

以对苯二甲酸、三乙烯二胺构筑的二维层状结构的 镉配位聚合物的晶体结构和荧光性质

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摘要: 溶剂热条件下采用 $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ 、对苯二甲酸和三乙烯二胺作为反应物合成出一个具有二维骨架结构的配位聚合物 $[\text{Cd}(\text{bdc})(\text{dabco})(\text{DMF})] \cdot 2\text{H}_2\text{O}$ (**1**), 并采用元素分析、红外光谱、差热分析和 X-射线单晶衍射进行了研究及表征。晶体结构分析结果表明: 对苯二甲酸离子(bdc)将 $\text{Cd}(\text{II})$ 离子连接成一维链, 相邻链之间进一步被三乙烯二胺(dabco)构筑成二维层状结构。沿 *c* 轴方向, 垂直于二维层状结构中存在大小为 $0.74 \text{ nm} \times 0.65 \text{ nm}$ 的一维通道。荧光谱图表明常温固态下配合物 **1** 发射蓝色荧光, 荧光寿命为 38.2 ns 。

关键词: 镉配位聚合物; 晶体结构; 对苯二甲酸; 三乙烯二胺; 荧光性质

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A 2D Layer-Like Cadmium Coordination Polymer Based on Terephthalate and Triethylenediamine Ligands: Crystal Structures and Luminescence

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Abstract: The self-assembly of terephthalic acid, triethylenediamine and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ under solvothermal condition gave one 2D cadmium coordination polymer, $[\text{Cd}(\text{bdc})(\text{dabco})(\text{DMF})] \cdot 2\text{H}_2\text{O}$ (**1**) (bdc=terephthalate, dabco=triethylenediamine), which has been characterized by elemental analysis, IR, TGA and single-crystal X-ray diffraction. The bdc ligands linked the $\text{Cd}(\text{II})$ centers to form an infinite Cd-carboxylate chain. The chains are further bridged by dabco ligands, forming a two-dimensional layered network. Interestingly, 2D layered network contains small channels of $0.74 \text{ nm} \times 0.65 \text{ nm}$ along the *c* axis. The photoluminescence and lifetime of **1** in the solid state have been studied. CCDC: 847762.

Key words: cadmium coordination polymer; crystal structure; terephthalic acid; triethylenediamine; luminescent

0 Introduction

As a new class of porous materials, metal-organic frameworks (MOFs) have received widespread attention

due to their fascinating topology and potential applications in gas storage, separation, catalysis and detection of high explosives^[1-6]. The selection of the suitable organic ligands to be attached to the metal

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centres plays a vital role in constructing desirable MOFs. It has been proved that the coordination of *N*-conating ligands and carboxylate ligands to metal centers will be an excellent tool in the assembly process and highly influenced by the structural characteristic of tectonic spacers. Bidentate ligands such as triethylene diamine (dabco) and bi- or tri-carboxylic acid are very common^[7-9]. Especially, the metal-organic frameworks (MOFs), constructed by transition metal ions with organic carboxylate ligands, not only possess micro-porous framework, but also keep their rigid structures after removing the guest molecules^[10-11]. In recent years, several terephthalate (bdc)-dabco complexes with transition metals have been reported^[12-21]. For example, He et al.^[12] have successfully synthesized a new 2D micro-porous zinc-organic framework, $[\text{Zn}_2(\text{bdc})(\text{dabco})(\text{H}_2\text{O})_2]$. Chun et al.^[14] obtained two new cobalt-organic frameworks based on trinuclear pinwheel motifs, which perform highly efficient hydrogen sorption capabilities. However, so far, work on the construction of new porous cadmium MOFs based on bdc and dabco ligands, and their photoluminescent properties have not been reported to date. Herein, we report a new cadmium coordination polymer, $\{\text{Cd}(\text{bdc})(\text{dabco})(\text{DMF})\} \cdot 2\text{H}_2\text{O}_n$ (**1**) (bdc=terephthalate, dabco=triethylenediamine), that features two-dimensional coordination network with 1D open channels of 0.74 nm×0.65 nm running along the *c* axis. Complex **1** has been characterized by IR spectroscopy, elemental analysis, single-crystal X-ray diffraction, TGA, and by photoluminescence.

1 Experimental

1.1 Materials and measurements

All chemicals purchased were of reagent grade and used without further purification. All syntheses were carried out in 23 mL Teflon-lined autoclaves under autogenous pressure. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240 CHN elemental analyzer. The IR spectra were acquired using Nicolet Avatar 360 FTIR spectrophotometer. Luminescence spectra and lifetime for crystal solid samples were recorded at room temperature on an Edinburgh FLS920 phosphorimeter. Thermogravimetry analyses

(TGA) were performed on a automatic simultaneous thermal analyzer (DTG-60, Shimadzu) under a flow of N_2 at a heating rate of $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$ between ambient temperature and $800\text{ }^\circ\text{C}$.

1.2 Synthesis of **1**

$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.1 g; 0.3 mmol) and H_2bdc (0.047 g; 0.3 mmol) were dissolved in 15 mL of DMF. After adding dabco (0.15 mmol; 0.017 g), the mixture was stirred for 1 h at room temperature. The milk-white precipitate was filtered off after centrifugation, and the colorless filtrate was sealed in a 23 mL Teflon reactor and kept under autogenous pressure at $120\text{ }^\circ\text{C}$ for 72 h. The mixture was cooled to room temperature as a rate of $5\text{ }^\circ\text{C} \cdot \text{h}^{-1}$. (yield: 45% based on bdc). Anal. Calcd. for $\text{C}_{17}\text{H}_{27}\text{CdN}_3\text{O}_7$ (%): C, 40.98; H, 5.42; N, 8.44. Found (%): C, 41.00; H, 5.39; N, 8.49. IR (KBr pellet, cm^{-1}): 3 400(vs), 2 956(m), 1 621(w), 1 554(vs), 1 499(s), 1 384(vs), 1 235(m), 1 172(w), 1 054(m), 1 003(w), 948(w), 847(m), 774(m), 665(w), 577(w), 512(w).

1.3 Crystal structure analysis

A single crystal with dimensions of 0.30 mm×0.28 mm×0.19 mm was mounted on a glass fiber for data collection which was performed on a Rigaku/MS C Mercury CCD diffractometer equipped with a graphite-monochromatic Mo $K\alpha$ radiation ($\lambda=0.071\ 073\text{ nm}$) at 293(2) K by using an φ - ω scan mode. In the range of $3.06^\circ < \theta < 25.19^\circ$, a total of 18 248 reflections were collected, of which 2 365 were unique ($R_{\text{int}}=0.076\ 7$) and 1 866 observed ones ($I > 2\sigma(I)$) were used in the succeeding structure calculations. Empirical absorption corrections were performed using the program Crystal Clear^[22]. The structure was solved by direct methods and refined on F^2 by full-matrix least squares technique using the SHELX-97 program package^[23]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. For complex **1**, electron density in two regions were attributed to two badly disordered water molecules. The regions of electron density were removed from the reflections data using the program SQUEEZE (PLATON)^[24], leaving a total void of 0.384 nm^3 . The final $R=0.060\ 9$ and $wR=0.166\ 9$ ($w=1/[\sigma^2(F_o^2)+(0.120\ 3P)^2+0.451\ 4P]$),

where $P=(F_o^2+2F_c^2)/3$ for 1 866 observed reflections with $I>2\sigma(I)$. $S=1.046$, $(\Delta/\sigma)_{\max}=0.000$, $(\Delta\rho)_{\max}=1\ 361\ \text{e}\cdot\text{nm}^{-3}$ and $(\Delta\rho)_{\min}=-640\ \text{e}\cdot\text{nm}^{-3}$. Crystal parameters and details of the data collection and refinement are given

in Table 1. Selected bond lengths and angles are given in Table 2.

CCDC: 847762.

Table 1 Crystal data and structure refinement information for compound 1

Formula	$\text{C}_{17}\text{H}_{27}\text{CdN}_3\text{O}_7$	Z	4
Formula Weight	461.78	$D_c / (\text{g}\cdot\text{cm}^{-3})$	1.265
Temperature / K	293(2)	Adsorption coefficient / mm	0.925
Crystal system	Orthorhombic	$F(000)$	936
Size / mm	$0.30\times0.28\times0.19$	θ range / ($^\circ$)	$3.06\sim25.19$
Space group	$Pnma$	Limiting indices	$-25\leq h\leq 25, -8\leq k\leq 8, -18\leq l\leq 18$
a / nm	$2.092\ 7(6)$	Reflections collected / unique	$18\ 248 / 2\ 365$
b / nm	$0.734\ 9(3)$	Goodness-of-fit	1.046
c / nm	$1.577\ 1(3)$	Final R indices ($I>2\sigma(I)$)	$R_1=0.060\ 9, wR_2=0.166\ 9$
V / nm^3	$2.425\ 5(13)$	R indices (all data)	$R_1=0.076\ 7, wR_2=0.178\ 7$

Table 2 Selected bond distances (nm) and angles ($^\circ$)

Cd1-O1	0.233 1(6)	Cd1-O5	0.237 1(6)	Cd1-O4 ⁱⁱ	0.250 0(6)
Cd1-O3 ⁱⁱ	0.234 5(6)	Cd1-N1	0.237 2(5)	Cd1-O2	0.259 7(8)
O1-Cd1-O3 ⁱⁱ	136.3(2)	O3-Cd1-N1	90.25(9)	O5-Cd1-O2	82.0(2)
O1-Cd1-O5	135.2(2)	N1-Cd1-N ⁱⁱⁱ	175.4(2)	N1-Cd1-O2	89.38(9)
O3-Cd1-O5	88.54(19)	N1-Cd1-O4 ⁱⁱ	92.00(10)	O4 ⁱⁱ -Cd1-O2	136.0(2)
O1-Cd1-N1	91.41(9)	O1-Cd1-O2	53.1(2)	O5-Cd1-O4 ⁱⁱ	142.0(2)

Symmetry codes: ⁱ $-1/2+x, y, 1/2-z$; ⁱⁱⁱ $x, 1/2-y, z$.

2 Results and discussion

2.1 IR spectra and TGA

The IR spectra of compound **1** shows broad bands in the $3\ 400\ \text{cm}^{-1}$, which may be assigned to the $\nu(\text{O-H})$ stretching vibrations of the free water molecules. The absence of broad band at $2\ 956\ \text{cm}^{-1}$ could be attributed to $\nu(\text{C-H})$ stretching vibrations of methylene (dabco) and methyl (DMF), respectively. The feature at $1\ 621\ \text{cm}^{-1}$ may be assigned to the $\nu(\text{C=O})$ stretching vibrations of DMF. Whilst the features at about $1\ 554$ and $1\ 499\ \text{cm}^{-1}$ are associated with the asymmetric (COO^-) and symmetric (COO^-) stretching vibrations. The $\Delta\nu(\nu_{\text{as}}(\text{COO}^-)-\nu_{\text{s}}(\text{COO}^-))$ values are $55\ \text{cm}^{-1}$ (less than $105\ \text{cm}^{-1}$), indicating the coordination of H_2bdc with Cd(II) in chelating mode^[25], which is well consistent with X-ray diffraction structural analysis.

Thermal gravimetric analyses (TGA) were carried out to examine the thermal stability of **1**. The samples were heated up in flowing N_2 with a heating rate of 10

$^\circ\text{C}\cdot\text{min}^{-1}$. The TGA curve is depicted in Fig.1, which shows that a gradual weight-loss step of 20.7% ($50\sim190\ ^\circ\text{C}$), corresponding to the escape of the two uncoordinated water molecules and one coordinated DMF molecule (calcd. 21.4%). The weight-loss step that occurs above $350\ ^\circ\text{C}$ corresponds to the decomposition of the framework.

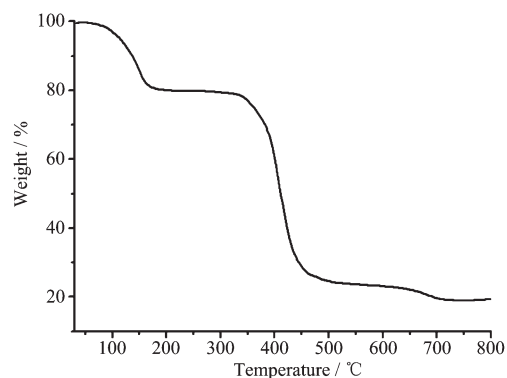


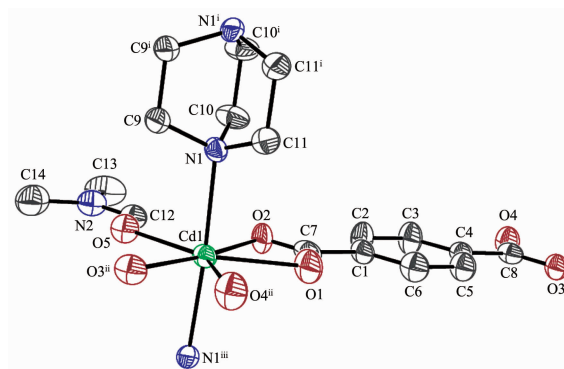
Fig.1 TGA trace of compound **1**

2.2 Structure description

Single-crystal X-ray diffraction analysis reveals

that compound **1** displays a 2D layered network, which built by Cd-carboxylate chains and diamine pillars. **1** crystallizes in the centrosymmetric space group *Pnma* with the complex located on a mirror plane. Coordination environment of Cd(II) atom of **1** is shown in Fig.2. Each Cd^{II} ion is seven-coordinated by four oxygen atoms from two bdc ligands, two nitrogen atoms from two dabco ligands and one oxygen atom from DMF molecule, adopting a distorted pentagonal bipyramidal coordination geometry with Cd-O, Cd-N bond lengths and O-Cd-O, O-Cd-N bond angles are within the range of those reported in other seven-coordinated Cd(II) compounds with oxygen and nitrogen donating ligand^[26-27]. The four carboxylate O atoms (O1, O2, O3ⁱⁱ, O4ⁱⁱ) involved in chelation and one O atom (O5) of DMF molecule form a pentagonal plane around the Cd atom, while two N atoms of the dabco ligands occupy the axial sited of the pentagonal bipyramid.

In the complicated polymeric structure of **1**, the bdc ligands exhibit μ_2 chelation bridging to link two Cd(II) ions. Whilst the dabco ligand acts in trans coordination motif and bidentate bridging to link two Co(II) ions. On the basis of these connections of μ_2 linear bridging bdc ligands, Cd(II) centers were con-



Symmetry codes: ⁱ $x, -1/2-y, z$; ⁱⁱ $-1/2+x, y, 1/2-z$; ⁱⁱⁱ $x, 1/2-y, z$;
Displacement ellipsoids at the 30% probability level

Fig.2 Coordination environment of Cd(II) atom in complex **1**

ected together to form a cadmium-carboxylate chain in the *b*-axis direction (Fig.3a), with the adjacent separation of Cd(II) ions is 1.134 1(2) nm. These chains are further connected into a 2D layered network through dabco ligands which functional as pillars (Fig.3b). Interestingly, 2D layered network contains small channels of 0.74 nm×0.65 nm along the *c* axis (Fig.3b). The size of the total void created by the formal removal of the coordinated DMF and uncoordinated water molecules is 1.189 5 nm³, which is about 49.0% of the unit cell volume^[24].

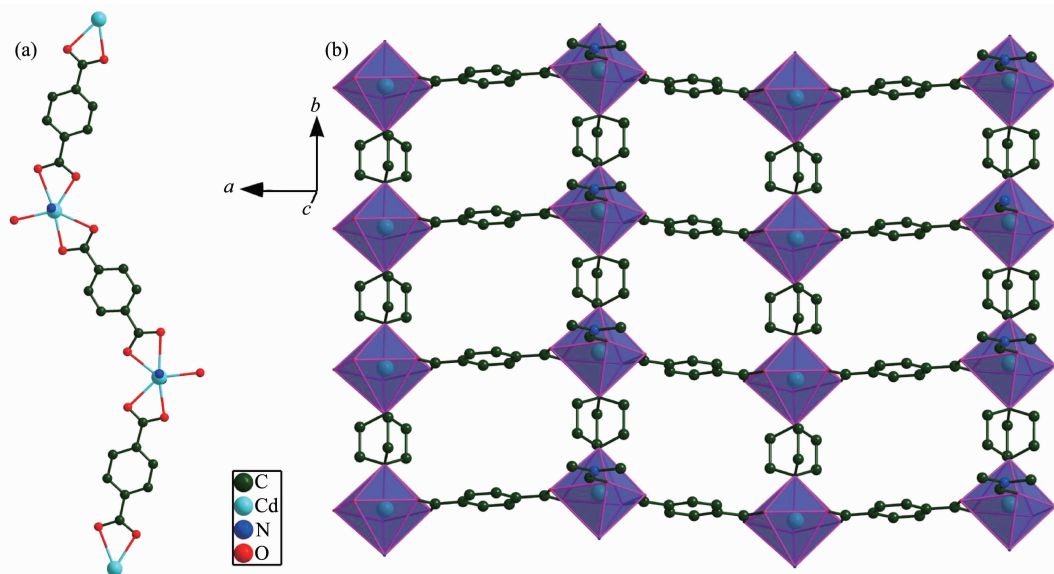


Fig.3 (a) 1D Cd-carboxylate chain of **1** in the *b* axis; (b) View of the 2D layered network of **1** with 1D channels of 0.74 × 0.65 nm² along the *c* axis

2.3 Luminescent properties

Due to the excellent luminescent properties of Cd(II) ions, the photoluminescence of **1** was investiga-

ted. The emission spectrum of compound **1** in the solid state at room temperature is shown in Fig.4a. It can be observed that compound **1** exhibits indigotin photolu-

minescence with an emission maximum at *ca.* 430 nm upon excitation at 320 nm. From the emission maximum of compound **1**, which is clearly red-shifted compared with the free ligand H₂bdc^[28]. The title compound represents an obvious qualitative change of luminescence property resulted from the interaction between metal ion and ligand. The emission of title compound probably origins from ligand-to-metal charge transfer

(LMCT)^[29] excited state, because the ligand H₂bdc has relatively large π -conjugated system of phenyl ring and uses carboxylato-oxygen donors to coordinate to Cd(II) ions, which benefits the charge transfer between Cd(II) ion and organic ligands. Moreover, as shown in Fig.4b, the luminescent lifetime of solid **1** using an Edinburgh FLS920 phosphorimeter with a 450 W xenon lamp as excitation source show lifetime for **1** of 38.2 ns.

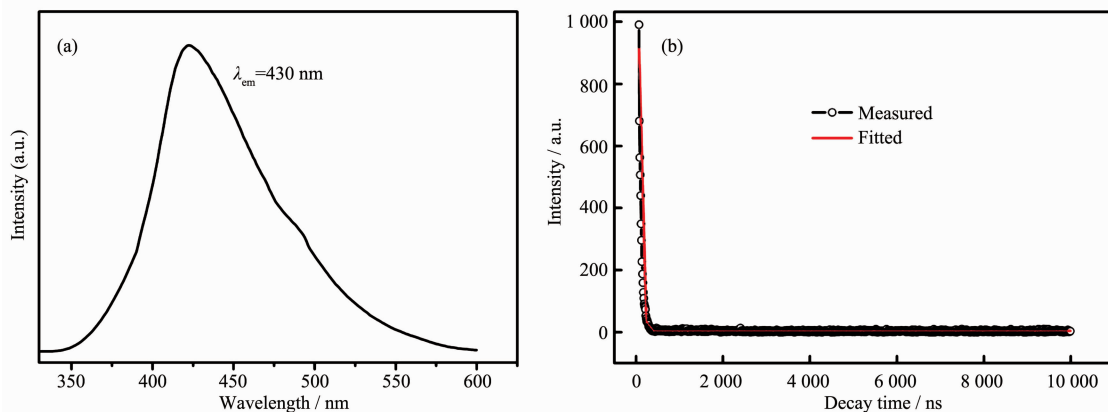


Fig.4 (a) Solid-state emission spectrum of **1** at room temperature; (b) Luminescent lifetime of **1**

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