Synthesis, crystal structures, and characterization of two Co(II) coordination polymers with 3-pyrid-3-ylbenzoic acid

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Two pyridinecarboxylato-bridged coordination polymers $\{[Co(pbc)_2(H_2O)]\cdot H_2O\}_n$ (**1**) and $[Co(pbc)_2]_n$ (**2**) (Hpbc = 3-pyrid-3-ylbenzoic acid) have been synthesized by the hydrothermal method and characterized by X-ray single crystal diffraction. In **1**, pbc$^-$ ligands link two Co(II) centers as μ_2-N,O and μ_2-N,O,O. Co(II) is six coordinate, octahedral. In **2**, Co(II) is coordinated by four oxygens and two nitrogens. The ligands are μ_2-N,O,O and μ_3-N,O,O. Through different pbc$^-$ ligands, **2** generates a 3-D network composed of six-connected nodes. Compound **2** exhibits good photoluminescence, whereas **1** is nonemissive at room temperature.

Keywords: Coordination polymer; Co(II); Crystal structure

1. Introduction

The design and synthesis of metal-organic frameworks (MOFs) are of current interest [1–7]. Coordination polymers are constructed by connectors and linkers; transition metal ions are connectors due to their versatility in coordination and linkers afford a variety of linking sites. A common strategy to construct these polymeric transition metal complexes is to select suitable multidentate ligands to integrate metal ions to a desired framework. Multidentate ligands with suitable spacers between linking groups are good choices to get architectures. Hydrogen bonds are frequently used as a powerful crystal engineering tool to form frameworks [8–11]. Pyridine-carboxylates result in a variety of new complexes. Coordination polymers exhibit various properties such as electrical conductivity, luminescence, nonlinear optics, zeolitic behavior, catalysis, magnetism, etc. [12–16].

As part of our work toward the rational design and preparation of functional coordination frameworks, we present the synthesis and characterization of two coordination polymers $\{[Co(pbc)_2(H_2O)]\cdot H_2O\}_n$ (**1**) and $[Co(pbc)_2]_n$ (**2**) assembled from Co(II) and 3-pyrid-3-ylbenzoic acid.

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2. Experimental

2.1. *Physical measurements*

Elemental analysis was carried out on a Carlo Erba 1106 full-automatic trace organic elemental analyzer. FT-IR spectra were recorded with a Bruker Equinox 55 FT-IR spectrometer in dry KBr pellet from 400 to 4000 cm^{-1}.

2.2. *Syntheses*

2.2.1. {[Co(pbc)$_2$(H$_2$O)]·H$_2$O}$_n$ (1). A mixture of CoCl$_2$·6H$_2$O (0.5 mmol, 0.1190 g), Hpbc (1 mmol, 0.199 g), and H$_2$O (12 mL) with the pH adjusted to *ca* 8.0 by NaOH was heated in a 20 mL Teflon-lined stainless steel reactor at 16°C for 120 h and then cooled to room temperature at 2°C for 1 h. Elemental analysis: Anal. Calcd (%): C, 58.67; H, 4.10; N, 5.70. Found: C, 57.23; H, 4.06; N, 5.62. IR (KBr, cm^{-1}): 3440(br), 1636(s), 1541(s), 1412(s), 1178(m), 819(s).

2.2.2. [Co(pbc)$_2$]$_n$ (2). A mixture of CoCl$_2$·6H$_2$O (0.5 mmol, 0.1190 g), Hpbc (1 mmol, 0.199 g), and H$_2$O (12 mL) with the pH adjusted to *ca* 6.5 by NaOH was heated in a 20 mL Teflon-lined stainless steel reactor at 160°C for 120 h and then cooled to room temperature at 2°C for 1 h. Elemental analysis: Anal. Calcd (%): C, 63.31; H, 3.54; N, 6.15. Found: C, 62.85; H, 3.46; N, 6.18. IR (KBr, cm^{-1}): 1610(s), 1586(s), 1442(s), 1184(m), 824(s).

2.3. *X-ray crystallography*

Suitable single crystals of **1** and **2** were selected under a polarizing microscope and fixed with epoxy on fine glass fibers, which were mounted on a Bruker Smart 1000 CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å) at 293(2) K using an ω scan mode for cell determination and data collection. All non-hydrogen atoms were located by direct methods and subsequent difference Fourier syntheses. Hydrogens bound to carbon were located by geometrical calculations and their positions and thermal parameters were fixed during the structure refinement. All non-hydrogen atoms were refined by full-matrix least-squares techniques. Calculations were performed by the SHELXTL 97 program [17]. Crystal data, intensity collection, and structure refinement details are summarized in table 1. Selected interatomic distances and angles are given in tables 2 and 3.

3. Results and discussion

3.1. *Structure description*

Figure 1 shows a perspective view of **1** {[Co(pbc)$_2$(H$_2$O)]·H$_2$O}$_n$ with atomic numbering scheme. Co(II) is coordinated by three carboxylate oxygens (Co–O(2) = 2.0125(16) Å, Co–O(3) = 2.166(15) Å, Co–O(4) = 2.211(15) Å) and two nitrogens

Table 1. Summary of crystal data, data collection, structure solution, and refinement details of **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{24}H_{20}CoN_2O_6$	$C_{24}H_{16}CoN_2O_4$
Formula weight	491.35	455.32
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/c$	$P2(1)/c$
Unit cell dimensions (Å)		
a	10.496(5)	10.167(5)
b	12.964(5)	20.048(5)
c	16.115(5)	10.780(5)
Volume (Å^3), Z	2183.9(15), 4	1969.7(14), 4
Calculated density (g cm^{-3})	1.494	1.535
Absorption coefficient (mm^{-1})	0.830	0.907
$F(000)$	1012	932
θ range for data collection ($^\circ$)	2.50–27.20	2.03–28.63
Limiting indices	$-13 \leq h \leq 12, -16 \leq k \leq 15,$ $-21 \leq l \leq 12$	$-13 \leq h \leq 12, -26 \leq k \leq 26,$ $-14 \leq l \leq 10$
Reflections collected	5041	4902
Independent reflection	3846 [R(int) = 0.0237]	4022 [R(int) = 0.0213]
Goodness-of-fit on F^2	1.047	1.022
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0346, wR_2 = 0.0871$	$R_1 = 0.0322, wR_2 = 0.0780$
R indices (all data)	$R_1 = 0.0524, wR_2 = 0.0953$	$R_1 = 0.0427, wR_2 = 0.0827$
Largest difference peak and hole (e Å^{-3})	0.322 and -0.599	0.371 and -0.358

$wR_2 = [\sum w(F_o^2 - F_c^2)^2 / w(F_o^2)^2]^{1/2}$.
$w = 1/[\sigma^2(F_o)^2 + (AP)^2 + BP]$ with $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected interatomic distances (Å) and angles ($^\circ$) of **1**.

Co(1)–O(2)	2.013(16)	Co(1)–O(3)		2.166(15)	Co(1)–O(4)	2.211(15)
Co(1)–O(1w)	2.098(15)	Co(1)–N(1)$^{\#1}$		2.152(17)	Co(1)–N(2)$^{\#2}$	2.166(17)
O(2)–Co(1)–O(1w)	94.05(6)	O(2)–Co(1)–N(1)$^{\#1}$		91.26(7)	O(1w)–Co(1)–N(1)$^{\#1}$	88.40(6)
O(2)–Co(1)–N(2)$^{\#2}$	90.48(7)	O(1w)–Co(1)–N(2)$^{\#2}$	175.47(6)	N(1)$^{\#1}$–Co(1)–N(2)$^{\#2}$	91.41(7)
O(2)–Co(1)–O(3)	169.20(6)	O(1w)–Co(1)–O(3)		88.34(6)	N(1)$^{\#1}$–Co(1)–O(3)	99.34(6)
N(2)$^{\#2}$–Co(1)–O(3)	87.22(6)	O(2)–Co(1)–O(4)	109.57(6)	O(1w)–Co(1)–O(4)	88.22(6)
N(1)$^{\#1}$–Co(1)–O(4)	159.08(6)	N(2)$^{\#2}$–Co(1)–O(4)		90.35(6)	O(3)–Co(1)–O(4)	59.93(6)

Hydrogen-bonding contacts

D–H$\cdots$A	d(D–H)	d(H–A)	$\angle$(D–H–A)	d(D–H–A)
O(1w)–H(1wA)$\cdots$O(1)$^{\#3}$	0.85(14)	1.82(14)	173	2.664(2)
O(1w)–H(1wB)$\cdots$O(3)$^{\#3}$	0.85(14)	1.94(17)	156	2.738(2)
O(2w)–H(2wB)$\cdots$O(3)$^{\#1}$	0.86(2)	2.28(2)	130	2.907(4)
O(2w)–H(2wA)$\cdots$O(1)	0.86(2)	2.05(3)	141	2.762(4)
C(1)–H(1)$\cdots$O(2)$^{\#1}$	0.93	2.56	115	3.067(3)
C(15)–H(15)$\cdots$O(2w)$^{\#4}$	0.93	2.36	161	3.250(4)
C(21)–H(21)$\cdots$O(2w)$^{\#4}$	0.93	2.53	172	3.455(5)
C(22)–H(22)$\cdots$O(2)	0.93	2.56	116	3.085(3)
C(23)–H(23)$\cdots$O(3)	0.93	2.42	120	2.998(3)

Symmetry transformations used to generate equivalent atoms: #1: $-1+x, y, z$; #2: $1-x, 0.5+y, 1.5-z$; #3: $2-x, 1-y, -z$; #4: $1+x, y, z$.

(Co–N(1) = 2.152(17) Å, Co–N(2) = 2.166(17) Å) of four different pbc$^-$ ligands, and one water (Co–O(1w) = 2.098(15)Å) in a distorted octahedral geometry. O2, O3, O4, and N1 form the equatorial plane (the equation of plane is $0.620x + 6.550y - 13.903z = 8.310$, the maximal and mean deviation are 0.3178 and 0.2082, respectively).

Table 3. Selected interatomic distances (Å) and angles (°) of **2**.

Co(1)–O(1)	2.321(16)	Co(1)–O(2)	2.094(13)	Co(1)–O(3)	1.991(14)
Co(1)–O(4)$^{\#1}$	2.033(14)	Co(1)–N(1)$^{\#2}$	2.151(17)	Co(1)–N(2)$^{\#3}$	2.177(17)
O(3)–Co(1)–O(4)$^{\#1}$	114.03(6)	O(3)–Co(1)–O(2)	152.00(6)	O(2)–Co(1)–O(4)$^{\#1}$	93.77(6)
O(3)–Co(1)–N(1)$^{\#2}$	95.68(6)	O(4)$^{\#1}$–Co(1)–N(1)$^{\#2}$	90.16(6)	O(2)–Co(1)–N(1)$^{\#2}$	87.16(6)
O(3)–Co(1)–N(2)$^{\#3}$	90.53(6)	O(4)$^{\#1}$–Co(1)–N(2)$^{\#3}$	85.49(6)	O(2)–Co(1)–N(2)$^{\#3}$	88.28(6)
N(1)$^{\#2}$–Co(1)–N(2)$^{\#3}$	173.48(5)	O(3)–Co(1)–O(1)	93.24(6)	O(4)$^{\#1}$–Co(1)–O(1)	152.73(5)
O(2)–Co(1)–O(1)	59.02(6)	N(1)$^{\#2}$–Co(1)–O(1)	86.82(6)	N(2)$^{\#3}$–Co(1)–O(1)	94.83(6)

Symmetry transformations used to generate equivalent atoms: #1: $1-x$, $-y$, $2-z$; #2: $-1+x$, $0.5-y$, $-0.5-y$, $-0.5+z$; #3: $1+x$, y, $1+z$.
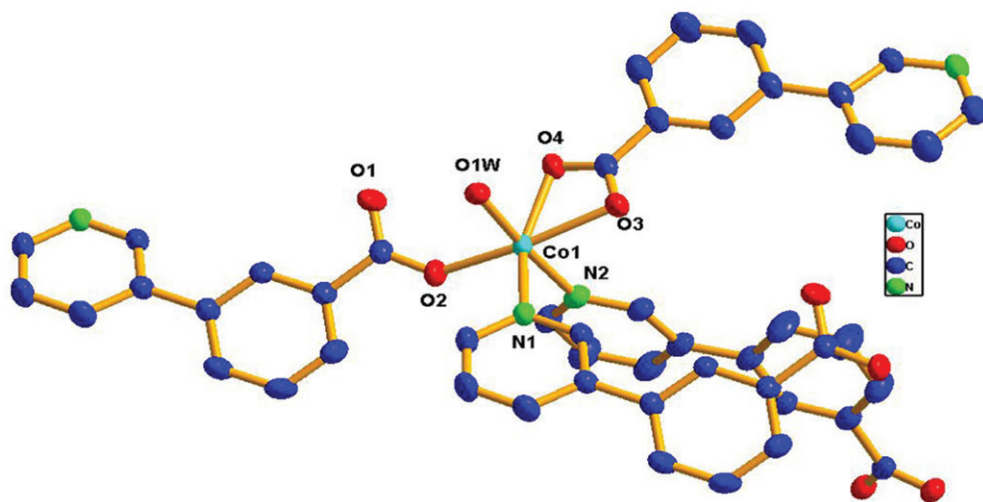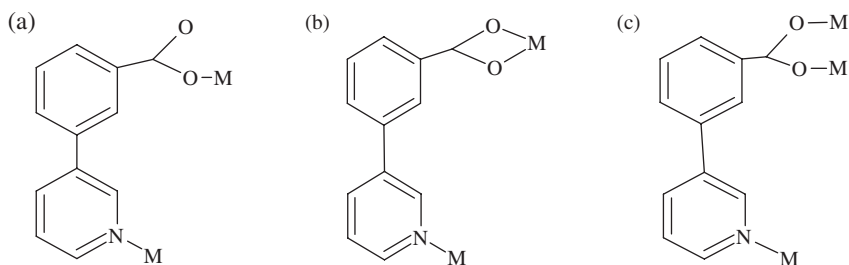

Figure 1. View of the coordination environment of Co(II) ion with thermal ellipsoids drawn at 50% probability level for **1**. All hydrogen atoms and lattice water molecules are omitted for clarity.

Scheme 1. The coordination modes of pbc⁻. (a) μ_2-N,O; (b) μ_2-N,O,O; and (c) μ_3-N,O,O.

Axial positions are occupied by one water and a nitrogen from pbc⁻. All pbc⁻ ligands are diconnectors linking two Co(II) centers through μ_2-N,O (scheme 1a) and μ_2-N,O,O (scheme 1b) forming a zigzag 1-D chain along the *a*-axis (figure 2). As shown in figure 3, pbc⁻ ligands adopt μ_2-N,O coordination mode in chains a and b. The chains a and b
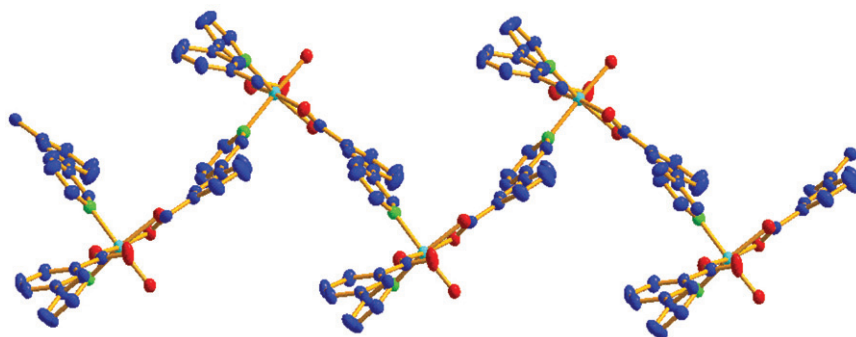
Figure 2. View of the 1-D zigzag chain along the *a*-axis for **1**.

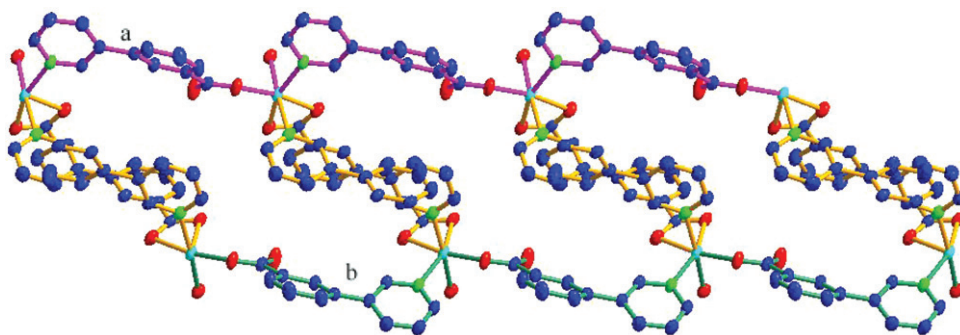Figure 3. Molecular packing of **1**, view along the *b*-axis. Purple: a chain. Green: b chain.

are connected by pbc⁻ functioning in a μ_2-N,O,O bridging mode. The dihedral angles are 32.73° (μ_2-N,O) and 15.59° (μ_2-N,O,O) between pyridine and phenyl rings in pbc⁻.

Intermolecular and intramolecular hydrogen bonds exit in **1**. As shown in table 2, inter-chain (O–H···O) hydrogen bonds form between O–H of coordinated water and carboxylate oxygen (O1 and O4), with a H1WA···O1 distance of 1.82(14) Å and a H1WB···O4 distance of 1.94(17) Å. Intermolecular hydrogen bonds exist between lattice water and carboxylate oxygen (O1 and O3) (H2WA···O1 distance of 2.05(3) Å and H2WB···O3 distance of 2.28(2) Å). There also exist intramolecular hydrogen bonds between the C–H groups and O of pbc⁻, with a H1···O2 distance of 2.56 Å and H22···O2 distance of 2.57 Å.

Complex **2** crystallizes in monoclinic space group $P2_1/c$ with each Co(II) coordinated by four O atoms (Co–O = 1.991–2.094 Å) and two N atoms (Co(1)–N(1) = 2.151(17) Å and Co(1)–N(2) = 2.177(17) Å) from five different pbc⁻ ligands in octahedral geometry. The Co–O and Co–N bond lengths agree well with related complexes [18], and bond angles of O(N)–Co–O(N) are from 59.02° to 173.48°. Four oxygens form the equatorial plane (equation of plane is $7.734x - 12.618y - 2.101z = 1.7382$, the maximal and mean deviation are 0.3957 Å and 0.1979 Å, respectively), and two nitrogens occupy axial sites (figure 4). The ligands have two coordination modes, one as a diconnector linking two Co(II) centers (μ_2-N,O,O) and the other as a triconnector linking three Co(II) centers (μ_3-N,O,O) with O_{COO} bis-monodentate *syn–anti* bridging to construct a dinuclear octahedral [$Co_2C_2O_4$] secondary structure unit (SBU), with nonbonding Co···Co
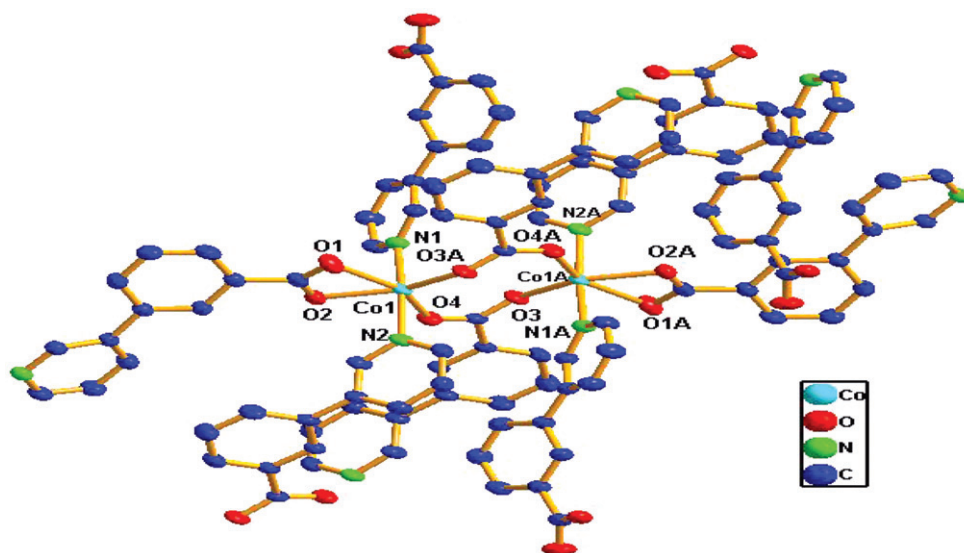
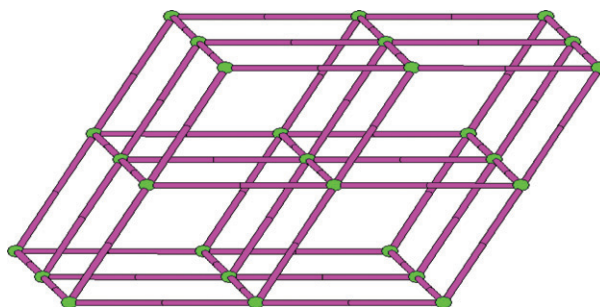Figure 4.   A perspective view of **2** (ellipsoids at 50% probability).

Figure 5.   Topological representation of the structure of **2** leading to a $4^{12}6^3$ topology.

distances of 4.242 Å. The SBUs are further interconnected through different pbc⁻ ligands, thereby generating a 3-D extended network composed of six-connected nodes (figure 5).

Intramolecular hydrogen bonds exist in **2** between C–H groups and O atom of pbc⁻, with a H20$\cdots$O2 distance of 2.31 Å and H21$\cdots$O3 distance of 2.59 Å.

3.2. *IR spectra*

IR spectra of **1** exhibit characteristic bands of carboxylate at 1646 and 1541 cm⁻¹ for the asymmetric stretching and at 1412 cm⁻¹ for symmetric stretching. The separation values between $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ indicate that the carboxylate groups coordinate in monodentate (224 cm⁻¹) and chelating (129 cm⁻¹) fashion. The IR spectrum of **2** shows characteristic bands of carboxylate at 1610 and 1586 cm⁻¹ for the asymmetric stretching and 1442 cm⁻¹ for symmetric stretching. The separations
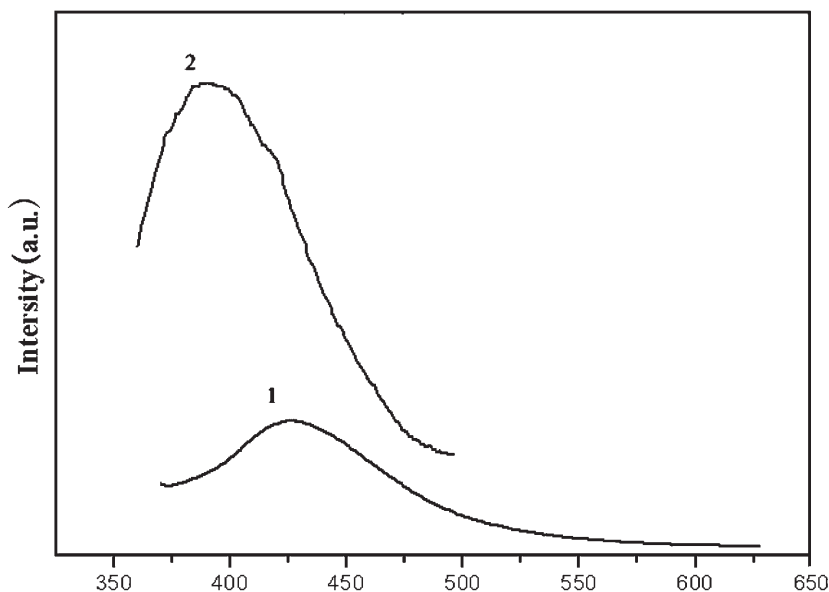
Figure 6. Solid-state photoluminescence emission spectra at room temperature (line 1 is the emission spectrum of free Hpbc and line 2 is the emission spectrum of **2**).

between $v_{asym}(CO_2)$ and $v_{sym}(CO_2)$ indicate that carboxylates coordinate to the metal atoms in a chelating ($144\,cm^{-1}$) and bis-monodentate ($168\,cm^{-1}$) fashion [19].

3.3. *Photoluminescence*

Compound **2** exhibits intense emission at $388\,nm$ ($\lambda_{ex} = 320\,nm$) in the blue region at room temperature (figure 6). To understand the emission band, we analyzed the photoluminescence of free Hpbc which displays an emission band at $427\,nm$ ($\lambda_{ex} = 345\,nm$). The intense emission of **2**, which is different from that of the free Hpbc, might be the ligand-to-metal charge transfer which reduces the loss of energy through radiationless decay of the intraligand emission excited state [20–22]. For **1**, LMCT cannot happen in the blue region and **1** does not exhibit photoluminescence. Co(II) is not an excellent metal source for photoluminescence but **2** exhibits strong emission, indicating that photoluminescence is closely related with the structure of **2**. $[Co_2C_2O_4]$ SBU cross-linked by pbc^{-} may promote the ligand-to-metal charge transfer (LMCT) and thus enhance photoluminescence [23].

4. Conclusion

Using hydrothermal technique we synthesized and characterized two coordination polymers, **1** and **2**. Compound **2** exhibits good photoluminescence, whereas **1** is nonemissive at room temperature. The structure has great influence on photoluminescence; **2** may be an excellent candidate for photoactive materials.

Supplementary material

Crystallographic data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC $\{[Co(pbc)_2(H_2O)] \cdot H_2O\}_n$ (710869) and CCDC $[Co(pbc)_2]_n$ (710870). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033 or Email: deposit@ccdc.cam.ac.uk).

Acknowledgment

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