

基于 1,2,4-苯三酸与[2,3-f]吡嗪并[1,10]菲咯啉配体的 钴(II)及镉(II)配合物的水热合成与晶体结构

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摘要: 利用水热技术, 合成了 2 个新的配合物 $[\text{Co}(\text{Hbtc})(\text{Pyphen})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (**1**) 和 $[\text{Cd}_2(\text{btc})(\text{Pyphen})_2\text{Cl}] \cdot 2\text{H}_2\text{O}$ (**2**) (H_3btc =1,2,4-苯三酸, Pyphen =[2,3-f]吡嗪并[1,10]菲咯啉), 并通过 X-射线单晶衍射、元素分析、热重分析和荧光进行了表征。配合物 **1** 属三斜晶系, 空间群 $P\bar{1}$, $a=0.643\ 44(13)$ nm, $b=1.202\ 9(2)$ nm, $c=1.371\ 6(3)$ nm, $\alpha=95.03(3)^\circ$, $\beta=90.46(3)^\circ$, $\gamma=103.54(3)^\circ$, $V=1.027\ 7(4)$ nm³, $Z=2$, $\text{CoC}_{23}\text{H}_{16}\text{N}_4\text{O}_8$, $M_r=535.31$, $D_c=1.730$ g·cm⁻³, $\mu(\text{Mo K}\alpha)=0.900$ mm⁻¹, $F(000)=546$, $\text{GOOF}=1.089$, $R=0.099\ 2$, $wR=0.249\ 0$; 配合物 **2** 属三斜晶系, 空间群 $P\bar{1}$, $a=0.968\ 93(8)$ nm, $b=1.223\ 82(10)$ nm, $c=1.592\ 21(14)$ nm, $\alpha=67.486\ 0(10)^\circ$, $\beta=73.158\ 0(10)^\circ$, $\gamma=78.468\ 0(10)^\circ$, $V=1.660\ 9(2)$ nm³, $Z=2$, $\text{Cd}_2\text{C}_{37}\text{H}_{23}\text{N}_8\text{O}_8\text{Cl}$, $M_r=967.88$, $D_c=1.935$ g·cm⁻³, $\mu(\text{Mo K}\alpha)=1.432$ mm⁻¹, $F(000)=956$, $\text{GOOF}=1.051$, $R=0.077\ 9$, $wR=0.141\ 2$ 。结构分析表明: 配合物 **1** 为无限一维双链结构, 配合物 **2** 为二维层状结构。此外, 氢键和 π - π 相互作用在加固配合物的结构中起到重要作用。

关键词: 钴(II); 镉(II); 1,2,4-苯三酸; [2,3-f]吡嗪并[1,10]菲咯啉; 晶体结构

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Hydrothermal Syntheses and Crystal Structures of Cobalt(II) and Cadmium(II) Complexes with 1,2,4-Benzenetricarboxylic Acid and Pyrazino[2,3-f][1,10]-phenanthroline Ligands

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Abstract: The title complexes, $[\text{Co}(\text{Hbtc})(\text{Pyphen})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (**1**) and $[\text{Cd}_2(\text{btc})(\text{Pyphen})_2\text{Cl}] \cdot 2\text{H}_2\text{O}$ (**2**) (H_3btc =1,2,4-benzenetricarboxylic acid, Pyphen =pyrazino [2,3-f][1,10]-phenanthroline) have been hydrothermally synthesized and structurally characterized by X-ray single-crystal diffraction, elemental analyses, thermal gravimetry analysis (TGA) and luminescent property. Crystal **1** is of triclinic, space group $P\bar{1}$ with $a=0.643\ 44(13)$ nm, $b=1.202\ 9(2)$ nm, $c=1.371\ 6(3)$ nm, $\alpha=95.03(3)^\circ$, $\beta=90.46(3)^\circ$, $\gamma=103.54(3)^\circ$, $V=1.027\ 7(4)$ nm³, $Z=2$, $\text{CoC}_{23}\text{H}_{16}\text{N}_4\text{O}_8$, $M_r=535.31$, $D_c=1.730$ g·cm⁻³, $\mu(\text{Mo K}\alpha)=0.900$ mm⁻¹, $F(000)=546$, $\text{GOOF}=1.089$, the final $R=0.099\ 2$ and $wR=0.249\ 0$ for 2 933 observed reflections ($I>2\sigma(I)$). Crystal **2** is of triclinic, space group $P\bar{1}$ with $a=0.968\ 93(8)$ nm, $b=1.223\ 82(10)$ nm, $c=1.592\ 21(14)$ nm, $\alpha=67.486\ 0(10)^\circ$, $\beta=73.158\ 0(10)^\circ$, $\gamma=78.468\ 0(10)^\circ$, $V=1.660\ 9(2)$ nm³,

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$Z=2$, $\text{Cd}_2\text{C}_{37}\text{H}_{23}\text{N}_8\text{O}_8\text{Cl}$, $M_r=967.88$, $D_c=1.935\text{ g}\cdot\text{cm}^{-3}$, $\mu(\text{Mo } K\alpha)=1.432\text{ mm}^{-1}$, $F(000)=956$, $\text{GOOF}=1.051$, the final $R=0.0779$ and $wR=0.1412$ for 4817 observed reflections ($I>2\sigma(I)$). Structural analyses show that the complex **1** presents an infinite one-dimensional polymeric double-chain structure and the complex **2** shows a two-dimensional layered structure. Furthermore, the hydrogen-bonding and π - π stacking interactions play key roles in consolidating the complex structures. CCDC: 829207, **1**; 829208, **2**.

Key words: cobalt(II); cadmium(II); 1,2,4-benzenetricarboxylic acid; pyrazino[2,3-f][1,10]-phenanthroline; crystal structure

0 Introduction

The construction of novel metal-organic frameworks is of considerable interest and importance in coordination chemistry, owing to not only their intriguing molecular topologies but also their tremendous potential applications in host-guest chemistry, medicine, catalysis, molecular selection, non-linear optics, ion exchange, magnetic materials and microelectronics^[1-10]. During the past decade, many novel and fascinating framework have been synthesized and characterized using symmetrical multicarboxylate ligands such as 1,4-benzenetetracarboxylate, 1,3,5-benzenetricarboxylate, 1,2,4,5-benzenetetracarboxylate, but the asymmetrical multicarboxylate ligands, have been less studied up to now^[11-15]. Compared with those symmetrical ligands, the inherent geometric asymmetric of 1,2,4-benzenetricarboxylate ligand provide more advantages in constructing novel network topologies^[16]. Furthermore, metal carboxylate and 1,10-phenanthroline (phen) systems have been widely studied^[17-18]. However, far less attention has been given to the derivatives of phen. Pyrazino [2,3-f] [1,10]-phenanthroline (Pyphen) as an important phen derivative possesses fruitful aromatic systems and may be a good candidate for the construction of metal-organic supramolecular architectures. Withal, no example of coordination complexes based on Pyphen in combination with 1,2,4-benzenetricarboxylic acid (H_3btc) ligand has been reported so far. Ongoing research in our work, we adopted H_3btc as an organic linker, Pyphen as a secondary ligand, divalent cobalt ion and divalent cadmium ion as the metal centers, synthesized two new metal-organic coordination polymers: $\{[\text{Co}(\text{Hbtc})(\text{Pyphen})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**1**) and

$\{[\text{Cd}_2(\text{btc})(\text{Pyphen})_2\text{Cl}]\cdot 2\text{H}_2\text{O}\}_n$ (**2**). Additionally, the crystal structure, TG and photoluminescent properties of these two polymers were also studied in detail.

1 Experimental

1.1 Generals

The Pyphen ligand was synthesized according to the literature method^[19] and all other materials were purchased from commercial sources and used without further purification. Elemental analysis was conducted on a Perkin-Elmer 240C analyzer. Thermogravimetric analysis (TGA) was carried out under air condition on a NETZSCH STA 449C analyzer. The photoluminescent behaviors of the complexes were studied using a Perkin-Elmer LS55 spectrometer.

1.2 Syntheses and crystal growth

Compound **1** was hydrothermally synthesized under autogenous pressure. A mixture of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.2 mmol, 0.0581 g), H_3btc (0.2 mmol, 0.0420 g), Pyphen (0.2 mmol, 0.0464 g), NaOH (0.4 mmol, 0.0160 g) and deionized water (15 mL) was stirred for 30 min in air, then transferred to a 25 mL Teflon-lined stainless steel autoclave and heated to 160 °C for 3 d. After cooling to room temperature at a rate of 5 °C \cdot h⁻¹, brown block crystals of **1** were obtained. The crystals were filtered, washed with distilled water and dried at ambient temperature getting a yield of about 72% based on Co(II). Anal. calcd. for $\text{CoC}_{23}\text{H}_{16}\text{N}_4\text{O}_8$ (%): C, 51.60; H, 3.01; N, 10.47. Found(%): C, 51.79; H, 2.69; N, 10.50.

The synthesis procedure for **2** was the same as that for **1** except that $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ was replaced by CdCl_2 . Yellow block crystals of **2** were collected in 68% yield based on Cd(II). Anal. calcd. for $\text{Cd}_2\text{C}_{37}\text{H}_{23}\text{N}_8\text{O}_8\text{Cl}$ (%): C, 45.91; H, 2.39; N, 11.58. Found(%): C, 45.94; H, 2.43; N, 11.56.

1.3 X-ray structure determination

Crystallographic data of two compounds were collected at room temperature on a Rigaku RAXIS-RAPID single crystal diffractometer equipped with a narrow-focus, 5.4 kW sealed tube X-ray source (graphite-monochromated Mo $K\alpha$ radiation, $\lambda=0.071\ 073\ \text{nm}$) by using an ω - 2θ scan mode at 292 (2) K. For **1**, a total of 8 078 reflections were collected in the range of $2.98^\circ \leq \theta \leq 25.01^\circ$, of which 3 604 were unique with $R_{\text{int}}=0.056\ 0$ and 2 933 were observed with $I>2\sigma(I)$. And for **2**, a total of 9 365 reflections were collected in the range of $1.42^\circ \leq \theta \leq 26.03^\circ$, of which 6 378 were unique with $R_{\text{int}}=0.026\ 1$ and 4 817 were observed with $I>2\sigma(I)$. All

the structures were solved by direct methods using the program SHELXS-97^[20] and refined by full-matrix least-squares techniques against F^2 using the SHELXTL-97 crystallographic software package^[21]. All non-hydrogen atoms were easily found from the difference Fourier map and refined anisotropically, whereas the hydrogen atoms of the organic molecules were placed by geometrical considerations and were added to the structure factor calculation. The detailed crystallographic data and structure refinement parameters for two compounds are summarized in Table 1.

CCDC: 829207, **1**; 829208, **2**.

Table 1 Crystal data and structure refinements for **1** and **2**

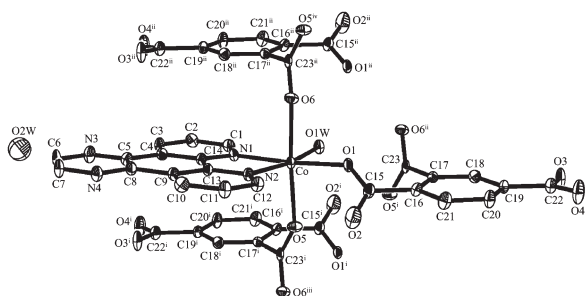
Compound	1	2
Empirical formula	$\text{CoC}_{23}\text{H}_{16}\text{N}_4\text{O}_8$	$\text{Cd}_2\text{C}_{37}\text{H}_{23}\text{N}_8\text{O}_8\text{Cl}$
Formula weight	535.33	967.88
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a / nm	0.643 44(13)	0.968 93(8)
b / nm	1.202 9(2)	1.223 82(10)
c / nm	1.371 6(3)	1.592 21(14)
$\alpha / (^\circ)$	95.03(3)	67.486 0(10)
$\beta / (^\circ)$	90.46(3)	73.158 0(10)
$\gamma / (^\circ)$	103.54(3)	78.468 0(10)
V / nm^3	1.027 7(4)	1.660 9(2)
Z	2	2
$R_1 [I>2\sigma(I)]$	0.099 2	0.077 9
$wR_2 [I>2\sigma(I)]$	0.249	0.141 2
$D_c / (\text{g}\cdot\text{cm}^{-3})$	1.73	1.935
μ / mm^{-1}	0.9	1.432
$F(000)$	546	956
Unique reflections	3 604	6 378
Observed reflections $[I>2\sigma(I)]$	2 933	4 817
Goodness-of-fit on F	1.089	1.051

2 Results and discussion

2.1 Description of the structure

A single-crystal X-ray diffraction study performed on **1** reveals an extended unique three-dimensional supramolecular coordination framework that crystallizes in space group $P\bar{1}$. The asymmetric unit of **1** (Fig.1) consists of one Co(II) atom, one Pyphen molecule, one Hbte^{2-} ligand and one coordinated water molecule.

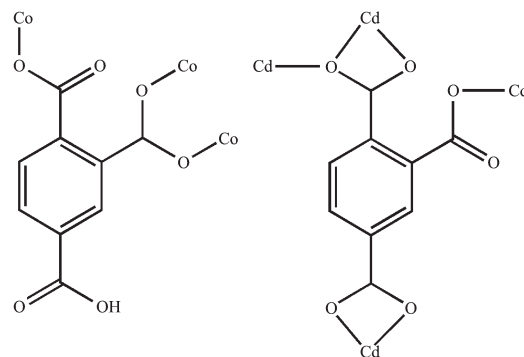
Furthermore, there exist disorder water molecules in complex **1**. The centre Co(II) atom is six-coordinated by two nitrogen atoms (Co-N(1) 0.214 7(5) nm, Co-N(2) 0.211 3(5) nm) from one Pyphen ligand, four oxygen atoms (Co-O(1) 0.207 6(4) nm, Co-O(5) 0.212 7(4) nm, Co-O(6) 0.214 4(4) nm, Co-O(1W) 0.210 0(4) nm) from three different Hbte^{2-} ligands and one water molecule, exhibits a slightly distorted octahedral coordination environment. The equatorial plane is composed of N(1),



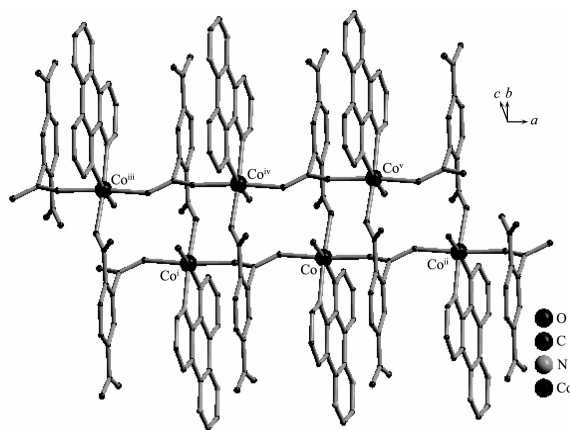
Symmetry codes: ⁱ $-x, 1-y, 2-z$; ⁱⁱ $1-x, 1-y, 2-z$; ⁱⁱⁱ $-1+x, y, z$; ^{iv} $1+x, y, z$; Hydrogen atoms were omitted for clarity

Fig.1 ORTEP view of compound **1** with 20% probability displacement ellipsoids

N(2), O(1), O(1W) atoms, whereas O(5) and O(6) atoms occupy the axial positions of the octahedron. The selected bond lengths and bond angles are given in Table 2. In complex **1**, two carboxylate groups of a Hbtc²⁻ ligand display monodentate and bis(monodentate) bridging coordination mode, respectively, whereas another carboxylate oxygen atoms are uncoordinated (Scheme 1). Each pair of adjacent Co atoms are bridged through the carboxyl group of Hbtc²⁻ to finish a one-dimensional double-chain along the *a* axis, with Pyphen ligands decorated on each side (Fig.2). Intermolecular O—H···O hydrogen bonds are observed between the deprotonated carboxylate oxygen atom O(3) and the carboxylate oxygen atom O(4). Furthermore, the



Scheme 1 Observed coordination modes of 1,2,4-btc in the complexes **1** and **2**



Symmetry codes: ⁱ $-1+x, y, z$; ⁱⁱ $1+x, y, z$; ⁱⁱⁱ $-1-x, 1-y, 2-z$; ^{iv} $-x, 1-y, 2-z$; ^v $1-x, 1-y, 2-z$

Fig.2 One-dimensional polymeric double chain of compound **1**

Table 2 Selected Bond lengths (nm) and bond angles(°) for **1** and **2**

Complex 1					
Co-O(1)	0.207 9(4)	Co-O(5)	0.212 6(4)	Co-N(1)	0.214 6(5)
Co-O(1W)	0.210 1(4)	Co-O(6)	0.214 5(4)	Co-N(2)	0.210 7(5)
O(1)-Co-O(5)	89.64(16)	O(1)-Co-O(6)	83.87(15)	O(1)-Co-N(2)	102.65(17)
O(1)-Co-O(1W)	89.35(16)	O(5)-Co-N(1)	94.90(17)	O(1W)-Co-N(1)	89.97(17)
Complex 2					
Cd(1)-N(1)	0.241 9(6)	Cd(1)-O(5)	0.244 5(5)	Cd(1)-O(6)	0.244 7(5)
Cd(1)-N(2)	0.234 3(6)	Cd(1)-O(1)	0.224 0(5)	Cd(1)-Cl ⁱ	0.216 3(6)
Cd(2)-Cl	0.218 2(4)	Cd(2)-O(5)	0.227 7(5)	Cd(2)-N(5)	0.235 5(6)
Cd(2)-N(6)	0.235 5(6)	Cd(2)-O(3)	0.228 2(5)	Cd(2)-O(4)	0.249 8(5)
Cl ⁱ -Cd(1)-O(1)	111.7(2)	Cl ⁱ -Cd(1)-N(2)	124.6(2)	O(1)-Cd(1)-N(2)	95.7(2)
Cl ⁱ -Cd(1)-N(1)	88.4(2)	Cl ⁱ -Cd(1)-O(6)	142.9(2)	N(1)-Cd(1)-O(5)	90.93(19)
Cl-Cd(2)-O(5)	88.7(2)	Cl-Cd(2)-O(3)	100.1(2)	O(5)-Cd(2)-O(3)	98.23(19)
Cl-Cd(2)-N(6)	115.3(2)	N(5)-Cd(2)-N(6)	70.6(2)	O(3)-Cd(2)-N(6)	139.8(2)

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

coordinated water molecule O(1W) is also involved in hydrogen bonding interactions with carboxylate oxygen atom (Table 3). Simultaneously, the neighboring one-dimensional chains interact via π - π stacking interactions between the Pyphen ligands (centroid-to-centroid

distance 0.353 3 nm), as well as the π - π type interactions between Hbtc²⁻ and Pyphen ligands (centroid-to-centroid distance 0.342 0 nm). Therefore, an intriguing three-dimensional supramolecular motif is formed via hydrogen bonds and π - π stacking interactions.

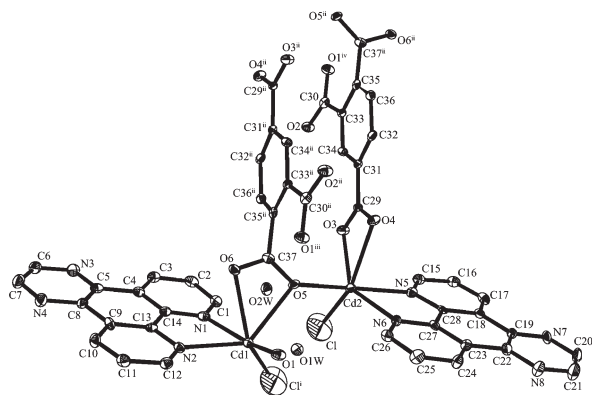
Table 3 Hydrogen bond lengths and bond angles for **1** and **2**

D-H \cdots A	<i>d</i> (D-A) / nm	<i>d</i> (H \cdots A) / nm	<i>d</i> (D \cdots A) / nm	\angle DHA / (°)
Complex 1				
O(3)-H(3A) \cdots O(4) ⁱ	0.082	0.184	0.264 8	170.4
O(1W)-H(1WA) \cdots O(1) ⁱⁱ	0.088	0.198	0.284 8	170.7
O(1W)-H(1WB) \cdots O(5)	0.090	0.208	0.288 5	147.8
O(1W)-H(1WB) \cdots O(6)	0.090	0.224	0.289 5	129.0
Complex 2				
O(1W)-H(1WA) \cdots O(3) ⁱⁱⁱ	0.085	0.193	0.275 5	164.6
O(1W)-H(1WB) \cdots O(2) ^{iv}	0.085	0.202	0.284 0	161.3
O(2W)-H(2WA) \cdots O(1W)	0.086	0.205	0.282 9	150.5

Symmetry transformations used to generate the equivalent atoms: **1**: ⁱ $-x+1, -y+2, -z+3$; ⁱⁱ $-x+1, -y+1, -z+2$; **2**: ⁱⁱⁱ $x-1, y, z$;

^{iv} $-x+1, -y, -z+1$.

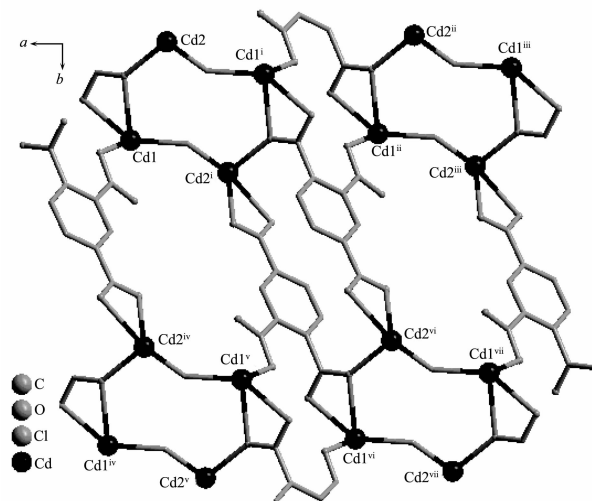
Compound **2** crystallized in a layered network structure, composed of interlinking of btc³⁻ ligands with Cd(II) ions. The asymmetric unit contains two crystallographically unique Cd(II) atoms, two Pyphen molecules, one btc³⁻ ligands, one Cl⁻ and two uncoordinated water molecules (Fig.3). Cd(1) and Cd(2) all adopt distorted octahedral geometries coordinated by two N atoms (N(1), N(2) or N(5), N(6)) from one Pyphen ligand, three O atoms (O(1), O(5), O(6) or O(3), O(4), O(5)) from two different btc³⁻ ligands, and one Cl⁻ ion (Clⁱ or Cl). The selected bond lengths and bond angles are given in



Symmetry codes: ⁱ $2-x, 1-y, 1-z$; ⁱⁱ $3-x, -y, 1-z$; ⁱⁱⁱ $3-x, 1-y, 1-z$;
^{iv} $x, -1+y, z$; Hydrogen atoms were omitted for clarity

Fig.3 ORTEP view of compound **2** with 20% probability displacement ellipsoids

Table 2. Cd(1) and Cd(2) centers are linked by one chelate/monodentate carboxylate group of btc³⁻ ligand to form a dimeric unit, the adjacent dimeric units are further linked by two bridging μ_2 -Cl ions to form an unusual tetranuclear cluster. Then such tetranuclear clusters are linked by btc³⁻ ligand to form novel two-dimensional layer structure along the *ab* plane (Fig.4), and the Pyphen ligands are attached to both sides of the layer. In contrast to compound **1**, the carboxylate groups



Symmetry codes: ⁱ $2-x, 1-y, 1-z$; ⁱⁱ $-1+x, y, z$; ⁱⁱⁱ $1-x, 1-y, 1-z$; ^{iv} $x, 1+y, z$; ^v $2-x, 2-y, 1-z$; ^{vi} $-1+x, 1+y, z$; ^{vii} $1-x, 2-y, 1-z$

Fig.4 2D framework structure of **2** and the Pyphen ligands are omitted

of the btc^{3-} ligand in **2** adopt different coordination modes: chelate-monodentate, chelate and monodentate coordination mode (Scheme 1). Finally, the π - π stacking interactions (centroid-to-centroid distance ca. 0.361 9 nm) between the Pyphen ligands and O-H \cdots O hydrogen bonds between water molecules as donors and carboxylate oxygen atoms and another water molecule as acceptors (Table 3), contributed to the stabilization of the overall crystal structure.

By a comparison of complexes **1** and **2**, structural dissimilarity reveals that the coordination behavior of metal center has pronounced effect on formation of building units, when the Co(II) ion is replaced by Cd(II) ion, structurally different complex is obtained. In addition, the noncovalent interactions such as hydrogen bonding and π - π stacking interactions, which guide the formation and stabilize the extended network structures.

2.2 TGA

The stability of **1**, **2** was investigated by TGA, three distinct weight losses were observed for both. For **1**, the first weight loss of 6.60% is in the range 80~220 °C, assigned to the decomposition of the water molecules (calcd. 6.75%). The second weight loss of 38.85% is ascribable to the loss of Hbtc^{2-} ligand (calcd. 39.03%) from 250 to 340 °C. The last weight loss of 43.25% is in the temperature range of 400~520 °C, corresponding to the release of Pyphen ligand (calcd. 43.55%). The final product may be CoO.

The reasons for the weight losses of **2** are the same, whereas the losses are 3.69% in the temperature range 90~150 °C for the first (calcd. 3.72%), 21.09% from 260 to 360 °C for the second (calcd. 21.42%), and 47.99% in the range of 390~519 °C for the last (calcd. 48.04%), respectively. And CdO could be the final product.

2.3 Photoluminescent property

Cd(II) can produce a variety of complexes that not only exhibit appealing structures but also possess excellent photoluminescence (PL) properties^[5,7,10]. The PL property of compound **2** was investigated in the solid state at room temperature (RT). It can be observed that the maximum emission peak of **2** occurs at 572 nm

(λ_{ex} =365 nm), which is red-shifted compared with that of pure Pyphen ligand (λ_{em} =439 nm, λ_{ex} =300 nm)^[22] (Fig.5). The H_3btc is nearly non-fluorescent emission in the range 300~700 nm for excitation wavelengths between 200 and 400 nm at RT. Compared with the PL spectra, the emission spectrum shape of **2** has slightly changeable to Pyphen ligands', which might be attributable to chelating coordination of the planar Pyphen ligand in complex and change its HOMO and LUMO energy levels. The photoluminescent emission of **2** also mainly originates from the intraligand fluorescent emission^[10].

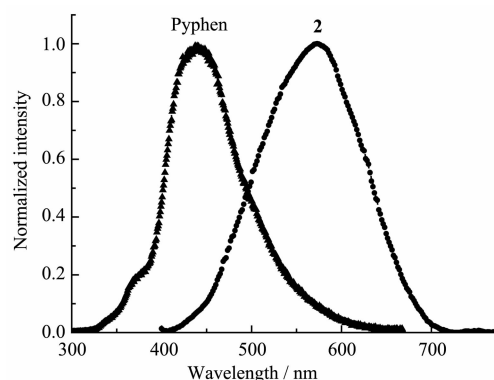


Fig.5 Normalized PL spectra of the complex **2** and Pyphen ligand

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