

## 3-羧基苯氧乙酸构筑的 Cd(II)配位聚合物的合成、 晶体结构及荧光性质

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**摘要:** 通过水热方法, 采用 3-羧基苯氧乙酸 (3-H<sub>2</sub>CPOA=3-carboxyphenoxyacetic acid) 和 phen (phen=1,10-phenanthroline) 与 Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O 反应, 合成了一个具有一维双链结构的配位聚合物 [Cd(3-CPOA)(phen)]<sub>n</sub> (**1**), 并对其结构和荧光性质进行了研究。结构分析结果表明该聚合物的晶体属于单斜晶系, C2 空间群。2 个镉(II)离子、2 个 3-CPOA<sup>2-</sup>配体和 2 个 phen 配体形成了 1 个 [Cd<sub>2</sub>(3-CPOA)<sub>2</sub>(phen)<sub>2</sub>] 环, 这些环通过镉(II)离子与 3-CPOA<sup>2-</sup>配体的配位作用形成了 1 个一维双链结构。链与链之间又通过 C-H···O 氢键作用形成了 1 个三维的配位框架。研究表明, 该聚合物在室温下能发出很强的蓝色荧光。

**关键词:** 配位聚合物; 镉(II)配合物; 氢键; 荧光性质

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## Synthesis, Crystal Structure and Luminescent Properties of a Cd(II) Coordination Polymer Constructed by 3-Carboxyphenoxyacetic Acid

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**Abstract:** A coordination polymer, namely [Cd(3-CPOA)(phen)]<sub>n</sub> (**1**) has been constructed hydrothermally using 3-H<sub>2</sub>CPOA (3-H<sub>2</sub>CPOA=3-carboxyphenoxyacetic acid), phen (phen=1,10-phenanthroline) and Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O. The complex crystallizes in the monoclinic system, space group C2 with *a*=1.575 3(7) nm, *b*=1.035 4(5) nm, *c*=1.133 9(5) nm, *β*=97.806(4)°, *V*=1.832 3(15) nm<sup>3</sup>, *D<sub>c</sub>*=1.764 g·cm<sup>-3</sup>, *Z*=4, *R*=0.020 4 and *wR*=0.039 7 (*I*>2σ(*I*)). Two Cd(II) atoms, two CPOA<sup>2-</sup> ligands and two phen ligands form a [Cd<sub>2</sub>(CPOA)<sub>2</sub>(phen)<sub>2</sub>] ring. The rings are connected by the coordination interactions of CPOA<sup>2-</sup> ligands and Cd(II) ions to generate a 1D double-chain, which are further extended into a 3D metal-organic supramolecular framework by C-H···O hydrogen bond interactions. Luminescent studies show that complex **1** displays strong blue emission at room temperature. CCDC: 853932.

**Key words:** coordination polymer; cadmium(II) complex; hydrogen bond; luminescent properties

Recently, the design and synthesis of transition metal coordination polymers is a rapid growth field due to their fascinating structures as well as their

potential application in magnetism, gas adsorption, catalysis, luminescence, and so on<sup>[1-6]</sup>. According to previous studies, organic ligands play a crucial role in

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directing the final structures and properties<sup>[7-8]</sup>. Many multi-carboxylate or heterocyclic carboxylic acids have been used for this purpose<sup>[9-15]</sup>. Compared to rigid carboxylate containing ligands, flexible multi-carboxylate ligands are of special interests because their varied coordination modes, abundant structural motifs, and flexible molecular backbones can lead to a variety of coordination polymers with appealing structures and related functions<sup>[8,14,16]</sup>. 3-H<sub>2</sub>CPOA is a flexible ligand that not only includes a rigid carboxylate group attached to the central aromatic ring directly but also exhibits additional interesting characteristics, such as the existence of a -OCH<sub>2</sub>-spacer between the benzene ring and the carboxylate moiety that allows more flexibility and may result in rich topologies, including coordination modes, packing fashions, and dimensionalities of supramolecular coordination complexes<sup>[17-18]</sup>.

Taking into account these factors, we herein report the synthesis, crystal structure, luminescent properties of Cd(II) compound with 3-CPOA ligands.

## 1 Experimental

### 1.1 Reagents and physical measurements

The 3-carboxyphenoxyacetic acid was prepared by the reaction of chloroacetic acid with 3-hydroxybenzoic acid, and all other chemicals were of analytical reagent grade and used without further purification. Carbon, hydrogen and nitrogen were determined using an Elementar Vario EL elemental

analyzer. IR spectra were recorded using KBr pellets and a Bruker EQUINOX 55 spectrometer. Thermogravimetric analysis (TG) data were collected on a Netzsch TG-209 instrument with a heating rate of 10 °C·min<sup>-1</sup>. Powder X-ray diffraction patterns (PXRD) were determined with a Rigaku-Dmax 2400 diffractometer using Cu-K $\alpha$  radiation. Excitation and emission spectra were recorded on an Edinburgh FLS920 fluorescence spectrometer at room temperature for the solid samples.

### 1.2 Synthesis of [Cd(3-CPOA)(phen)]<sub>n</sub> (**1**)

A mixture of Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.027 g, 0.1 mmol), 3-H<sub>2</sub>CPOA (0.020 g, 0.1 mmol), phen (0.020 g, 0.1 mmol), NaOH (0.004 g, 0.1 mmol) and H<sub>2</sub>O-EtOH (10 mL, V<sub>H<sub>2</sub>O</sub>:V<sub>EtOH</sub>=5:1) was stirred at room temperature for 15 min, and then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 d, followed by cooling to room temperature at a rate of 10 °C·h<sup>-1</sup>. Clouress block-shaped crystals of **1** were isolated manually, and washed with distilled water. Yield: 76% (based on Cd). Anal. Calcd. for C<sub>21</sub>H<sub>14</sub>CdN<sub>2</sub>O<sub>5</sub>(%): C 51.82, H 2.90, N 5.76; found(%): C 51.96, H 3.27, N 5.38. IR (KBr, cm<sup>-1</sup>): 2 927m, 1 614s, 1 583s, 1 395s, 1 273m, 1 226m, 1 077m, 856s, 767m, 674m. The compound is insoluble in water and common organic solvents, such as methanol, ethanol, acetone, and DMF.

### 1.3 Structure determinations

Single-crystal data of **1** were collected at 296(2) K on a Bruker Smart Apex 1000 CCD diffractometer

Table 1 Crystal data for complex **1**

Complex	<b>1</b>	Crystal size / mm	0.30×0.24×0.24
Chemical formula	C <sub>21</sub> H <sub>14</sub> CdN <sub>2</sub> O <sub>5</sub>	$\theta$ range for data collection / (°)	2.36–25.49
Molecular weight	486.74	Limiting indices	$-19 \leq h \leq 19, -12 \leq k \leq 12, -13 \leq l \leq 12$
Crystal system	Monoclinic	Reflections collected / unique ( $R_{int}$ )	6 662 / 3 362 (0.018 8)
Space group	<i>C</i> 2	$D_c$ / (g·cm <sup>-3</sup> )	1.764
<i>a</i> / nm	1.575 3(7)	$\mu$ / mm <sup>-1</sup>	1.229
<i>b</i> / nm	1.035 4(5)	Data / restraints / parameters	3 362 / 1 / 262
<i>c</i> / nm	1.1339(5)	Goodness-of-fit on $F^2$	1.035
$\beta$ / (°)	97.806(4)	Absolute structure parameter	0.006(18)
<i>V</i> / nm <sup>3</sup>	1.8323(15)	Final <i>R</i> indices ( $I \geq 2\sigma(I)$ ) $R_1, wR_2$	0.020 4, 0.039 7
<i>Z</i>	4	<i>R</i> indices (all data) $R_1, wR_2$	0.023 4, 0.040 8
<i>F</i> (000)	968	Largest diff. peak and hole / (e·nm <sup>-3</sup> )	218 and -271

**Table 2** Selected bond distances (nm) and bond angles ( $^{\circ}$ ) for compound **1**

Cd(1)-O(1)	0.246 5(2)	Cd(1)-O(2)	0.227 4(2)	Cd(1)-O(4)#2	0.223 7(2)
Cd(1)-O(5)#3	0.225 3(3)	Cd(1)-N(1)	0.237 0(3)	Cd(1)-N(2)	0.233 4(3)
O(4)#2-Cd(1)-O(5)#3	92.53(10)	O(4)#2-Cd(1)-O(2)	98.29(9)	O(5)#3-Cd(1)-O(2)	95.55(10)
O(4)#2-Cd(1)-N(2)	115.81(10)	O(5)#3-Cd(1)-N(2)	102.94(10)	O(2)-Cd(1)-N(2)	139.92(11)
O(4)#2-Cd(1)-N(1)	84.18(8)	O(5)#3-Cd(1)-N(1)	170.63(10)	O(2)-Cd(1)-N(1)	93.61(9)
N(2)-Cd(1)-N(1)	70.91(11)	O(4)#2-Cd(1)-O(1)	149.11(8)	O(5)#3-Cd(1)-O(1)	104.46(10)
O(2)-Cd(1)-O(1)	55.11(8)	N(2)-Cd(1)-O(1)	85.70(10)	N(1)-Cd(1)-O(1)	82.46(8)

Symmetry transformations used to generate equivalent atoms: #2:  $-x, y, -z+1$ ; #3:  $x, y, z+1$ .

with Mo  $K\alpha$  radiation ( $\lambda=0.071\ 073\ \text{nm}$ ). A summary of the crystallography data and structure refinement is given in Table 1, and selected bond lengths and angles of the complex **1** are listed in Table 2. The structure was solved using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. All the hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL-97 system<sup>[19]</sup>.

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## 2 Results and discussion

### 2.1 Description of the structure

As shown in Fig.1, the asymmetrical unit of the cell of compound **1** contains one crystallographically unique Cd(II) atom, one 3-CPOA<sup>2-</sup> ligand, one phen ligand. The Cd(II) center is six-coordinated by two N atoms of the phen ligand, four carboxylate O atoms from three different 3-CPOA<sup>2-</sup> ligands, resulting in a distorted octahedral coordination geometry. The distances of Cd-O and Cd-N bonds span the range of 0.223 7(2)~0.246 5(2) and 0.233 4(3)~0.237 0(3) nm,

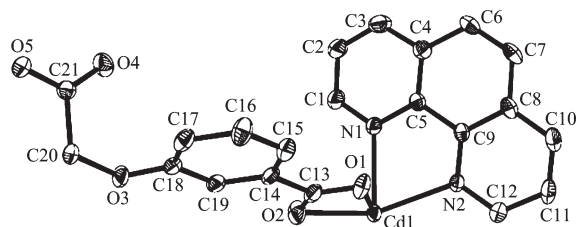


Fig.1 Drawing of the asymmetric unit of complex **1**, H atoms were omitted for clarity

which are in good with the bond lengths observed in other Cd(II) complexes<sup>[6,14-15]</sup>.

Notably, the two carboxylate groups of 3-CPOA<sup>2-</sup> ligand exhibit two different coordination modes: one links one Cd(II) atom in a chelating mode, while the other connects two Cd(II) atoms in a bridging mode. In this way, two CPOA<sup>2-</sup> ligands linked two neighboring Cd(II) atoms, form a  $[\text{Cd}_2(\text{CPOA})_2(\text{phen})_2]$  ring (Fig.2). The rings are connected by the coordination interactions of CPOA<sup>2-</sup> ligands and Cd(II) ions to generate a 1D double chain, which are further extended into a 3D metal-organic supramolecular framework by C-H $\cdots$ O hydrogen bond interactions (Fig.3, Fig.4).

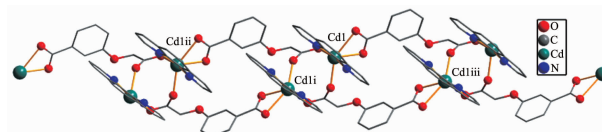
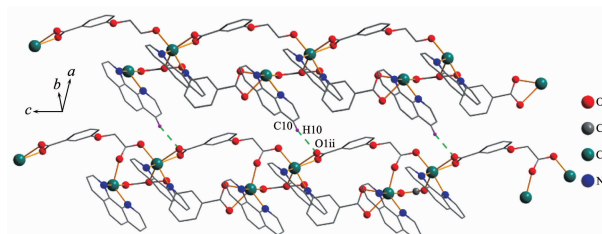


Fig.2 View of the 1D double chain structure of complex **1** along  $b$  axis

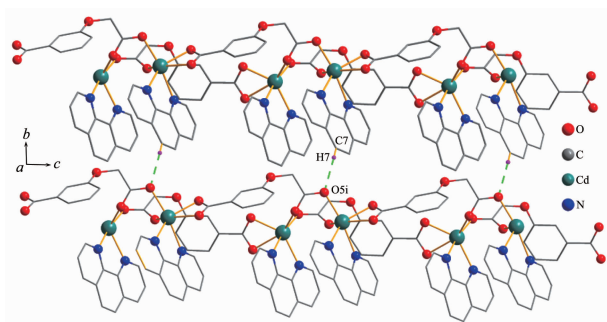


Green dashed lines present the C-H $\cdots$ O hydrogen bond interactions; Symmetry code: ii:  $-0.5+x, -0.5+y, z$

Fig.3 2D structure formed by C-H $\cdots$ O hydrogen bond interactions in the adjacent chains in **1**

### 2.2 TG analysis and PXRD results

Powder X-ray diffraction experiment was carried out for compound **1**. The pattern for the as-synthesized bulk material closely matches the



Green dashed lines present the C-H...O hydrogen bonds; Symmetry code:  $i: -x, -1+y, 1-z$

Fig.4 3D structure formed by C-H...O hydrogen bonds in the adjacent sheets in **1**

simulated one from the single-crystal structure analysis, which is indicative of the pure solid-state phase (Fig.5). To study the stability of compound **1**, thermal gravimetric analyses (TG) were performed. As shown in Fig.6, complex **1** was stable up to 300 °C, and then began to decompose. The final residual weight is 26.24% (Calcd. 26.38%), corresponding to CdO.

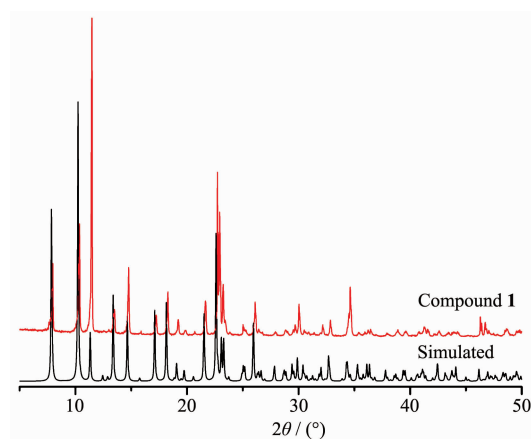


Fig.5 PXRD pattern of compound **1** at room temperature

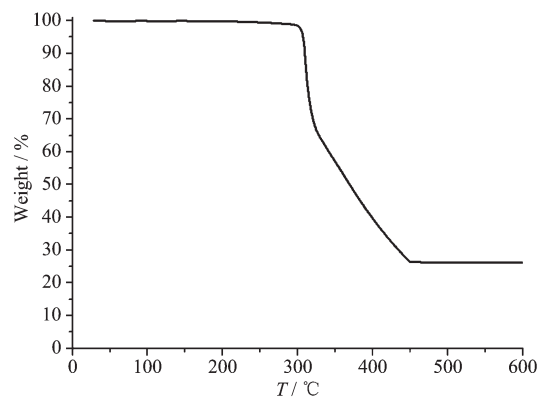


Fig.6 TG plot of complex **1**

## 2.3 Photoluminescence properties

Coordination polymers with  $d^{10}$  metal centers and conjugated organic linkers are promising candidates for photoactive materials with potential applications such as chemical sensors and photochemistry<sup>[6,14-15]</sup>. Hence, the solid state photoluminescence properties of complex **1** was investigated at room temperature (Fig. 7). The free 3-H<sub>2</sub>CPOA does not display any luminescent, while compound **1** emits a strong blue fluorescent emission band with a maximum peak at 480 nm ( $\lambda_{\text{ex}}=384$  nm), which is probably caused by the ligand-to-metal charge transfer (LMCT)<sup>[20]</sup>. The luminescent analysis indicates that complex **1** is a good candidate for blue-light luminescent material.

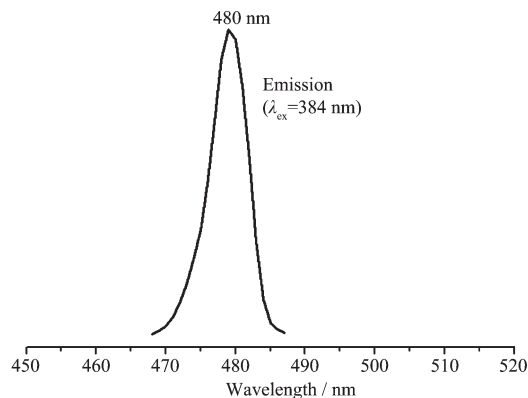


Fig.7 Emission spectrum of complex **1** in the solid state at room temperature

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