$ environment, with the equatorial positions taken up by carboxylate oxygen atom donors from two HFA³⁻ ligands and two *trans* aqua oxygen atom donors. Axial positions are filled by two *trans* triazole nitrogen donor atoms belonging to BTX ligands. The Cd-N bond lengths are 2.260(3) and 2.269(3) Å and the Cd-O bond lengths are in the range 2.228(3)-2.628(3) Å.

The HFA trianions in complex **1** adopt an exopentadentate $\mu_5-\kappa^5O:O':O'':O''':O''''$ binding mode, connecting one Cd2

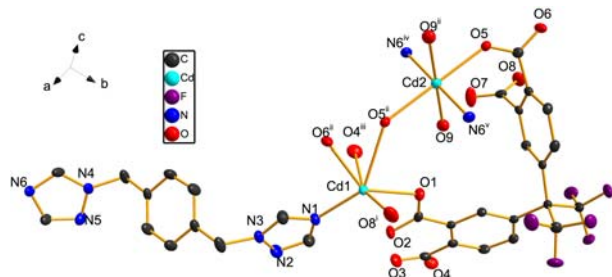
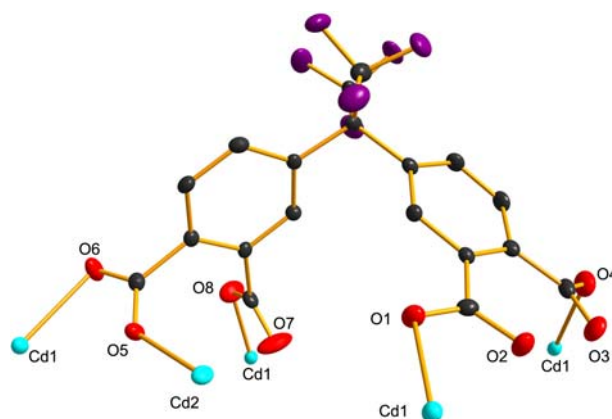


Figure 1. An ORTEP drawing of **1** showing 30% ellipsoid probability (hydrogen atoms are omitted for clarity). Symmetry codes: ⁱx+1, y, z; ⁱⁱ-x+1, -y+1, -z+2; ⁱⁱⁱ-x+1, -y+1, -z+1; ^{iv}x-1, -y+1/2, z+1/2; ^v-x+2, y+1/2, -z+3/2.



Scheme 1. View of the coordination mode of HFA³⁻ ligand in complex **1**.

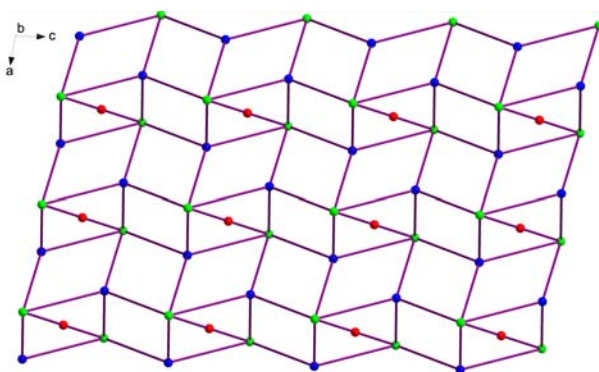


Figure 2. Network perspective of the 4,5-connected binodal $\{3.4^3.5^2\}\{3^2.4^4.5^2.6^2\}$ point symbol in complex **1**. The blue, red and bright green spheres represent the Cd1, Cd2 atom nodes and HFA³⁻ ligands, respectively.

and four Cd1 atoms (Scheme 1). The Cd1 atoms and HFA trianion construct $[Cd_1(HFA)]_n^{n-}$ (4,4) rhomboid gridlike layers that are arranged parallel to the crystallographic *b*-axis direction. The $[Cd(HFA)]_n^{n-}$ layers are linked into $[Cd_3(HFA)_2 \cdot 2H_2O]$ neutral layers by $[Cd_2(H_2O)]^+$ complex fragments. The topology of a neutral $[Cd_3(HFA)_2 \cdot 2H_2O]$ layer pattern can be simplified by the Cd1 atoms, HFA ligands as 4- and 5-connected nodes, respectively, while the Cd2 atoms are considered as simply linkers. The resulting network has a 4, 5-connected binodal net topology of $\{3.4^3.5^2\}\{3^2.4^4.5^2.6^2\}$ point symbol (Figure 2).

Adjacent $[Cd_3(HFA)_2 \cdot 2H_2O]$ layers are connected into a 3D $[Cd_3(BTX)_2(HFA)_2 \cdot 2H_2O]_n$ coordination polymer by bridging BTX ligands, which connect Cd1 and Cd2 atoms in neighboring layers with a metal-metal contact distance of 15.245 Å. The 3-D net can be simplified by considering the Cd1 atoms, Cd2 atoms, HFA³⁻ ligands as 4-, 5-, and 5-connected nodes. The Cd1 and Cd2 atoms connect directly HFA³⁻ ligands, while each HFA³⁻ ligand nod connects to four Cd1 and Cd2 atoms. A calculation with TOPOS software reveals that the coordination polymer is an unprecedented 4,5,5-connected 3-D network of $\{4.8^5\}\{4^4.6^2.8^4\}_2\{4^6.6^4\}_2$ point symbol (Figure 3).¹⁴ To the best of our knowledge, this trinodal topology has neither been reported. The unligated

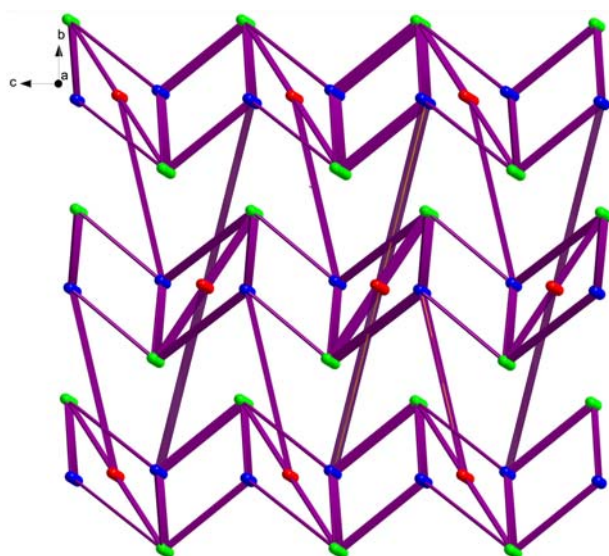


Figure 3. Network perspective of the 4-, 5-, and 5-connected 3-D trinodal $\{4.8^5\}\{4^4.6^2.8^4\}_2\{4^6.6^4\}_2$ point symbol in complex **1**. The blue, red and bright green spheres represent the Cd1, Cd2 atom nodes and HFA³⁻ ligands, respectively.

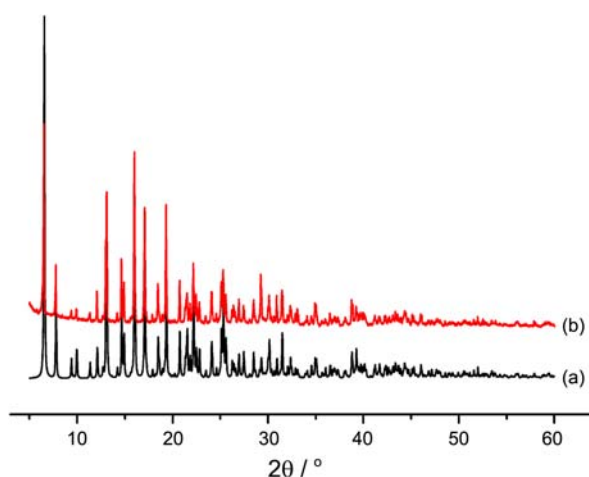


Figure 4. The simulated (Black) and experimental (Red) PXRD of complex **1**.

water molecules occupy a solvent-accessible incipient space comprising 2.4% of the unit cell volume, according to PLATON.¹⁵

To confirm the phase purity of the as-synthesized complex **1**, its PXRD pattern was performed. The peak positions of the experimental and simulated PXRD patterns are in good agreement with each other, which demonstrates that complex **1** has been obtained successfully as a pure crystalline phase (Figure 4). The differences in intensity may be owing to the preferred orientation of the powder sample.

Thermogravimetric analysis of **1** (Figure 5) demonstrates that the water molecules of crystallization were ejected from 100 °C to 150 °C (2.24% weight loss observed, 1.99% calcd). The organic ligands began to decompose at 170 °C, with the 21.01% mass remnant at 765 °C consistent with production of CdO (21.30% calcd).

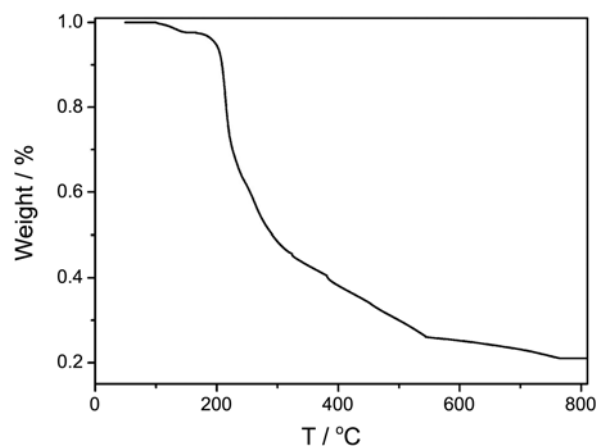


Figure 5. Thermogravimetric curve of complex **1**.

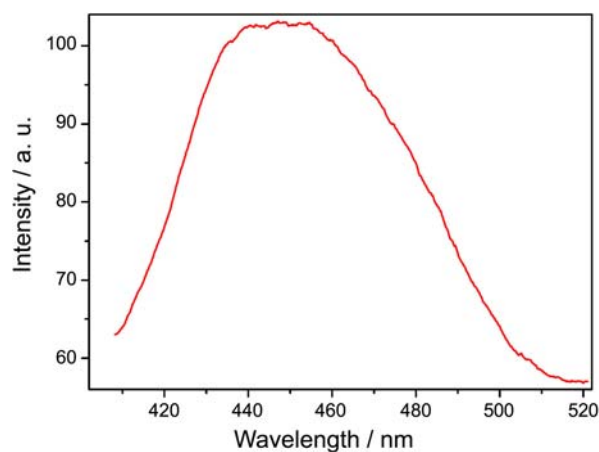


Figure 6. The solid-state emission spectrum of complex **1** recorded at room temperature.

The uorescent property of complex **1** was studied in the solid state at room temperature. The free ligands exhibit emissions at 462 nm for BTX (excitation at 395 nm) and at 362 nm for H₄FA (excitation at 330 nm).¹⁶ The emission bands of these free ligands are probably caused by the $\pi^*-\pi$ or $\pi^*-\pi$ transition. Irradiation of complex **1** with ultraviolet light ($\lambda_{\text{ex}} = 350$ nm) in the solid state resulted in a relatively broad emission band centered on ~ 447 nm (Figure 6), which is blue-shifted by 15 nm with respect to the free BTX. According to a recent review of d¹⁰ metal coordination polymer luminescence, the emissive behavior of **1** can be ascribed to ligand-centered electronic transitions.¹⁷

In conclusion, we have successfully synthesized a new cadmium(II) coordination polymer based on 4,4'-(hexafluoroisopropylidene)diphthalic 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 crystal structure of complex **1** shows a novel three-dimensional framework with 4-, 5-connected 3-D trinodal $\{4.8^5\}\{4^4.6^2.8^4\}_2\{4^6.6^4\}_2$ topology. In addition, complex **1** exhibits strong fluorescent emissions in the solid state at room temperature.

Supplementary Material. CCDC-851201(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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