

Research Article

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Twofold interpenetrated 3D Cd(II) complex: Crystal structure and luminescent property

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Abstract: A novel Cd(II) compound, namely $[\text{Cd}_6(\text{TCA})_4(4\text{-bpmh})(\text{DMA})_2(\text{H}_2\text{O})_2]_n \cdot 4n(\text{H}_2\text{O})$ (denoted as **1**, $\text{H}_3\text{TCA} = 4,4',4''$ -tricarboxytriphenylamine, 4-bpmh = *N,N*-bis(pyridin-4-ylmethylene)hydrazine, and DMA = *N,N*'-dimethylacetamine), has been solvothermally prepared via a dual-ligand strategy that employs two organic ligands to fulfill different functions. The solid of compound **1** shows blue luminescence at room temperature.

Keywords: Cd(II) compound, dual ligand, luminescence

1 Introduction

Metal–organic frameworks (MOFs) have been deemed as among the promising hybrid functional materials that show huge application potential in a variety of fields, including magnetism, gas adsorption/separation, luminescence sensing, heterogeneous catalysis, and nonlinear optics [1–3]. In this field, MOFs are structured through coordination bond-driven self-assembly of multi-dentate organic ligands and metal ions under appropriate conditions. Despite great progress made in building functional MOF materials, the manufacturing of MOFs with performance and ideal structures has remained a great challenge so far [4–7]. Hence, we need to choose the right metal center, organic ligands, and synthesis strategy that may help to construct the desired MOFs [8–10]. Zinc and cadmium, as transition metal elements, have unfilled d orbitals. These unfilled d orbitals can interact with electrons in ligands, leading to charge transfer or energy

transitions, resulting in fluorescence. Therefore, complexes prepared with zinc and cadmium as metal centers often exhibit excellent fluorescent properties and can be used for the quantitative detection of specific target analytes [11–14]. Among the widely used combinations of dual ligands, polycarboxylate ligand and bis(pyridyl) or bis(imidazole)-based ligand are commonly used as the dual ligand to produce new high-dimensional MOFs [15–18]. In comparison with the single ligand, the dual-ligand strategy is more favorable to enrich the structural diversities of MOFs and can even endow MOFs with more excellent performance [19,20]. Bearing the aforementioned considerations, in this research, we have chosen two kinds of organic ligands, namely, 4,4',4''-tricarboxytriphenylamine (H_3TCA) and *N,N*-bis(pyridin-4-ylmethylene)hydrazine (4-bpmh), both of which have large conjugated groups that can act as a chromophore to construct new luminescent MOFs. We succeeded in getting a novel compound via the solvothermal reactions of the transition metal Cd(II) ions in combination with H_3TCA and 4-bpmh. The XRD analysis displayed that compound **1** reveals a framework of twofold interpenetrated 3D pillar layers, which can be topologically reduced to a (3,8)-linked network. Under 350 nm excitation, it exhibits visible blue luminescence at room temperature (RT).

2 Experimental

2.1 Materials and instrumentation

The 4-bpmh and H_3TCA ligand were purchased from Jinan Henghua Technology Co., Ltd (Shandong, P.R. China) with 98% purity. The *N,N*-dimethylacetamine (DMA) solvent in analytical grade was purchased from Shanghai Sinopharm Reagent Co., Ltd (Shanghai, P.R. China). N, H, and C elemental analyses were implemented on the elemental Vario EL III analyzer. On a PANalytical X'Pert Pro powder diffractometer with 1.54056 Å Cu/K α radiation, a powder x-ray diffraction (PXRD) experiment was carried out with 0.05° step size. Thermogravimetric analysis (TGA) for **1** was conducted under a nitrogen atmosphere using the NETSCHZ

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STA-449C thermoanalyzer. The luminescent spectrum data were collected on the Edinburg FLS920 TCSPC fluorescence spectrophotometer at RT.

2.2 Synthesis of $[\text{Cd}_6(\text{TCA})_4(4\text{-bpmh})(\text{DMA})_2(\text{H}_2\text{O})_2]_n \cdot 4n(\text{H}_2\text{O})$ (**1**)

The reaction was carried out in a small glass vial (20 mL) by adding 4-bpmh (10.51 mg, 0.05 mmol), H_3TCA (18.87 mg, 0.05 mmol), and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (30.85 mg, 0.100 mmol) in a solvent mixture of H_2O (1 mL) and DMA (3 mL). The reaction was sealed and heated in an oven (110°C) for 48 h. When the reaction mixture was cooled down to room temperature, it yielded the desired compound **1** as colorless block crystals (32%). Elemental analysis for $\text{C}_{116}\text{H}_{98}\text{Cd}_6\text{N}_{14}\text{O}_{32}$ (2874.49) Calcd.: N, 4.02; H, 3.41; C, 48.43%. Found: N, 4.05; H, 3.43; C, 48.38%. IR (KBr pallet, cm^{-1}): 535(s), 580(w), 618(w), 689(s), 710(m), 756(s), 776(s), 836(m), 925(s), 1,005(w), 1,026(m), 1,108(s), 1,150(m), 1,162(m), 1,233(s), 1,312(s), 1,338(s), 1,364(m), 1380(m), 1,451(s), 1,489(s), 1,563(s), 1,593(s), 2,783(m), 2,934(m), 3,063(m), 3,423(m).

2.3 X-ray structural determination

The compound **1**'s crystal structure data were gathered at RT through a PC-controlled Rigaku Mercury CCD diffractometer that was equipped with Mo-K α radiation in graphite monochrome. SADABS was employed for the empirical absorption correction [21], and the solution and refinement of structure were conducted through the SHELXS program and SHELXL refinement package, separately [22]. All non-H atoms were refined in an anisotropic manner, while H atoms were geometrically produced. Utilized the SQUEEZE function in the PLATON program to remove solvent molecules from the material's pores, thereby enhancing the quality of the data [23]. The compound **1**'s crystallographic data and their refinements are presented in detail in Table 1.

3 Results and discussion

3.1 Description of the crystal structure for **1**

The compound **1**'s single crystal is crystallized in the monoclinic space group of $P2_1/c$ and displays a 3D skeleton with (3,8)-linked topology. Its asymmetric unit is composed of two coordinated DMA molecules, four TCA^{3-} ligands, six Cd(II) ions, two coordinated H_2O , and four lattice H_2O

Table 1: The crystal data for **1**

Formula	$\text{C}_{116}\text{H}_{98}\text{Cd}_6\text{N}_{14}\text{O}_{32}$
Fw	2874.49
Crystal system	Monoclinic
Space group	$P2_1/c$
<i>a</i> (Å)	23.9216(4)
<i>b</i> (Å)	23.7196(3)
<i>c</i> (Å)	27.6715(5)
α (°)	90
β (°)	113.003(2)
γ (°)	90
Volume (Å ³)	14452.6(4)
<i>Z</i>	4
Density (calculated)	1.288
Abs. coeff. (mm^{-1})	0.931
Total reflections	156,894
Unique reflections	50,285
Goodness of fit on F^2	1.078
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R = 0.0574$, $wR_2 = 0.1480$
<i>R</i> (all data)	$R = 0.0897$, $wR_2 = 0.1607$

molecules. Figure 1 presents that Cd1, Cd2, and Cd3 are linked into a trinuclear $[\text{Cd}_3(\text{COO})_4(\mu_2\text{-H}_2\text{O})]$ cluster via a $\mu_2\text{-H}_2\text{O}$ ligand and four carboxylic acid groups, with the mean Cd...Cd distance of 3.73 Å. In the above trinuclear cluster, Cd1, Cd2, and Cd3 all exhibit a distorted octahedral geometry in a hexacoordination mode, coordinated with five carboxylic acid O atoms come from three TCA^{3-} ligands and a N atom come from a 4-bpmh ligand, four carboxylic acid O atoms come from a $\mu_2\text{-H}_2\text{O}$ ligand, a DMA molecule and four TCA^{3-} ligands, and four carboxylic acid O atoms come from a $\mu_2\text{-H}_2\text{O}$ ligand and three TCA^{3-} ligands, and a N atom from a 4-bpmh ligand, separately. Three other Cd(II) ions (Cd4, Cd5, and Cd6), which are independently crystallographic, are also linked together via a $\mu_2\text{-H}_2\text{O}$ ligand and four carboxylic acid groups to form another trinuclear $\{\text{Cd}_3(\text{COO})_4(\mu_2\text{-H}_2\text{O})\}$ cluster, and the mean distance of Cd...Cd is 3.65 Å. In such a trinuclear cluster, Cd4 exists in a heptacoordination mode through one N atom from the 4-bpmh ligand and six carboxylate O atoms from three TCA^{3-} ligands, displaying a distorted pentagonal bipyramidal geometry. Cd5 exhibits an octahedral coordination environment defined by four carboxylate O atoms from three TCA^{3-} ligands, one $\mu_2\text{-H}_2\text{O}$ ligand, and one N atom from the 4-bpmh ligand. On the other hand, the coordination sphere around Cd6 is achieved through four carboxylate O atoms from four TCA^{3-} ligands, one $\mu_2\text{-H}_2\text{O}$ ligand, and one DMA molecule. Table 1 presents the bond parameters around the Cd(II) ions. Four crystallographic-independent TCA^{3-} ligands show three different coordination fashions: $(\kappa^1\text{-}\kappa^1\text{-})(\kappa^1\text{-}\kappa^1\text{-})(\kappa^2\text{-}\mu_2)\text{-}\mu_6$, $(\kappa^2\text{-})(\kappa^2\text{-})(\kappa^1\text{-}\kappa^1)\text{-}\mu_4$, and $(\kappa^2\text{-})(\kappa^2\text{-})(\kappa^2\text{-}\mu_2)\text{-}\mu_4$. Two different trinuclear $\{\text{Cd}_3\}$ clusters are linked by

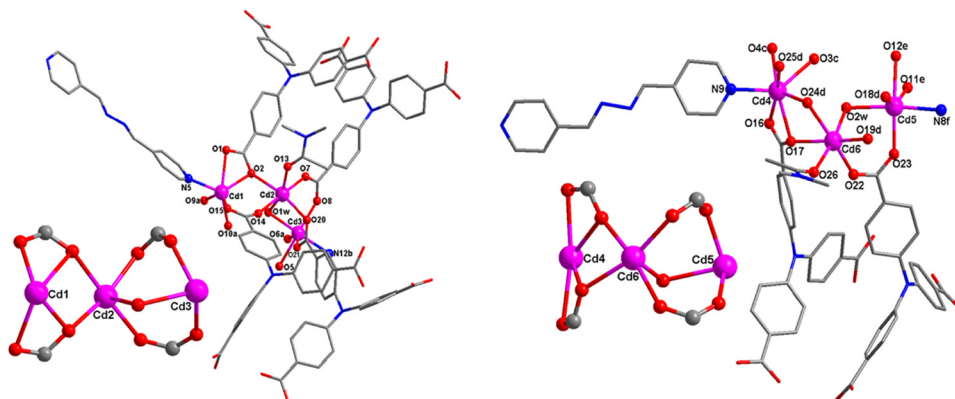


Figure 1: The coordination environments of Cd(II) ions in **1** and the trinuclear $\{Cd_3\}$ clusters (symmetrical code a: $1 - X, 1/2 + Y, -1/2 - Z$; b: $2 - X, 1/2 + Y, 1/2 - Z$; c: $1 + X, +Y, +Z$; d: $-1 + X, +Y, -1 + Z$; e: $+X, +Y, -1 + Z$; f: $1 + X, +Y, 1 + Z$).

the TCA^{3-} ligands to form a 2D layer (Figure 2a). These 2D layers are layered further with 4-bpmh ligands to produce a framework of 3D pillar layers with large 1D open channels (Figure 2b). It is noteworthy that the 1D opened channels of the 3D pillar-layered framework are interpenetrated by another same 3D pillar-layered skeleton, resulting in the development of a twofold interpenetrating 3D columnar layer framework (Figure 2c). By carefully analyzing this 3D framework, it can be found that each TCA^{3-} ligand links three distinct trinuclear clusters of $\{Cd_3(COO)_4(\mu_2-H_2O)\}$, and each trinuclear $\{Cd_3(COO)_4(\mu_2-H_2O)\}$ cluster is connected to eight distinct

TCA^{3-} ligands. In topological terms, this 3D framework can be simplified to a (3,8)-linked topological net with $\{4^3 \cdot 6^{24} \cdot 8\} \{4^3\}_2$ point symbol by looking at the trinuclear $\{Cd_3(COO)_4(\mu_2-H_2O)\}$ clusters and TCA^{3-} ligands as 8- and 3-connected nodes, respectively (Figure 2d).

3.2 PXRD and TGA

The test of PXRD was performed to confirm the phase purity of the bulk solids. The findings display that for the

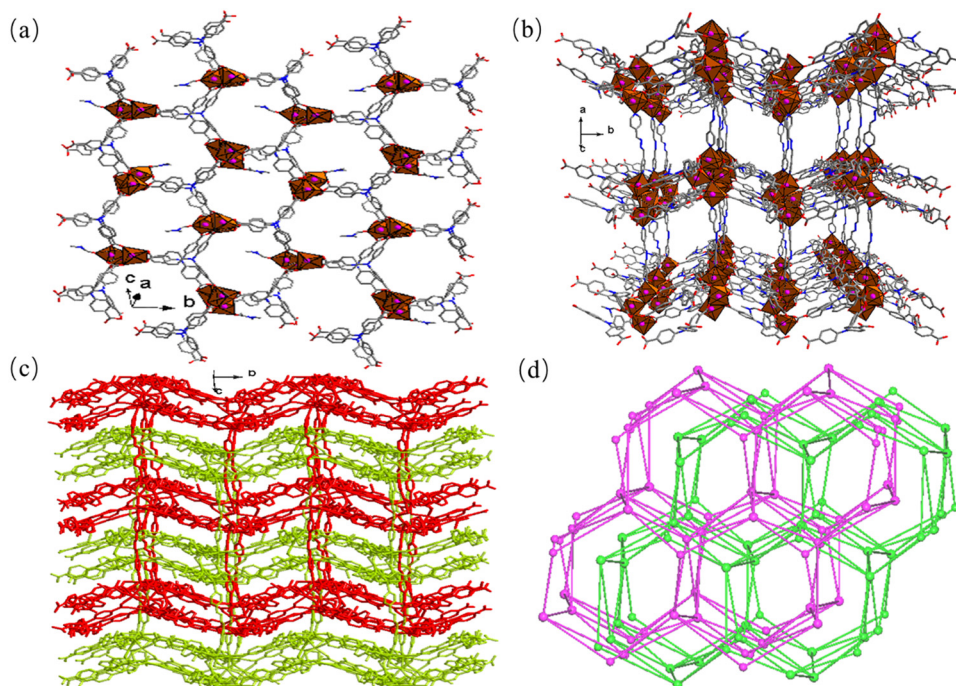


Figure 2: (a) The 2D layer structure built from the trinuclear $\{Cd_3\}$ cluster and TCA^{3-} ligands. (b) The single 3D pillar-layered skeleton. (c) The **1**'s twofold interpenetrated 3D pillar-layered skeleton. (d) The **1**'s twofold interpenetrated (3,8)-linked topological net.

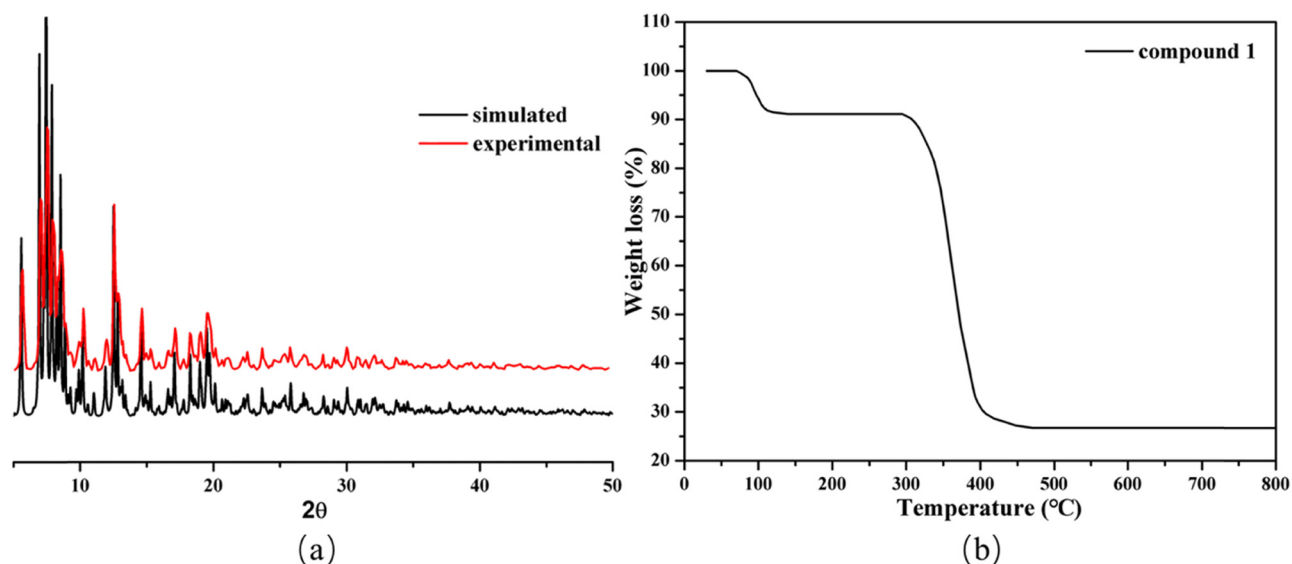


Figure 3: (a) **1**'s PXRD pattern (b) and its TGA curve.

bulk solid, the experimental pattern fits closely with the simulated pattern that was determined from the single-crystal diffraction data, thereby substantiating the bulk solid's single phase (Figure 3a).

TGA analysis indicated an initial weight loss of approximately 9.85% between 70 and 140°C, attributed to the complete release of lattice water molecules, as well as coordinated DMA and H₂O molecules (calculated: 9.82%). Beyond 295°C, as solvent molecules were removed, the solvent-free framework started collapsing, and the organic ligands began to

decompose, ultimately leaving behind a residue of 26.73%, which closely matched the composition of CdO (calculated: 26.80%).

3.3 Luminescent property of **1**

Transition metals, due to their partially filled d orbitals in the valence shell, readily form coordination polymers with aromatic organic ligands, exhibiting intriguing luminescent

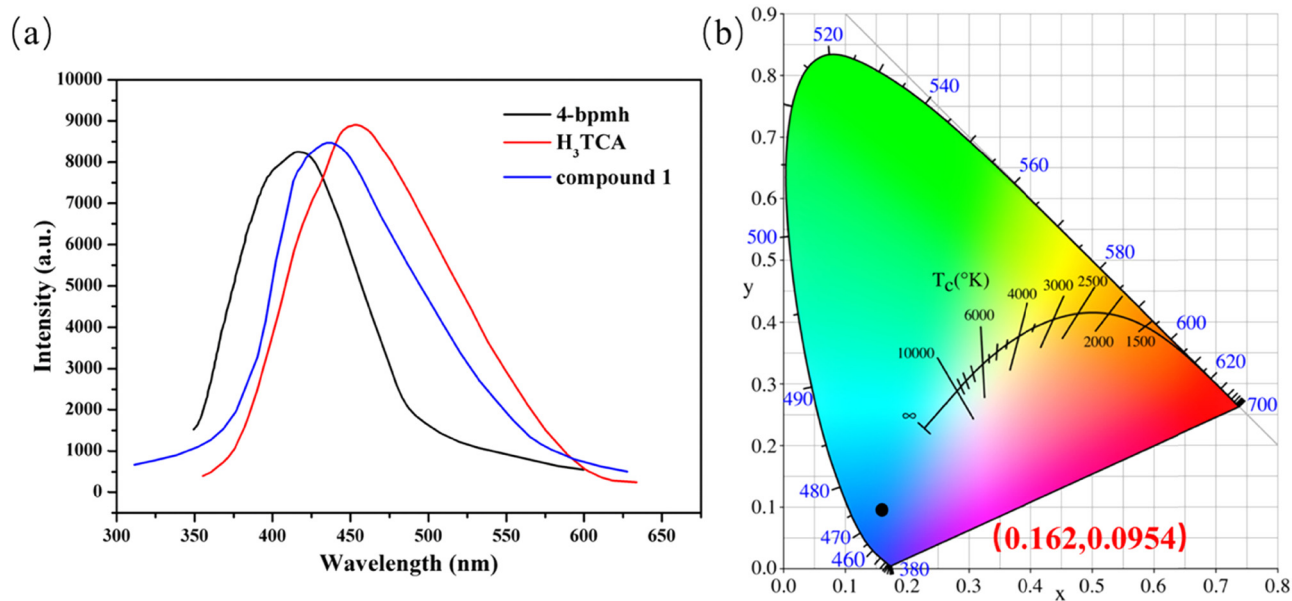


Figure 4: (a) The luminescent spectra of **1**, 4-bpmh, and H₃TCA at room temperature. (b) The CIE chromaticity diagram for **1**.

properties. This makes them highly promising as luminescent probes for the detection of hazardous substances [24,25]. Given that, we determined the **1**'s luminescent spectra as well as the corresponding free ligands at RT. As illustrated in Figure 4a, the free ligands of H₃TCA and 4-bpmh display intense luminescence with the largest emission peaks at 452 nm ($\lambda_{\text{ex}} = 340$ nm) and 417 nm ($\lambda_{\text{ex}} = 350$ nm), respectively, and these emissions may be caused by the $\pi^* \rightarrow \pi$ transition of the conjugated groups inside the ligands [26,27]. Under 350 nm excitation, **1** displays a largest emission peak at 435 nm. Comparing the emission spectra of **1**, 4-bpmh, and H₃TCA, it can be found that **1**'s emission peak has an 18 nm redshift with respect to 4-bpmh and a 17 nm blueshift with respect to the H₃TCA ligand. Because of the d¹⁰ conformation of the Cd(II) ion, the **1**'s luminescence may come from a ligand-to-ligand charge transfer or a $\pi^* \rightarrow \pi$ transition within the ligand or a mixture of both [28]. The commission internationale de l'Eclairage (CIE) chromaticity coordination of **1** is (0.162, 0.0954) calculated by the CIE 1931 software, indicating that **1** may be applied as an excellent blue photoluminescent material.

4 Conclusion

In conclusion, a novel twofold interpenetrated 3D Cd(II) compound has been constructed from two different kinds of organic ligands. This 3D framework has two different trinuclear {Cd₃} cluster subunits and represents a (3,8)-linked topological net. Moreover, the intense blue luminescence indicates that **1** may be an excellent candidate for a blue-emitting material.

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Author contributions: Jing Li synthesized and characterized the compounds; Hongjiang Ren and Jiangtao Li performed other experiments.

Conflict of interest: The author(s) declare(s) that there is no conflict of interest regarding the publication of this article.

Ethical approval: Research experiments conducted in this article with animals or humans were approved by the

ethical committee and responsible authorities of our research organization(s) following all guidelines, regulations, legal, and ethical standards as required for humans or animals.

Data availability statement: The data used to support the findings of this study are included within the article.

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