

两个以 3-硝基邻苯二甲酸为配体构筑的锌和钴 配位聚合物的合成、晶体结构和性质

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摘要: 通过水热法合成了 2 种配位聚合物 $[\text{Zn}(\text{3-Nbdc})(\text{bpmp})] \cdot \text{H}_2\text{O}$ (**1**) 和 $[\text{Co}(\text{3-Nbdc})(\text{bpmp})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (**2**) (3-Nbdc²⁻=3-硝基邻苯二甲酸根, bpmp=1,4-二(4-吡啶甲基)哌嗪), 并通过 X-射线单晶衍射、元素分析和红外光谱对其结构进行了表征。配合物 **1** 和 **2** 均为二维(4,4)格子层结构, 其中 **1** 含有双核单元, **2** 含有螺旋金属羧酸盐链。此外, 对它们的热重、粉末 X-射线衍射、固体荧光和磁性性能进行了考察。**1** 显示与游离的 3-硝基邻苯二甲酸相似的荧光性质, 锌离子的配位环境和配体之间的耦合作用对其荧光性能几乎没有影响。**2** 在低温区表现出铁磁耦合作用, 高温区的 $\chi_{\text{M}}T$ 值降低主要是由于八面体钴的自旋轨道耦合导致的。

关键词: 水热合成; 钴; 光致发光; 磁性; 配合物

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Syntheses, Structures and Properties of Two Coordination Polymers Constructed by 3-Nitrobenzene-1,2-dicarboxylate Acid and Zn/Co

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Abstract: Two coordination polymers $[\text{Zn}(\text{3-Nbdc})(\text{bpmp})] \cdot \text{H}_2\text{O}$ (**1**) and $[\text{Co}(\text{3-Nbdc})(\text{bpmp})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (**2**) (3-Nbdc²⁻=3-nitrobenzene-1,2-dicarboxylate, bpmp=1,4-bis(4-pyridylmethyl)piperazine) were synthesized hydrothermally and characterized structurally by single-crystal X-ray diffractions, elemental analysis and infrared spectroscopy (IR). Both complexes **1** and **2** display (4,4) grid layers containing the dinuclear units in **1** and helix metal-carboxylate chains in **2**. Thermogravimetric Analyses (TGA), powder X-ray diffractions (PXRD), fluorescence property and magnetic property for compounds **1** and **2** are also investigated. The solid state fluorescence indicates that the complex **1** shows similar emission spectra to the free 3-NbdcH₂ ligand due to little contribution from the Zn-O inorganic motifs to the emission and very little degree change of interligand coupling upon metal coordination. The complex **2** exhibits a ferromagnetic coupling between the metal centers in the low-temperature region, and the decrease of $\chi_{\text{M}}T$ value in the high-temperature region may be attributed to the strong spin-orbit coupling through the ⁴T_{1g} state of the octahedral Co²⁺ centers. CCDC: 1042678, **1**; 1042679, **2**.

Key words: hydrothermal synthesis; cobalt; photoluminescence; magnetic property; coordination polymer

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Much attention has been paid to the design and assembly of metal-organic frameworks or porous coordination polymers in recent years not only because of their intriguing structures^[1-3], but also due to their potential applications in various areas such as gas adsorption, separation, heterogeneous catalysis, and photoluminescence^[4-9]. In this field, the organic bridging ligands play a crucial role in the design and construction of desirable metal-organic frameworks (MOF), because changes in flexibility, length, and symmetry of organic ligands can result in materials bearing diverse architectures and functions. The rigid aromatic benzenedicarboxylic acid and its derivatives (such as 1, *n*-benzenedicarboxylic acid, *n*=2, 3, 4) are widely used as building blocks to link metal ions to produce metal-organic frameworks with interesting structures and properties because of having strong coordination ability and diverse coordination modes^[10-14]. Recently, our group chose the nitro-1,2-benzenedicarboxylic acid (NbdcH₂) as organic bridging ligands to self-assemble and produce versatile 1D, 2D and 3D metal-organic frameworks with the diverse properties^[15-18]. Though the nitro group does not participate in coordination, NbdcH₂ may provide the potential to construct unpredictable and interesting network structures due to the existence of an electron-withdrawing nitro-group on the aromatic backbone^[19-21].

On the other hand, the N-donor ligand is also very important for the design and assembly of diverse coordination polymers. Throughout the multitudinous N-donor ligands, the bis-pyridyl-type ligand, such as bpe (1,2-bis(4-pyridyl)ethene), bpa (1,2-bis(4-pyridyl)ethane) and bpp (1,3-bis(4-pyridyl)propane), is one of the most common auxiliary ligands to combine with polycarboxylates main ligands, and has obtained a series of MOFs with different structures and properties^[22-24]. In this article, We use 1,4-bis(4-pyridylmethyl)piperazine (bpmp) as new bis-pyridyl-type coligand to construct coordination polymers not only because bpmp has twisted conformation, but also its four nitrogen atoms may improve the structures and properties of coordination polymers^[25-26]. We obtained two coordination polymers under similar hydrothermal

reaction conditions, namely, {[Zn(3-Nbdc)(bpmp)]·H₂O}_n (**1**) and {[Co(3-Nbdc)(bpmp)(H₂O)]·H₂O}_n (**2**). The synthesis, structures, stabilities, fluorescence and magnetic property for complexes **1** and **2** are given in this paper.

1 Experimental

1.1 Materials and methods

All reagents were commercially available and used as received without further purification. Elemental analyses were determined with on a Flash 2000 organic elemental analyzer. Infrared spectra (4 000~600 cm⁻¹) were recorded on powdered samples using a NICOLET 6700 FT-IR spectrometer. Thermogravimetric analyses (TGA) were performed on a SII EXStar 6000 TG/DTA6300 analyzer with a heating rate of 10 °C·min⁻¹ up to 900 °C under N₂ atmosphere. Powder X-ray diffraction (PXRD) patterns were taken on a Bruker D8-ADVANCE X ray diffractometer with Cu Kα radiation (λ=0.154 18 nm). Luminescence spectra were performed on an Aminco Bowman Series 2 luminescence spectrometer at room temperature. Variable temperature magnetic susceptibilities were measured by using a MPMS-7 SQUID magnetometer.

1.2 Synthesis of {[Zn(3-Nbdc)(bpmp)]·H₂O}_n (**1**)

A mixture of Zn(OAc)₂·2H₂O (0.021 g, 0.10 mmol), 3-NbdcH₂ (0.042 g, 0.20 mmol), bpmp (0.027 g, 0.10 mmol), KOH (0.006 g, 0.10 mmol), EtOH (4 mL) and H₂O (3 mL) was placed in a 23 ml Teflon-lined autoclave at 120 °C for 4 days, then cooled to room temperature. Colourless block crystals were obtained in 71% yield. Elemental analysis Calcd. (%) for C₂₄H₂₅N₅O₇Zn: C, 51.39; H, 4.49; N, 12.49. Found(%): C, 51.35; H, 4.51; N, 12.43. IR (KBr, cm⁻¹): 2 800~3 600(m), 1 639(s), 1 620(s), 1 597(s), 1 563(m), 1 523(s), 1 452(m), 1 433(m), 1 341(s), 1 291(m), 1 230(m), 1 156(w), 1 145(w), 1 129(w), 1 069(m), 1 032(m), 1 000(w), 921(w), 847(m), 825(s), 798(s), 779(s), 755(s), 713(s), 696(s), 667(w).

1.3 Synthesis of {[Co(3-Nbdc)(bpmp)(H₂O)]·H₂O}_n (**2**)

A mixture of Co(OAc)₂·4H₂O (0.025 g, 0.10 mmol), 3-NbdcH₂ (0.021 g, 0.10 mmol), bpmp (0.054 g, 0.20

mmol), KOH (0.006 g, 0.10 mmol), and H₂O (7 mL) was placed in a 23 mL Teflon-lined autoclave. The vessel was heated to 120 °C for 4 days, then cooled to room temperature. Pink block crystals were obtained in 87% yield. Elemental analysis Calcd.(%) for C₂₄H₂₇N₅O₈Co: C, 50.36; H, 4.75; N, 12.23. Found(%): C, 50.32; H, 4.92; N, 12.21. Selected IR (KBr, cm⁻¹): 2 800~3 600(w), 1 600(s), 1 577(s), 1 554(s), 1 525(s), 1 450(w), 1 427(m), 1 392(s), 1 341(s), 1 329(s), 1 295(m), 1 155(m), 1 133(m), 1 069(w), 1 013(m), 943(m), 922(m), 877(w), 834(s), 826(s), 785(m), 761(m), 754(w), 736(s), 713(w), 668(s).

1.4 X-ray crystallography

The crystallographic data collections for complexes **1** and **2** were recorded at room temperature on a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromated Mo *K*α radiation (λ = 0.071 073 nm). All structures were solved by direct

methods with SHELXS-97 and refined on *F*² by full-matrix least-squares using the SHELXL-97 program package^[27-28]. All hydrogen atoms were placed in calculated positions and refined isotropically with a riding model except for water H atoms, which were initially located in a difference Fourier map and included in the final refinement by use of geometrical restraints with *d*(O-H)=0.085 nm and *U*_{iso}=1.5*U*_{eq}(O). The details of the structure solutions and final refinements for two complexes are summarized in Table 1. Selected bond distances and angles and hydrogen bonds are listed in Table S1 and Table S2.

CCDC: 1042678, **1**; 1042679, **2**.

2 Results and discussion

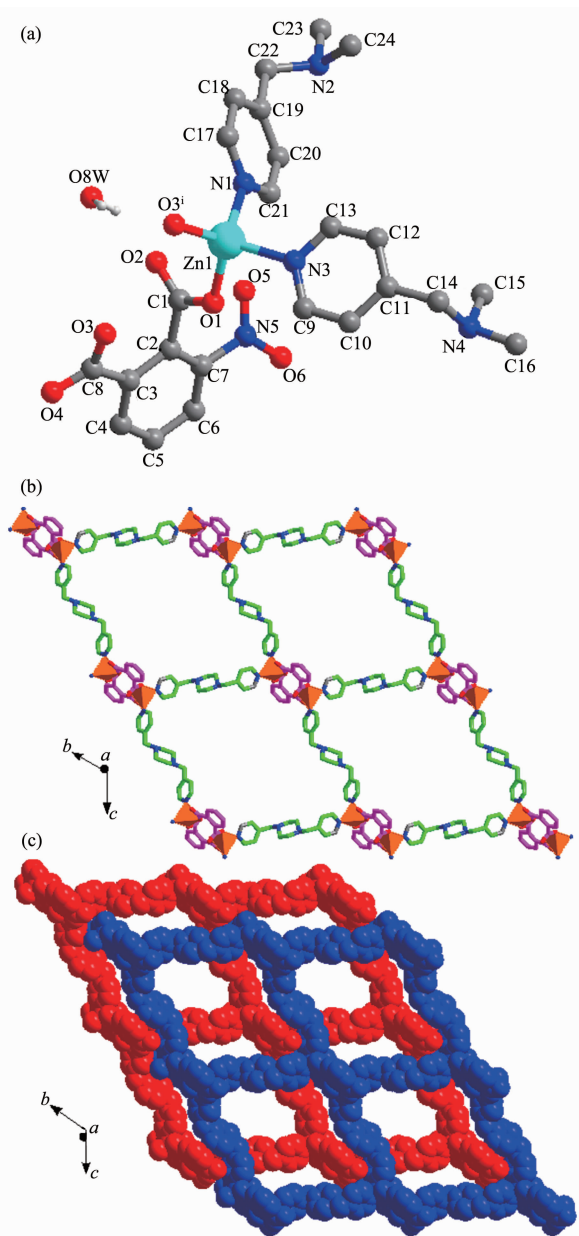
2.1 Structural description of {[Zn(3-Nbdc)(bpm)]·H₂O}_n (**1**)

X-ray crystallographic analysis reveals that **1**

Table 1 Crystal and structure refinement data for compounds **1** and **2**

	1	2
Empirical formula	C ₂₄ H ₂₅ N ₅ O ₇ Zn	C ₂₄ H ₂₇ N ₅ O ₈ Co
Formula weight	560.86	572.44
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> / nm	1.007 27(8)	1.626 03(4)
<i>b</i> / nm	1.192 17(8)	0.860 01(2)
<i>c</i> / nm	1.212 50(9)	1.915 62(6)
α / (°)	117.917(7)	90
β / (°)	96.693(6)	109.147(3)
γ / (°)	103.418(6)	90
<i>V</i> / nm ³	1.207 74(15)	2.530 63(12)
<i>Z</i>	2	4
<i>D</i> _c / (g·cm ⁻³)	1.542	1.502
μ / mm ⁻¹	1.073	0.737
<i>F</i> (000)	580	1 352
θ range for data collection / (°)	3.04~25.50	2.96~25.50
Reflections collected / unique	8 163 / 4 474	10 792 / 4 702
<i>R</i> _{int}	0.026 4	0.020 5
Completeness / %	99.8	99.8
Data / restraints / parameters	4 474 / 0 / 334	4 702 / 0 / 343
Goodness-of-fit on <i>F</i> ²	1.066	1.061
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> >2σ(<i>I</i>)]	0.036 3, 0.079 4	0.032 9, 0.076 2
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.043 9, 0.085 0	0.040 3, 0.080 6
Largest peak and hole / (e·nm ⁻³)	372 and -389	346 and -346

crystallizes in triclinic crystal system, space group $P\bar{1}$ and features a 2D (4,4) grid layer. The asymmetry unit contains one crystallographically unique Zn^{2+} cation, one completely deprotonated 3-Nbdc $^{2-}$, one bpmp molecule and one guest water, as shown in Fig.1(a). The Zn^{2+} center is coordinated by two carboxylate O atoms



Symmetry codes in (a): $^i -x+1, -y+1, -z+1$; $^{ii} -x+1, -y, -z+2$; $^{iii} -x, -y-1, -z$; All hydrogen atoms of carbon atoms and nitro groups of 3-Nbdc $^{2-}$ are omitted for clarity

Fig.1 (a) View of the asymmetric unit showing the local coordination environments of Zn ion in **1**;
(b) Polyhedral view of the 2D (4,4) grid layer;
(c) View of 3D packing of two adjacent layers

from two 3-Nbdc $^{2-}$ and two N atoms from two bpmp molecules to form a four-coordinated distorted pyramid $[\text{ZnN}_2\text{O}_2]$ geometry. The Zn-O bond lengths are 0.192 98(17) and 0.194 88(17) nm, and the Zn-N bond lengths are 0.203 5(2) and 0.204 9(2) nm, respectively.

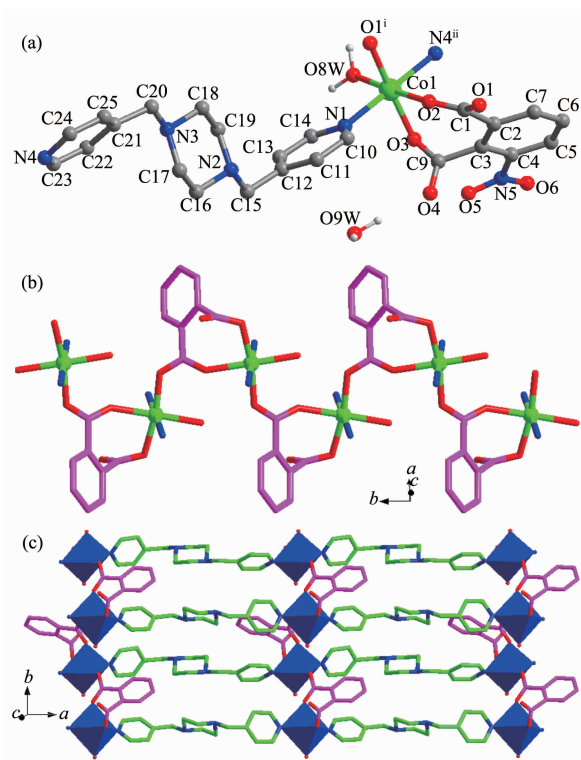
The adjacent Zn^{2+} centers are bridged by the 3-Nbdc $^{2-}$ ligands with two carboxyl groups adopting a monodentate coordination mode to form binuclear units with the $\text{Zn}\cdots\text{Zn}$ separation of 0.511 36(7) nm, as indicated in Fig.1(b). The binuclear units are interlinked together with bpmp coligands to form a (4,4) grid layer with parallelogram cavities. Individual layers stack together in an -ABAB- motif forming its entire three-dimensional supramolecular structure via weak Van der Waals interaction between the interlayers (Fig.1 (c)). The parallelogram cavities in single layer are almost completely covered due to the stacking of multilayers. There exist intralayer H-bond interactions between carboxylate O atom and free water O atom ($\text{O8W}-\text{H2W}\cdots\text{O1}^i$: 0.319 8 (3) nm, 136.1° ; $\text{O8W}-\text{H2W}\cdots\text{O3}^i$: 0.313 5 (3) nm, 144.7°). No significant $\pi\cdots\pi$ interactions are observed between all the aromatic rings of all the ligands due to the terraced arrangement of the adjacent layers.

2.2 Structural description of $\{[\text{Co}(\text{3-Nbdc})(\text{bpmp})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**2**)

X-ray crystallographic analysis reveals that **2** crystallizes in monoclinic crystal system, space group $P2_1/c$ and features a 2D (4,4) grid layer. The asymmetry unit contains one crystallographic Co^{2+} ion, one deprotonated 3-Nbdc $^{2-}$, one bpmp molecule, one coordination water and one guest water, as shown in Fig.2(a). The Co^{2+} center is a distorted octahedral $[\text{CoN}_2\text{O}_4]$ geometry by four oxygen atoms in the equatorial plane, three carboxylic oxygen atoms from two 3-Nbdc $^{2-}$ ligands and one oxygen atoms from the coordination water, and two nitrogen atoms from two bpmp coligands at the axial positions (Fig.2(a)). The Co-O bond distances fall in the range of 0.205 88(14)~0.214 30(15) nm, and the Co-N bond lengths are 0.213 76(17) and 0.214 77(17) nm, respectively.

The two carboxyl groups of a 3-Nbdc $^{2-}$ adopt a

bidentate-bridging and a monodentate coordination mode, respectively. The adjacent Co^{2+} cations are connected by two μ_2 -carboxylates forming 1D carboxylate-metal zigzag chain along *b* direction with the $\text{Co}\cdots\text{Co}$ distance of 0.527 22 (4) nm, as indicated in Fig.2(b). Each zigzag chain connects with through-ligand $\text{Co}\cdots\text{Co}$ separation of 1.626 03(6) nm across bpmp ligands to form a 2D (4,4) grid layer (Fig.2(c)). The adjacent layers are stacked in a parallel mode along *c* direction with the 3-Nbdc^{2-} anions occupying the interlayer regions to form a three-dimensional supramolecular framework by interlayer H-bond interactions between the guest water O atom and the carboxylate O atom of 3-Nbdc^{2-} anions ($\text{O9W}\cdots\text{H4W}\cdots\text{O4}$: 0.286 2(2) nm, 171.5°; $\text{O9W}\cdots\text{H3W}\cdots\text{O4}^{\text{v}}$: 0.286 4(2) nm, 169.7°), between coordination water O atom and free water O atom ($\text{O8W}\cdots\text{H1W}\cdots\text{O9W}^{\text{iii}}$: 0.276 8(2) nm, 165.1°). There also exist intralayer H-bond inter-



Symmetry codes: ⁱ $-x+2, y-1/2, -z+1/2$; ⁱⁱ $x+1, y, z$; All hydrogen atoms of carbon atoms and nitro groups of 3-Nbdc^{2-} are omitted for clarity

Fig.2 (a) View of the coordination environments of Co ion for **2**; (b) View of 1D Co-carboxylate chain along *b* direction; (c) Polyhedral view of the 2D grid layer

actions between the coordination water O atom and the carboxylate O atoms of 3-Nbdc^{2-} anions ($\text{O8W}\cdots\text{H2W}\cdots\text{O2}^{\text{ii}}$: 0.301 5(2) nm, 123.7°; $\text{O8W}\cdots\text{H2W}\cdots\text{O1}^{\text{i}}$: 0.286 3(2) nm, 154.4°; Symmetry codes: ⁱ $x, y-1, z$; ⁱⁱ $-x+2, y-1/2, -z+1/2$; ⁱⁱⁱ $-x+2, -y+1, -z+1$; ^v $-x+2, -y+2, -z+1$) (Fig.S1). There exists the weak face to face $\pi\cdots\pi$ interaction between phenyl rings of 3-Nbdc^{2-} and pyridyl rings of bpmp coligands within the layer (centroid distance: 0.395 17(1) nm, dihedral angle: 22.103°) (Fig.S2). It is obvious that the H-bonding bonds and $\pi\cdots\pi$ interactions among the coordination polymers play important roles in the self-assembly and enhanced stability of the resultant structure.

2.3 Thermogravimetric analyses and powder X-ray diffractions

The thermogravimetric analyses (TGA) of **1** and **2** performed by heating the polycrystalline samples display significantly different thermal degradations between room temperature and 900 °C under N_2 atmosphere, as shown in Fig.3. The TGA curve for **1** suggests that the first weight loss of 3.34 % from 85 to 190 °C corresponds to the loss of one lattice water (Calcd. 3.21%). The residual framework starts to decompose above 250 °C with a series of complicated weight losses and does not stop until heating ends. The observed final mass remnant of 25.75% cannot be specifically identified and may be the mixtures of metal oxide and carbonaceous material, because the theoretical remaining mass of 14.44% is calculated by assuming a final phase ZnO . The TGA curve of **2** shows that the weight loss of about 6.45% in the range of 80~165 °C is corresponded to one coordination

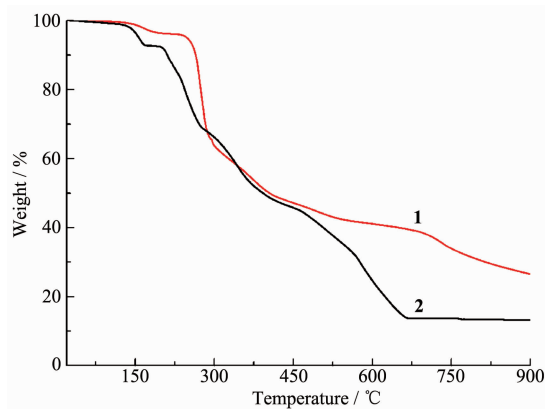


Fig.3 TGA curves of complexes **1** and **2**

water and one guest water per formula unit (Calcd. 6.30%), and the framework can keep stability up to about 200 °C. The observed final mass remnant of 13.18% likely representing deposition of CoO is agreement with the calculated value of 13.09%.

The powder X-ray diffractions of two compounds are in good agreement with the patterns simulated from the respective single-crystal data, implying their good phase purity (Fig.S3 and Fig.S4).

2.4 Fluorescence property

The photoluminescent properties of **1** and powdered free 3-NbdcH₂ ligand were investigated in the solid state at room temperature, as illustrated in Fig.4. Upon excitation at 300 nm, it is observed that the emission spectra of complex **1** is very similar to the free 3-NbdcH₂ ligand in rough shape, displaying a wide range of the emissions with maximum peaks at ~433 nm, ~472 nm and ~548 nm. Since the Zn²⁺ ions are difficult to oxidize or reduce due to their *d*¹⁰ configuration, the emissions of the compound is neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature. It can probably be assigned to the ligand-centered charge transfer ($n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$)^[17-18,29] based on 3-NbdcH₂ ligand because a similar emission is observed for the free 3-NbdcH₂ ligand, whereas the bpmp coligand shows almost no contribution to the emission of the compound **1** due to its weak fluorescent emission in the high energy emission region^[25-26]. All the results

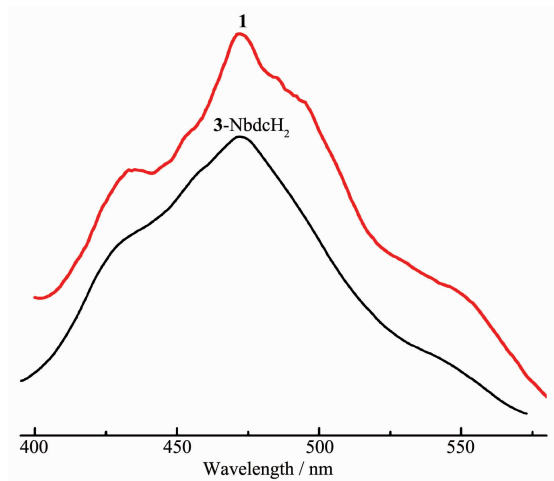


Fig.4 Solid-state emission spectra of compound **1** and the free 3-NbdcH₂ at room temperature

suggest little contribution from the Zn-O inorganic motifs to the emission and very little degree change of interligand coupling upon metal coordination^[30].

2.5 Magnetic property

The magnetic susceptibility (χ_M) of **2** was measured in the 2~300 K temperature range in a 2 000 Oe applied field, and shown as $\chi_M T$ and χ_M^{-1} versus *T* plots in Fig.5. From a magnetic point of view, it is clear that the much larger Co...Co separation across bridging bpmp (more than 1.2 nm) when compared to the shorter value across carboxylate bridge (0.527 22(4) nm) allow us to discard the exchange pathways through N-donor ligands. So complex **2** can be considered as pseudo-1D metal-carboxylate chain polymers with the nonplanar syn-anti coordination mode, in which adjacent Co²⁺ ions are linked by carboxyl bridges since couplings through bpmp are almost negligible.

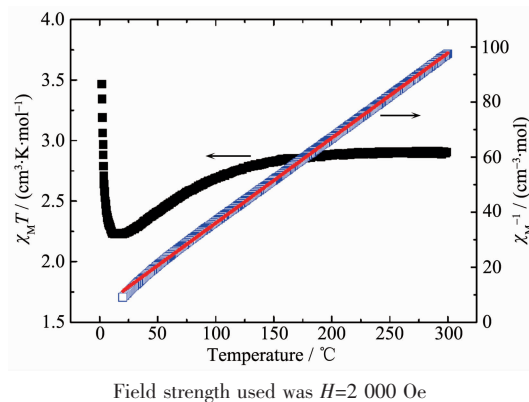


Fig.5 Plot of the $\chi_M T$ (■) and χ_M^{-1} (□) versus *T* in compound **2**

The $\chi_M T$ value at room temperature in **2** of 2.91 cm³·K·mol⁻¹ is significantly greater than the spin-only value (1.88 cm³·K·mol⁻¹, *S*=3/2) expected for an isolated high-spin Co²⁺ ion. The product $\chi_M T$ firstly decreases smoothly to a rounded minimum of 2.23 cm³·K·mol⁻¹ at 18.9 K, then increases rapidly to a high maximum of 3.47 cm³·K·mol⁻¹ at 2.0 K, indicating the ferrimagnetic-like behavior in complex **2**^[31-32]. The temperature dependence of magnetic susceptibilities above 18.9 K follows the Curie-Weiss law $\chi_M = C/(T - \theta)$ with a Weiss constant $\theta = -16.6$ K and a Curie constant $C = 3.24$ cm³·K·mol⁻¹, which agrees well with those given in the literature for the Curie constant ($C = 2.8 \sim 3.5$ cm³·K·mol⁻¹)^[33]. The Curie

constant is much larger than the expected spin-only value, indicating that the orbital contribution of Co^{2+} ions exists in complex **2**. Thereby the negative value of θ cannot unambiguously confirm the existence of antiferromagnetic coupling between Co^{2+} ions because of the strong spin-orbital coupling through the $^4T_{1g}$ state of the octahedral Co^{2+} centers^[33-34]. All these data indicate that the ferromagnetic coupling between Co^{2+} ions occurs in complex **2** and is sufficient to compensate the single-ion behavior resulting from spin-orbital coupling. The magnetic property of Co compound is very complicated by the fact that the orbital moment, spin-orbit coupling, distortion from regular stereochemistry, electron delocalization, and crystal field anisotropy can influence the magnetic susceptibility. Therefore, the magnetic mechanism of compound **2** will be further investigated.

3 Conclusions

In summary, two Zn/Co coordination polymers were successfully synthesized based on 3-nitrophthalic acid and 1,4-bis(4-pyridylmethyl)piperazine coligands. Both complexes **1** and **2** exhibit (4,4) grid layers including the dinuclear units in **1** and metal-carboxylate chains in **2**. The solid state luminescence of compound **1** is attributed to intraligand $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ charge transfer since it shows similar emission spectra to the free 3-NbdcH₂ ligand. The magnetic property of complex **2** was also investigated and showed a ferromagnetic coupling between the Co^{2+} centers in the low-temperature region, and the decrease of $\chi_M T$ value in the high-temperature region may be attributed to the strong spin-orbit coupling, which is remarkable for the $^4T_{1g}$ state of Co^{2+} in an octahedral ligand field. The magnetic mechanism of compound **2** will be further investigated.

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Supporting information is available at <http://www.wjhxsb.cn>

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