

一维配位聚合物 $\{[\text{Co}(\text{dpa})(\text{H}_2\text{O})_4] \cdot (\text{dpdo}) \cdot (\text{H}_2\text{O})\}_n$ ($\text{H}_2\text{dpa}=2,2'$ -联苯二酸, $\text{dpdo}=N,N'$ -二氧化-4,4'-联吡啶)的晶体结构和光谱性质

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摘要: 采用水热合成法制备了一个一维配位聚合物 $\{[\text{Co}(\text{dpa})(\text{H}_2\text{O})_4] \cdot (\text{dpdo}) \cdot (\text{H}_2\text{O})\}_n$ (**1**) ($\text{H}_2\text{dpa}=2,2'$ -联苯二酸, $\text{dpdo}=N,N'$ -二氧化-4,4'-联吡啶), 通过红外光谱、紫外光谱、元素分析、XRPD、TGA 和 X-射线单晶衍射进行了表征。Co(II)原子采取了畸变的八面体构型, 6 个配位氧原子分别来自于 2 个 dpa^{2-} 配体和 4 个配位水分子。每一个 dpa^{2-} 配体桥联 2 个 Co(II)中心, 每一个 Co(II)原子与 2 个 dpa^{2-} 配体配位进而形成了 2_1 螺旋链结构。借助溶剂水分子的连接作用, 螺旋链之间通过多种 O—H \cdots O 氢键作用形成了 2D 网络, 通过 dpdo 和 2D 网络之间多种类型的氢键作用形成了三维超分子结构。测定了室温下聚合物 **1** 的固体荧光光谱。

关键词: 配位聚合物; 钴(II); 晶体结构

中图分类号: O614.81*2

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Crystal Structure and Spectral Properties of a One-Dimensional Coordination Polymer $\{[\text{Co}(\text{dpa})(\text{H}_2\text{O})_4] \cdot (\text{dpdo}) \cdot (\text{H}_2\text{O})\}_n$ ($\text{H}_2\text{dpa}=2,2'$ -biphenyldicarboxylate, $\text{dpdo}=4,4'$ -bipyridine- N,N' -dioxide)

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Abstract: A new Co(II) coordination polymer $\{[\text{Co}(\text{dpa})(\text{H}_2\text{O})_4] \cdot (\text{dpdo}) \cdot (\text{H}_2\text{O})\}_n$ (**1**) ($\text{H}_2\text{dpa}=2,2'$ -biphenyldicarboxylate, $\text{dpdo}=4,4'$ -bipyridine- N,N' -dioxide) has been synthesized and characterized by IR spectroscopy, UV-Vis spectroscopy, elemental analysis, XRPD, TGA and X-ray single-crystal structure analysis. The Co(II) atom has a distorted octahedral coordination environment with a set of oxygen donors from two dpa^{2-} ligands and four coordinated water molecules. Each dpa^{2-} ligand is bounded to two cobalt centers and each cobalt atom is coordinated by two dpa^{2-} ligands thereby generating a 2_1 helical chain. The helical chains further interact with each other and form a 2D network through multiform O—H \cdots O hydrogen bonds with the help of the solvent water. In the solid state the adjacent layers are separated by dpdo units to form a 3D framework. Upon the excitation at 275 nm, the polymer **1** shows one emission peak at 430 nm in the solid state. CCDC: 922034.

Key word: coordination polymer; cobalt(II); crystal structure

The construction of coordination polymers via self-assembly of predesigned ligands with appropriate

metal ions has attracted increasing interests, due to the intriguing structure motifs and their potential

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applications in catalysis, molecular adsorption, magnetism, optical devices and molecular sensors^[1-4]. The polycarboxylates as one important subfamily of ligands are often employed to construct interesting framework structures because of not only their abundant coordination modes (such as monodentate, bidentate and chelate) but also their abilities to act as hydrogen-bond acceptors and donors^[5-7]. Compare with rigid organic polycarboxylic ligands, the flexible V-shaped 2,2'-biphenyldicarboxylate (H_2dpa) are often used as bridging ligands to assemble different coordination polymers with metal ions via the cooperative effect of various possible coordination modes and the flexibility of the ligand around the C-C bond^[8-11]. On the other hand, the introduction of the second organic component affords interestingly extended structures and functional properties. This strategy is currently one of the powerful methods in the design of coordination polymers^[12-13].

As a part of our continuing investigations on coordination polymers^[14-20], herein, we reported the synthesis and crystal structure of a one-dimensional Co(II) coordination polymer $\{[\text{Co}(\text{dpa})(\text{H}_2\text{O})_4] \cdot (\text{dpdo}) \cdot (\text{H}_2\text{O})\}_n$ (**1**) containing the bridging ligand 2,2'-biphenyldicarboxylate (H_2dpa) and free organic component 4,4'-bipyridine- N,N' -dioxide (dpdo).

1 Experimental

1.1 Materials and methods

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Ligand dpdo was synthesized and characterized by a previously reported procedure^[21]. Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240C analytical instrument. IR spectra were recorded from KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the 4 000~400 cm^{-1} region. The UV-Vis spectra were obtained on a Shimadzu UV-250 spectrometer in the range of 800~190 nm in the solid state. X-ray powder diffraction patterns were recorded on a D/max- γ A rotating anode X-ray diffractometer with Cu sealed tube ($\lambda=0.154\ 178$ nm). The thermogravimetric analysis was carried out

on a Perkin-Elmer-7 thermal analyzer at a heating rate of 10 $^{\circ}\text{C} \cdot \text{min}^{-1}$ from 25 to 800 $^{\circ}\text{C}$, and the luminescent spectra were performed on a Hitachi F-7000 fluorescence spectrophotometer.

1.2 Synthesis of the polymer

$\{[\text{Co}(\text{dpa})(\text{H}_2\text{O})_4](\text{dpdo})(\text{H}_2\text{O})\}_n$ (**1**): A mixture containing $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ (0.125 g, 0.5 mmol), H_2dpa (0.121 g, 0.5 mmol), dpdo (0.094 g, 0.5 mmol) and NaOH (0.020 g, 0.5 mmol) in 8 mL deionized water was sealed in a 25 mL Teflon lined stainless steel container and heated at 120 $^{\circ}\text{C}$ for 3 d. Red block crystals of **1** were collected in a 62% yield. Anal. for $\text{C}_{24}\text{H}_{26}\text{CoN}_2\text{O}_{11}$: calcd. (%): C 49.92, H 4.54, N 4.85; found (%): C 50.15, H 4.48, N 4.95. IR (cm^{-1} , KBr pellet): $\nu=3\ 392$ (m), 3 107 (m), 1 601 (w), 1 574(m), 1 548(s), 1 475(m), 1 449(w), 1 406(s), 1 232(s), 1 190(s), 1 024(w), 839(s), 760(m), 547(m).

1.3 Crystal structure determination

A suitable sample of size 0.40 mm \times 0.31 mm \times 0.18 mm was chosen for the crystallographic study and then mounted on a Bruker Smart APEX II CCD diffractometer with ω and φ scan mode in the range of $1.77^{\circ} < \theta < 25.00^{\circ}$. All diffraction measurements were performed at room temperature using graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm). A total of 12 354 (4 299 independent, $R_{\text{int}}=0.034\ 6$) reflections were measured. The structure was solved by direct methods and refined on F^2 by using full-matrix least-squares methods with SHELXL-97 program^[22-23]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques. All hydrogen atoms associated with carbon atoms were placed in the calculated positions and refined as a riding mode. The hydrogen atoms of water molecules were located from the successive difference Fourier syntheses and refined with the isotropic displacement parameters setting to 1.2 times those of their carrier atoms. Structure solution and refinement based on 3 473 independent reflections with $I > 2\sigma(I)$. Space group, lattice parameters and other relevant information are listed in Table 1, and selected bond lengths and angles are given in Table 2.

CCDC: 922034.

Table 1 Summary of crystal data and refinement results for the polymer **1**

Chemical formula	C ₂₄ H ₂₆ CoN ₂ O ₁₁	<i>F</i> (000)	1 196
Formula weight	577.4	μ / mm ⁻¹	0.8
Temperature / K	296(2)	θ range for data collection / (°)	1.77~25.00
Wavelength /	0.710 73	Index ranges	-12 ≤ <i>h</i> ≤ 12, -12 ≤ <i>k</i> ≤ 27, -16 ≤ <i>l</i> ≤ 16
Crystal system	Monoclinic	Reflections collected	12 354
Space group	<i>P</i> 2 ₁ / <i>c</i>	Independent reflections, <i>R</i> _{int}	4 299 / 0.034 6
<i>a</i> / nm	1.0138 5(7)	Refinement method	Full-matrix least-squares on <i>F</i> ²
<i>b</i> / nm	2.296 13(15)	Data / parameters	4 299 / 343
<i>c</i> / nm	1.400 20(7)	Goodness of fit on <i>F</i> ²	1.051
β / (°)	131.420(3)	<i>R</i> ₁ (<i>F</i>), <i>wR</i> ₂ (<i>F</i> ²) (<i>I</i> > 2σ(<i>I</i>))	0.037 0, 0.099 8
Volume / nm ³	2.444 3(3)	<i>R</i> ₁ (<i>F</i>), <i>wR</i> ₂ (<i>F</i> ²) (all data)	0.050 0, 0.105 3
<i>Z</i>	4	Largest diff. peak and hole / (e·nm ⁻³)	430 and -390
<i>D</i> _c / (g·cm ⁻³)	1.569		

Table 2 Selected bond lengths (nm) and angles (°) of the polymer **1**

Co(1)-O(1)	0.202 3(2)	Co(1)-O(5)	0.212 5(2)	Co(1)-O(6)	0.216 2(2)
Co(1)-O(3A)	0.203 7(2)	Co(1)-O(7)	0.214 3(2)	Co(1)-O(8)	0.217 9(2)
O(1)-Co(1)-O(3A)	177.48(7)	O(5)-Co(1)-O(7)	177.83(7)	O(1)-Co(1)-O(8)	84.37(7)
O(1)-Co(1)-O(5)	90.66(7)	O(1)-Co(1)-O(6)	92.21(7)	O(3A)-Co(1)-O(8)	93.11(7)
O(3A)-Co(1)-O(5)	89.27(7)	O(3A)-Co(1)-O(6)	90.31(7)	O(5)-Co(1)-O(8)	86.19(7)
O(1)-Co(1)-O(7)	89.62(7)	O(5)-Co(1)-O(6)	90.71(7)	O(7)-Co(1)-O(8)	95.98(7)
O(3A)-Co(1)-O(7)	90.54(7)	O(7)-Co(1)-O(6)	87.13(7)	O(6)-Co(1)-O(8)	175.35(7)

Symmetry code: A: *x*, -0.5-*y*, 0.5+*z*.

2 Results and discussion

2.1 IR and UV-Vis spectra

In the IR spectrum of polymer **1**, the moderate broad band at 3 392 cm⁻¹ is assigned to the ν (OH) stretching frequency indicating the presence of water molecule. The characteristic bands of the carboxyl groups are shown at 1 548 cm⁻¹ for antisymmetric stretching and 1 406 cm⁻¹ for symmetric stretching. The separation value of 142 cm⁻¹ indicates that the carboxyl groups of H₂dpa function in the unidentate coordination mode^[24]. Moreover, two strong bands at 1 232 and 1 190 cm⁻¹ indicate the existence of dpdo^[25]. These assignments were finally confirmed by X-ray crystallography (see below).

As depicted in Fig.1, the electronic spectrum of the polymer **1** in the solid state shows three absorption bands in the region between 340 and 800 nm. The intense band around 355 nm is due to the π - π^* transition of the aromatic units. The bands

observed at 495 and 672 nm can be attributed to a parity forbidden *d-d* type transition of Co(II)^[26].

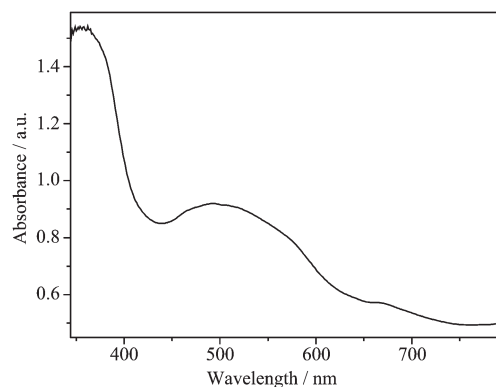


Fig.1 Electronic spectrum of the polymer **1** in the solid state at room temperature

2.2 Crystal and molecular structure

Single-crystal X-ray structural analysis revealed that the structure of **1** exhibits a three-dimensional supramolecular framework containing free organic units 4,4'-bipyridine-*N,N'*-dioxide (dpdo) based on one-dimensional polymeric chains, which formed

through the coordination interaction of $\text{Co}(\text{II})$ and the bridging organic ligands 2,2'-biphenyldicarboxylate (dpa^{2-}). Polymer **1** crystallizes in a monoclinic space group $P2_1/c$. The asymmetric unit consists of one $\text{Co}(\text{II})$ ion, one dpa^{2-} , one independent dpdo , four coordinated water molecules and one crystal water molecule. As shown in Fig.2, $\text{Co}(\text{I})$ atom is coordinated by two monodentate carboxylate oxygen atoms $\text{O}(1)$ and $\text{O}(3\text{A})$ from two dpa^{2-} ligands ($\text{O}(1)$ trans to $\text{O}(3\text{A})$, $\text{Co}(1)-\text{O}(1)$, 0.202 3(2) nm; $\text{Co}(1)-\text{O}(3\text{A})$, 0.203 7(2) nm, $\text{O}(1)-\text{Co}(1)-\text{O}(3\text{A})$, $177.48(7)^\circ$), four oxygen atoms $\text{O}(5)$, $\text{O}(6)$, $\text{O}(7)$ and $\text{O}(8)$ from four coordinated water molecules with the average $\text{Co}(1)-\text{O}$ distant of 0.215 nm to attain a distorted octahedral geometry. Each dpa^{2-} ligand is bound to two $\text{Co}(\text{II})$ centers through two monodentate carboxylate groups with the $\text{Co}(1) \cdots \text{Co}(1\text{B})$ (symmetry code B: $x, -0.5-y, -0.5+z$) separation of 0.701 nm and each $\text{Co}(\text{II})$ center is coordinated by two dpa^{2-} ligands thereby generating a one-dimension helical chain architecture (Fig.3). The helical pitch is 1.400 2(7) nm (the unit cell length along the crystallographic c axis), which is given by one full rotation around the 2_1 helical axis. Similar monohelical chain structure has also been observed in the related polymers^[27-28]. Consequently, the 2,2'-biphenyldicarboxylate adopts a twist conformation with the torsion angle of $-63.1(3)^\circ$ around $\text{C}(2)-\text{C}(7)-\text{C}(8)-\text{C}(13)$ bonds.

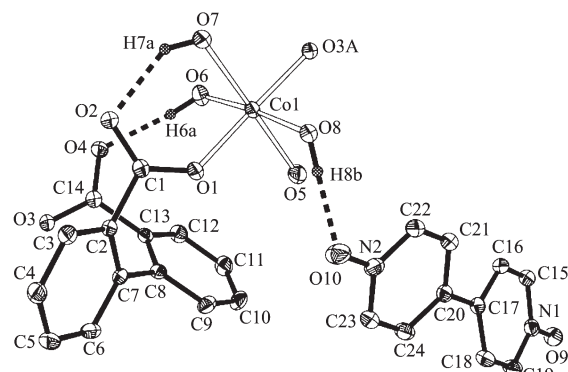
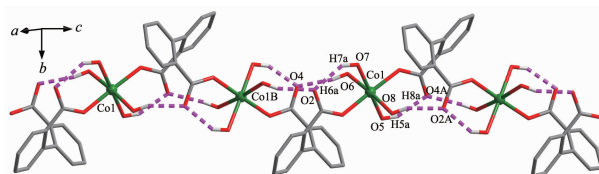


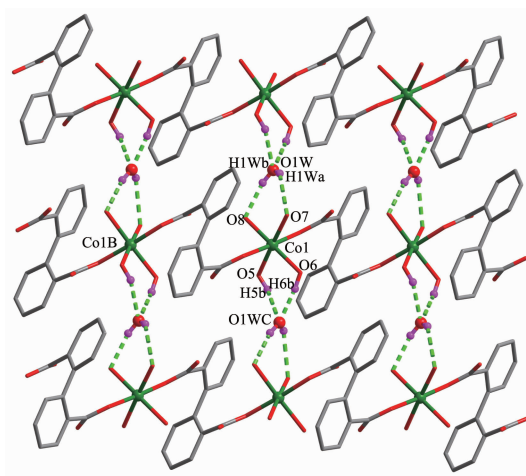
Fig.2 Asymmetric unit and coordination environment of $\text{Co}(\text{II})$ in polymer **1** with the atom numbering scheme showing hydrogen bonds (dashed line) and the coordination environment for Co atom

The angle between two phenyl rings is 63.5° . In addition, four types of $\text{O}(5)-\text{H}(5\text{a}) \cdots \text{O}(4\text{A})$, $\text{O}(6)-\text{H}(6\text{a}) \cdots \text{O}(4)$, $\text{O}(7)-\text{H}(7\text{a}) \cdots \text{O}(2)$ and $\text{O}(8)-\text{H}(8\text{a}) \cdots \text{O}(2\text{A})$ (symmetry code: A: $x, -1/2-y, 1/2+z$) hydrogen bonds are found in the 1D helical chain and also play an important role in stabilizing network (Table 3). It is interesting to note that the existence of $\text{O}(1\text{W})-\text{H}(1\text{Wa}) \cdots \text{O}(7)$, $\text{O}(1\text{W})-\text{H}(1\text{Wb}) \cdots \text{O}(8)$, $\text{O}(5)-\text{H}(5\text{b}) \cdots \text{O}(1\text{WC})$ and $\text{O}(6)-\text{H}(6\text{b}) \cdots \text{O}(1\text{WC})$ (symmetry code: C: $-1+x, -1/2-y, -1/2+z$) hydrogen bonds between the 1D chains and solvent water molecules gives further rise to a 2D supramolecular network, in which each solvent water molecule acts as a 4-connected node (Fig.4).



Symmetry codes: A: $x, -0.5-y, 0.5+z$; B: $x, -0.5-y, -0.5+z$

Fig.3 Illustration of the helical chain in the polymer **1** with four types of $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds in dashed lines



Each solvent water molecule acts as a 4-connected node; Symmetry codes: B: $x, -0.5-y, -0.5+z$; C: $-1+x, -1/2-y, -1/2+z$

Fig.4 Illustration of a layer in the polymer **1** with four types of $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds in dashed lines

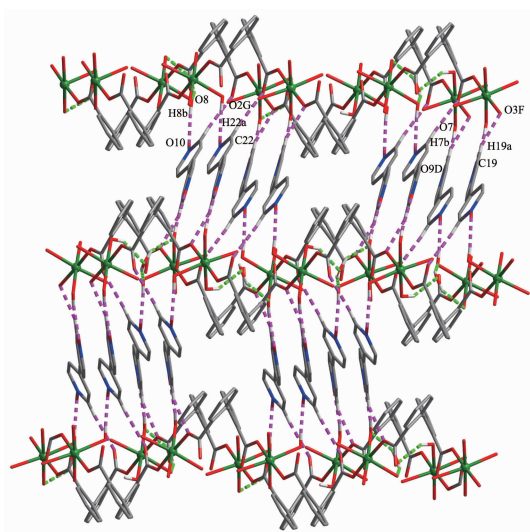
Detailed structural analysis revealed that in the solid state the adjacent layers are separated by dpdo units. The $\text{O}(7)-\text{H}(7\text{b}) \cdots \text{O}(9\text{D})$, $\text{O}(8)-\text{H}(8\text{b}) \cdots \text{O}(10)$ and two types of $\text{C}(19)-\text{H}(19\text{a}) \cdots \text{O}(3\text{F})$, $\text{C}(22)-\text{H}(22\text{a})$

Table 3 Hydrogen bonding interactions of the polymer **1**

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠DHA / (°)
O(1W)-H(1Wa)···O(7)	0.085	0.243	0.307 7(4)	133
O(1W)-H(1Wb)···O(8)	0.085	0.195	0.277 7(5)	164
O(5)-H(5a)···O(4A)	0.085	0.192	0.269 6(4)	151
O(5)-H(5b)···O(1WC)	0.085	0.227	0.302 9(4)	149
O(6)-H(6a)···O(4)	0.085	0.198	0.280 5(3)	163
O(6)-H(6b)···O(1WC)	0.085	0.190	0.274 3(5)	172
O(7)-H(7a)···O(2)	0.085	0.199	0.271 5(3)	143
O(7)-H(7b)···O(9D)	0.085	0.209	0.288 9(3)	156
O(8)-H(8a)···O(2A)	0.085	0.199	0.280 5(3)	159
O(8)-H(8b)···O(10)	0.085	0.186	0.270 6(2)	175
C(15)-H(15a)···O(10E)	0.093	0.243	0.330 2(5)	156
C(19)-H(19a)···O(3F)	0.093	0.225	0.315 0(3)	162
C(22)-H(22a)···O(2G)	0.093	0.258	0.350 3(3)	172
C(23)-H(23a)···O(9H)	0.093	0.240	0.332 4(5)	172

Symmetry codes: A: $x, -1/2-y, 1/2+z$; C: $-1+x, -1/2-y, -1/2+z$; D: $1-x, -1/2+y, 1/2-z$; E: $-1+x, y, z$; F: $1-x, -y, -z$; G: $x, -1/2-y, 1/2+z$; H: $1+x, y, z$.

···O(2G) (symmetry codes: D: $1-x, -1/2+y, 1/2-z$; F: $1-x, -y, -z$; G: $x, -1/2-y, 1/2+z$) hydrogen bonds are observed, which lead to a 3D supramolecular structure of **1** (Fig.5). The O-H···O are between O(7), O(8) of the coordinated water molecules as hydrogen-bond donors and the oxygen atoms O(9), O(10) of dpdo as acceptor. Two types of C-H···O hydrogen bonds are found between the carbon atoms of dpdo and the oxygen atoms of the two coordinated water molecules.



Symmetry codes: D: $1-x, -1/2+y, 1/2-z$; F: $1-x, -y, -z$; G: $x, -1/2-y, 1/2+z$

Fig.5 Packing diagram of the polymer **1** with hydrogen bonds in dashed lines

At the same time, the adjacent dpdo molecules are connected together through C(15)-H(15a)···O(10E) and C(23)-H(23a)···O(9H) (symmetry codes: E: $-1+x, y, z$; H: $1+x, y, z$) hydrogen bonds to form a dimer structure. Herein, each dpdo exhibits slightly twist conformation due to the existence of multiform hydrogen bonds with the dihedral angle of two pyridyl rings of 21.0° . Although these hydrogen bonds interactions are weak compared to the metal-oxygen coordination bonds, it is suggested that these interactions are important in the packing of the molecules.

2.3 Luminescence properties

The solid-state photoluminescent spectra of the polymer **1** and dpdo have been measured at room temperature. As shown in Fig.6, upon the excitation at 275 nm, the polymer **1** shows one emission peak at 430 nm, while the emission maximum of dpdo is at 460 nm upon excitation at 275 nm. Moreover, the results of the reported literatures reveal that 2,2'-biphenyldicarboxylate shows the main emission peak at 459 nm which is attributed to the $\pi^*-\pi$ or π^*-n transitions^[29-30]. Compared to that of ligands, the nature of the emissive behavior of the polymer **1** may be assigned mainly to the intraligand $\pi^*-\pi$ or π^*-n electronic transitions^[31-33]. Similar emissions have been

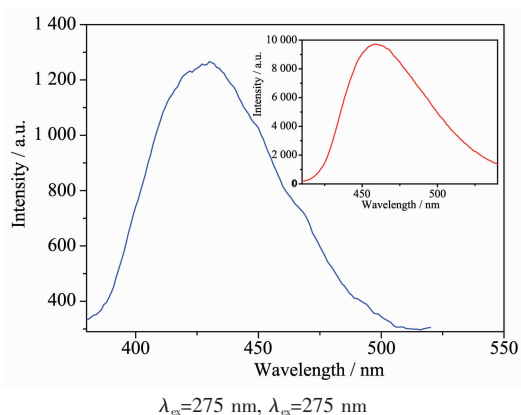


Fig.6 Emission spectrum of polymer **1** and dpdo ligand in solid state at room temperature

observed in the related complexes^[34-35].

2.4 X-ray powder diffraction (XRPD)

As shown in Fig.7, the experimental XRPD pattern of the bulk product of **1** is in good agreement with the simulated XRPD pattern from single-crystal X-ray diffraction, indicating the phase purity of the sample. The intensity difference between experimental and simulated XRPD patterns is due to the variation in preferred orientation of the powder sample during collection of the experimental XRPD.

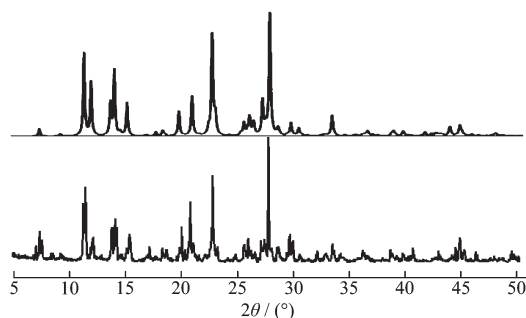


Fig.7 Pattern calculated from the single-crystal data for polymer **1** (top) and the power X-ray diffraction pattern of the samples (bottom)

2.5 Thermal analysis

The thermogravimetric analysis (TGA) of **1** is carried out under nitrogen condition at a heating rate of $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$ from 25 to $800\text{ }^\circ\text{C}$ (Fig.8). The TGA curve shows three-step weight loss processes. The first loss of 9.37% in the range of $105\sim 145\text{ }^\circ\text{C}$, corresponds to the release of three water molecules (Calcd. 9.35%), and one endothermal peak at $105\text{ }^\circ\text{C}$ is observed in the DTA curve. Upon further raising the temperature

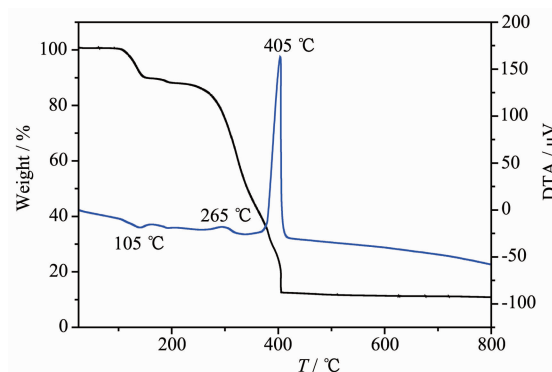


Fig.8 Thermogravimetric analysis (TGA) curve for polymer **1**

till $265\text{ }^\circ\text{C}$, another two water molecules are lost with the weight loss of 6.18% (Calcd. 6.24%), and one exothermal peak at $265\text{ }^\circ\text{C}$ in the corresponding DTA curve. The last step gives a loss of 71.80% (Calcd. 71.42%) in the range of $265\sim 405\text{ }^\circ\text{C}$, corresponding to the loss of all the organic ligands, and the final residue should be CoO. Moreover, a strong exothermal peak is observed at $405\text{ }^\circ\text{C}$ in DTA which suggests the occurrence of a phase transitions.

3 Conclusions

In this paper, a 1D polymer $\{[\text{Co}(\text{dpa})(\text{H}_2\text{O})_4] (\text{dpdo})(\text{H}_2\text{O})\}_n$ **1** containing two organic components, dpdo (4,4'-bipyridine- N,N' -dioxide) and H_2dpa (2,2'-biphenyldicarboxylate), has been synthesized and characterized by IR spectroscopy, electronic spectroscopy. **1** exhibits a three-dimensional supramolecular framework containing free dpdo components based on one-dimensional polymeric chains, which formed through the coordination interaction of Co (II) and dpa^{2-} . The photoluminescence measurement of **1** shows the main emission peak at 430 nm in the solid state.

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