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Synthesis, Crystal Structure, and Luminescent Properties of Two Zn^{II}/Cd^{II} Coordination Polymers Based on 1,4-Bis(pyridine-3-Ylmethoxy)benzene[1]

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Abstract—Two polymeric frameworks, $[Zn(Dpb)(Oba)]_n$ (**I**) and $[Cd(Dpb)(2,6\text{-}Pda)H_2O]_n \cdot nH_2O$ (**II**) (Dpb = 1,4-bis(pyridin-3-ylmethoxy)benzene, H_2Oba = 4,4'-oxybis(benzoic acid), 2,6-H_2Pda = 2,6-pyridyl- dicarboxylate), have been hydrothermally synthesized and structurally characterized by single crystal X-ray diffraction method (CIF files CCDC 1488269 (**I**), 1488270 (**II**)). Complex I is a 2D layer structure, which is constructed from 1D double chain. Complex **II** is a 1D chain. The luminescent properties of **I**, **II** have been investigated with fluorescent spectra in the solid state, **I** and **II** displayed a strong fluorescent emission at room temperature.

Keywords: hydrothermal synthesis, crystal structure, luminescent property, thermal stability

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INTRODUCTION

During the past few decades, the design and synthesis of metal-organic coordination polymers (Cps) have attracted increasing active research interest not only because of their intriguing variety of architectures and interesting topologies but also owing to their tremendous potential applications in gas storage, catalysis, ion-exchange, catalysis, magnetism, luminescence, nonlinear optics, drug delivery, and embedding of nanoparticles, and so on [1–6]. Although now a variety of Cps with beautiful topologies and interesting properties have been prepared, the rational predict and futher control the framework of a given crystalline product remains a great challenge in crystal engineering [7].

It is well-know that the construction of Cps is mainly dependent on the combination of several factors, such as metal atoms, organic ligands, templating, solvents, metal-ligand ratio, counteranion, and pH value [8–12]. Among these factors, the rational selection of organic ligands or coligands according to their length, rigidity and functional groups is important for the assembly of structural controllable Cps. The flexible N-bridging ligands, as good candidate for the construction of Cps, have aroused a good deal of interest from chemists [13–15]. Among the flexible N-bridging ligands, the flexible 4-bis(pyridin-3-ylmethoxy)benzene (Dpb) is a good candidate for the construction of Cps with novel architectures. For example, the flexible Dpb possesses the rotating $–O–CH_2$ group and the neutra pyridine moieties, which can exhibit a great variety of coordination modes. On the other hand, the large aromatic system can provide potential supramolecular recognition sites for π–π aromatic stacking and hydrogen-bond interactions to form interesting supramolecular structures.

In addition, introducing the O-donor ligands as auxiliary into a reaction system which has only neutral N-donor ligands can generate interesting structures which can not be obtained only through one type of ligands. The carboxylate group can act as the bridging group or chelating group, which may extend the structure into high dimensional Cps. In our attempt, to design and synthesize d^{10} metal-organic architectures with Dpb ligand, we choose different flexible dicarboxylic acids as auxiliary ligands, two Cps, namely $[Zn(Dpb)(Oba)]_n$ (**I**) and $[Cd(Dpb)(2,6\text{-}Pda)H_2O]_n \cdot nH_2O$ (**II**) (Dpb = 1, 4-bis(pyridin-3-ylmethoxy)benzene, H_2Oba = 4,4'-oxybis(benzoic acid), 2,6-H_2Pda = 2,6-pyridyl-dicarboxylate) have been synthesized and structurally characterized by elemental analyses, IR spectroscopy and single-crystal X-ray diffraction analyses.

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[1] The article is published in the original.

EXPERIMENTAL

Materials and measurements. All chemicals and reagents were purchased from commercial sources and used without further purification. Elemental analyses (C, H, N) were determined with a Vario EL III elemental analyzer. IR spectra were recorded on KBr pellets in the range of 4000–400 cm^{-1} with a Bruker EQUINOX-55 spectrometer. Thermogravimetric (**TG**) analyses were performed under nitrogen gas with a heating rate of 10°C min^{-1} using a METTLER TGA851 thermogravimetric analyzer.

Synthesis of complex I. A mixture of Dpb (0.013 g, 0.05 mmol), H_2Oba (0.013 g, 0.05 mmol) and $Zn(NO_3)_2 \cdot H_2O$ (0.015 g, 0.05 mmol) was put in a solution of water and methanol (10 mL, $V_{H2O} : V_{methanol} = 3 : 1$) and stirred for 30 min at the room temperature then sealed in a 25 mL Telfon-lined stainless steel container, which was heated to 180°C for 4 h and kept under autogenous pressure at 180°C for 3 days. After cooling to room temperature at a rate of 2°C per hour, the yellow block-shaped crystals were obtained in ~50% yield based on Zn.

For $C_{32}H_{18}N_2O_7Zn$ ($M = 607.85$)

Anal. calcd., %:	C, 63.22;	H, 2.98;	N, 4.61.
Found, %:	C, 63.24;	H, 2.96;	N, 4.64.

IR (KBr; ν, cm^{-1}): 3452.3 w, 3061.1 w, 1927.4 w, 1611. 6 s, 1496.2 m, 1356.3 s, 1237.9 s, 1030.8 m, 774.0 m, 686.1 m, 659.2 s,504.3 s.

Synthesis of complex II. A mixture of Dpb (0.013 g, 0.05 mmol), 2,6-H_2Pda (0.009 g, 0.05 mmol) and $CdCl_2 \cdot 2.5H_2O$ (0.012 g, 0.05 mmol) in water (10 mL) was stirred for 30 min in air, then sealed in a 25 mL Telfon-lined stainless steel container, which was heated to 160°C for 4 and kept under autogenous pressure at 160°C for 3 days. After cooling to room temperature at a rate of 2°C per hour, the yellow block-shaped crystals were obtained in ~46% yield based on Cd.

For $C_{50}H_{42}N_6O_{16}Cd_2$ ($M = 1203.66$)

Anal. calcd., %:	C, 49.72;	H, 3.51;	N, 6.96.
Found, %:	C, 49.75;	H, 3.53;	N, 6.94.

IR (KBr; ν, cm^{-1}): 3467.9 s, 3072.8 m, 1659.9 s, 1611. 9 s,1570. 5 s, 1498.5 m, 1427.3 m, 1369.4 s, 1265.4 w, 1239.6 s, 1181.7. m, 1065.1 w, 786. 5 m, 695.8 m, 650.4 w, 507.9 w.

X-ray crystallography. Intensity data were collected on a Bruker Smart APEX II CCD diffractometer with graphite-monochromated MoK_α radiation (λ = 0.71073 Å) at room temperature. Empirical absorption corrections were applied by the SADABS program. The structure was solved by direct methods [16] and refined by the full-matrix least-squares based on F^2 using SHELXTL-97 program [17]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed in calculated positions and refined as riding models. Crystal data and structural refinement parameters for I, II are summarized in Table 1 and selected bond distances and bond angles are listed in Table 2.

Supplementary material for complexes has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1488269 (**I**), 1488270 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.camac.uk).

RESULTS AND DISCUSSION

X-ray single crystal structural analysis reveals that complex I is a 2D layer structure. The asymmetric unit of **I** contains one Zn(II) atom, one Dpb and one $(Oba)^{2-}$ ligand. As shown in Fig. 1a, Zn(1) atom is surrounded by two nitrogen atoms (N(1), N(2*A*)) from two Dpb ligands (Zn(1)–N(1) 2.066(4), Zn(1)–N(2*A*) 2.053(4) Å) and two oxygen atoms (O(1), O4*A*)) from two $(Oba)^{2-}$ ligands (Zn–O 1.931(3), 1.983(3) Å). The coordination geometry can be described a distorted tetrahedron.

In I, the H_2Oba ligand is completely deprotonated to form $(Oba)^{2-}$ anion. One $(Oba)^{2-}$ and one Dpb ligands bridge two Zn(II) atoms with bidentate coordination mode to form two kinds of dinuclear units with 33-membere ring. The units of the two 33-membered rings are alternately arranged by sharing Zn(II) atoms to form an infinite 1D loop-and-chain running along the *x* axis (Fig. 1b). From the view of the c axis, dpb ligands bridge the adjacent Zn(II) atoms forming a 1D wave-like chains, the adjacent 1D chains are further linked by the $(Oba)^{2-}$ ligand to form a 2D layer structure (Fig. 1c).

The asymmetric unit of **II** has one cadmium(II) atom, one crystallographically independent Dpb ligand, one $(2,6\text{-Pda})^{2-}$ ligand, one coordination water molecule and one lattice water molecule. Each Cd(II) atom is coordinated to three nitrogen atoms (N(3) and N(3*A*) from two different Dpb ligands, N(1) from $(2,6\text{-Pda})^{2-}$ ligand) and four oxygen atoms (O(2),O(2*A*) and O(3) from two $(2,6\text{-Pda})^{2-}$ ligands and O(5) from coordination water molecule) (Fig. 2a). The coordination geometry of Cd(II) atom can be described as a distorted pentagonal bipyramid geometry. N(1), O(2), O(2*A*), O(3) and O(5) take up the equatorial plane and the other two nitrogen atoms from two Dpb occupy the axial positions. The Cd–O and Cd–N bond lengths are in the range of 2.269(3)–2.477(3) and 2.339(3)–2.394(3) Å, respectively, which are good agreement with previous studies [12]. Each pair of Cd(II) centers is bridged by two μ_2 oxygen atoms from two different $(2,6\text{-Pda})^{2-}$ ligands to form a Cd_2O_2 dimeric unit. The dimeric Cd_2O_2 units are

Table 1. Crystal data and structural refinement parameters for **I** and **II**

Parameter	Value	
	I	**II**
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a, Å	8.9424(8)	10.4778(9)
b, Å	24.376(2)	10.5014(9)
c, Å	13.5139(12)	11.9261(10)
α, deg	90	106.1140(10)
β, deg	108.970(2)	91.1190(10)
γ, deg	90	107.1020(10)
V Å^3	2785.8(4)	1197.61(18)
Z	4	1
ρ_{calcd}, g cm^{-3}	1.449	1.669
μ, mm^{-1}	0.934	0.968
F(000)	1240	604
Reflections collected	14147	6127
Unique reflections	4958	4220
Independent parameters	379	334
S on F^2	1.006	1.129
R_1, wR_2 ($I > 2\sigma(I)$)	0.0511, 0.1308	0.0411, 0.0891
R_1, wR_2 (all data)	0.0980, 0.1617	0.0466, 0.0930
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	0.436/–0.332	0.926/–0.841

linked by nitrogen atoms of two Dpb ligands generating a 1D double-chain running along the y axis (Fig. 2b), thus forming a novel $\{Cd_4O_6N_4C_{36}\}$ 42-membered ring.

The d^{10} transition-metal ions compounds are well known for their versatile fluorescence properties at room temperature. The photoluminescent properties of **I**, **II** and the free ligand in the solid state are investigated at room temperature (Fig. 3). The H_2Oba ligand exhibits one intense emission band at ~432 nm upon excitation at 260 nm. The emission spectra of **I** display strong fluorescence peak at ~414 nm which may be assigned to the π→π* intraligand fluorescence emission of ligand (Fig. 3a). Notably, a lower energy emission was also detected at 448 nm for I, which is indicative of metal-to-ligand charge-transfer (MLCT) transitions [18]. The reason leading to this emission peak may be assigned to the coordination of Zn^{2+}, which strengthens the electron acceptor ability of Oba^{2-} ligand and the stabilizes its MLCT state in **I**. The 2,6-H_2Pda ligand exhibits one intense emission band at ~342 nm upon excitation at 260 nm. The **II** exhibits one intense emission band at ~325 nm which means a hypsochromic shift of ~17 nm relative to that of the free ligand (Fig. 3b). The reason leading to this

Table 2. Selected bond distances (Å) and bond angles (deg) for **I** and **II***

Bond	*d*, Å	Bond	*d*, Å
I			
Zn(1)–O(1)	1.931(3)	Zn(1)–O(4)	1.983(3)
Zn(1)–N(2)	2.053(4)	Zn(1)–N(1)	2.066(4)
II			
N(2)–Cd(1)$^{\#1}$	2.343(3)	Cd(1)–O(5)	2.269(3)
Cd(1)–N(1)$^{\#2}$	2.339(3)	Cd(1)–O(2)	2.435(3)
Cd(1)–N(3)	2.394(4)	Cd(1)–O(3)$^{\#2}$	2.477(3)
Cd(1)–O(2)$^{\#2}$	2.454(3)		
Angle	ω, deg	Angle	ω, deg
I			
O(1)Zn(1)O(4)	112.07(15)	O(1)Zn(1)N(2)	125.38(15)
O(4)Zn(1)N(2)	104.34(14)	O(1)Zn(1)N(1)	108.26(14)
O(4)Zn(1)N(1)	97.40(15)	N(2)Zn(1)N(1)	105.71(13)
C(1)O(4)Zn(1)	106.9(3)	C(23)N(2)Zn(1)	124.9(3)
C(27)N(2)Zn(1)	117.6(3)	C(8)O(1)Zn(1)	112.4(3)
C(15)N(1)Zn(1)	119.8(3)	C(19)N(1)Zn(1)	122.8(3)
II			
O(5)Cd(1)N(1)$^{\#2}$	144.56(12)	O(5)Cd(1)N(2)$^{\#3}$	94.44(14)
N(1)$^{\#2}$Cd(1)N(2)$^{\#3}$	91.01(11)	O(5)Cd(1)N(3)	87.56(14)
N(1)$^{\#2}$Cd(1)N(3)	83.28(11)	N(2)$^{\#3}$Cd(1)N(3)	172.59(12)
O(5)Cd(1)O(2)	78.87(10)	N(1)$^{\#2}$Cd(1)O(2)	136.44(10)
N(2)$^{\#3}$Cd(1)O(2)	87.20(11)	O(5)Cd(1)O(2)$^{\#2}$	146.47(11)
N(3)Cd(1)O(2)	100.19(11)	N(1)$^{\#2}$Cd(1)O(2)$^{\#2}$	68.20(10)
N(2)$^{\#3}$Cd(1)O(2)$^{\#2}$	90.76(11)	N(3)Cd(1)O(2)$^{\#2}$	91.49(11)
O(2)Cd(1)O(2)$^{\#2}$	68.32(10)	O(5)Cd(1)O(3)$^{\#2}$	77.68(11)
N(1)$^{\#2}$Cd(1)O(3)$^{\#2}$	67.89(10)	N(2)$^{\#3}$Cd(1)O(3)$^{\#2}$	85.31(11)
N(3)Cd(1)O(3)$^{\#2}$	88.16(11)	O(2)Cd(1)O(3)$^{\#2}$	154.71(9)
O(2)$^{\#2}$Cd(1)O(3)$^{\#2}$	135.81(9)	C(15)O(2)Cd(1)	130.1(3)
C(15)O(2)Cd(1)$^{\#2}$	118.1(3)	Cd(1)O(2)Cd(1)$^{\#2}$	111.68(10)
C(8)N(3)Cd(1)	122.6(3)	C(39)N(3)Cd(1)	119.4(3)
C(16)O(3)Cd(1)$^{\#2}$	117.9(3)	C(24)N(1)Cd(1)$^{\#2}$	119.3(3)
C(14)N(1)Cd(1)$^{\#2}$	120.0(2)		

* Symmetry codes: $^{\#1}$ $x + 1, y, z - 1$; $^{\#2}$ $-x, -y, -z + 1$; $^{\#3}$ $x - 1, y, z + 1$ (**II**).

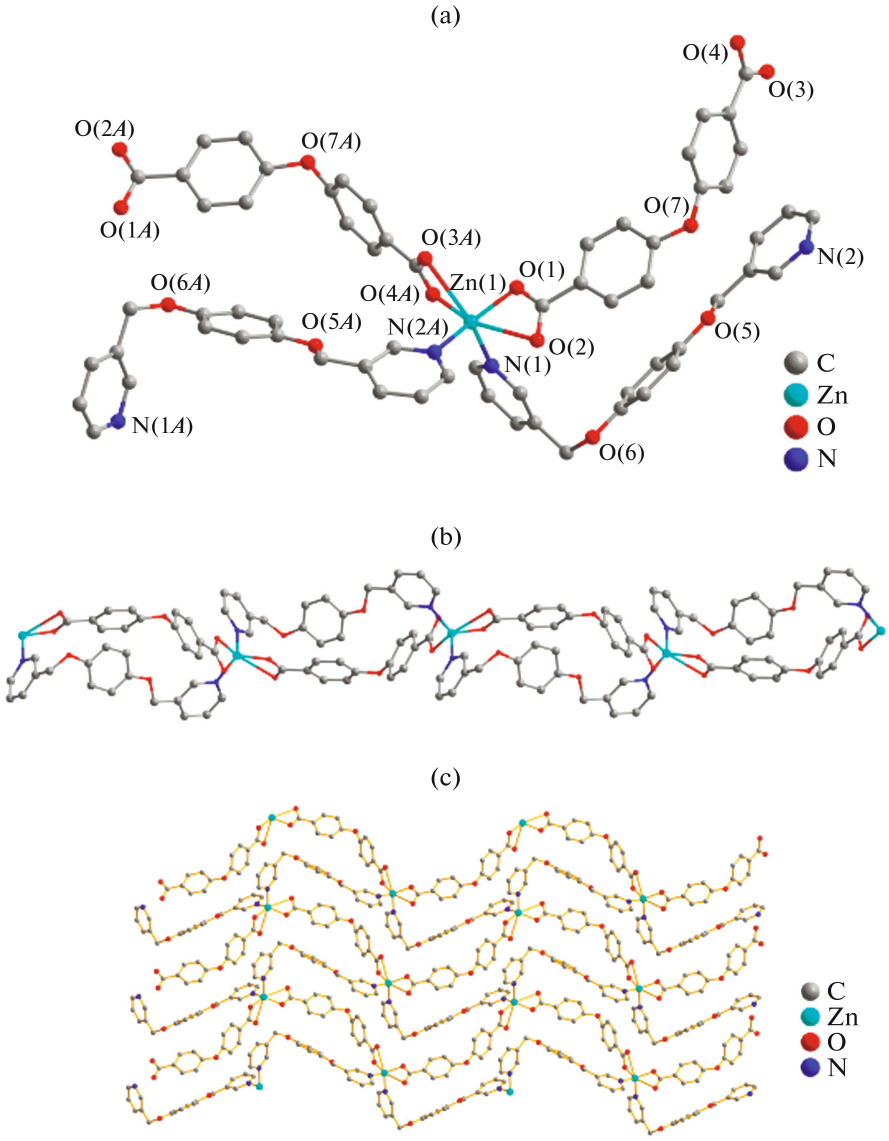

Fig. 1. Coordination environment of the Zn(II) atom in **I** (a); view of the 1D chain of **I** (b); the 2D layer framework of **I** (c).

emission peak may be assigned to the π→π* intraligand fluorescence emission of ligand.

In order to confirm the purities of the bulk samples, PXRD experiments were carried out for **I**, **II**. The experimental patterns are in good agreement with the corresponding simulated ones, indicating that the synthesized bulk materials and the measured singlecrystals are the same.

In order to examine the thermal stability of the two compounds, TG analyses were carried out for **I** and **II** at 30–1000°C (Fig. 4). When the temperature is below 355°C, the compound begin to lose ligands (calcd. 89.2%; found 90.5%). The residue product should be ZnO (calcd. 24.48%). The TG curve of **II** is divided into three stages. The first weight loss of 3.09% occurs in the temperature range 120–210°C, which can be attributed to the loss of lattice water molecules and coordinated water molecules (calcd. 5.9%, found 6.3%). The second continuous weight loss of 47.8% between 220 and 396°C was assigned to the decomposition of Dpb ligands (calcd. 47.6%). and the weight loss of 27.33% between 402 and 510°C attributed to the loss of coordinated $(2,6\text{-Pda})^{2-}$ ligands (calcd. 27.43%). The residue product should be CdO.

The IR spectra of compounds **I** and **II** were performed as KBr pellets in the range 4000–400 cm^{-1} (Fig. 5). The peaks of 1617 and 1647 cm^{-1} are assigned to the skeleton vibration of C=N in **I** and **II**, respectively, which display certain shifts in contrast with

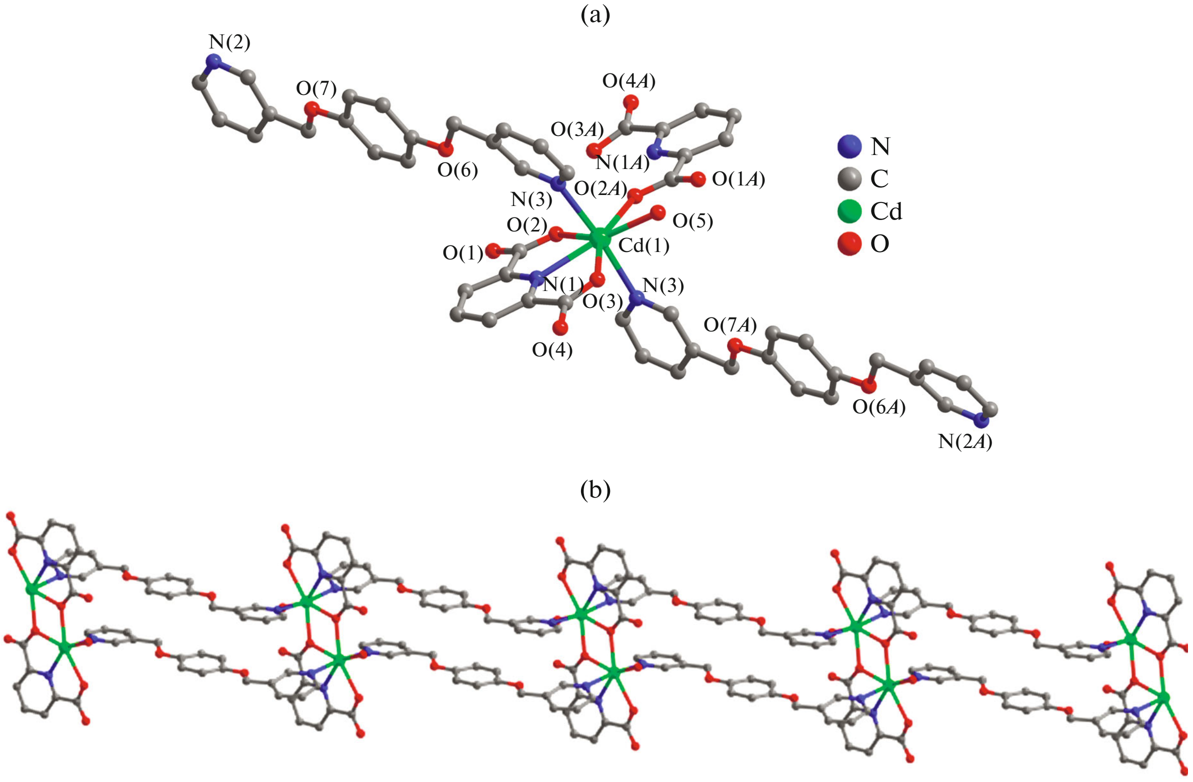

Fig. 2. Coordination environment of the Cd(II) atom in **II** (a); view of the 1D double-chain chain of **II** (b).

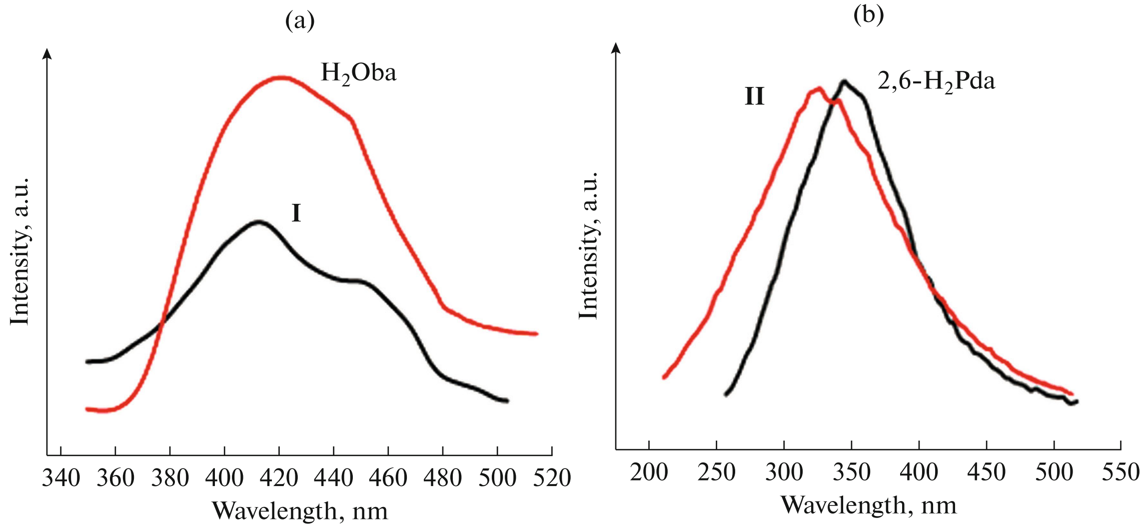

Fig. 3. The solid-state emission spectra: (a) H_2Oba (*1*) and **II** (*2*);(b) H_2Pda (*1*) and **II** (2) at room temperature.

1594 cm^{-1} in the ligand. It is thus assumed that nitrogen atoms in the ligand coordinate to metal atoms. The absence of any strong bands around 1700 cm^{-1} for **I**, **II** indicates that the carboxylate groups of organic-acid are completely deprotonated [19]. In the IR spectrum of **I**, $\Delta(\nu_{as}(OCO) - \nu_s(OCO)) < 200$ (Δ = 115 cm^{-1}), Δ value suggests that the carboxylate is coordinated to metal ions only in a bidentate mode. In the IR spectra of II, the difference between ν_{as}(COO) and ν_s(COO) (Δ = 211 cm^{-1}) suggests that the carbox-

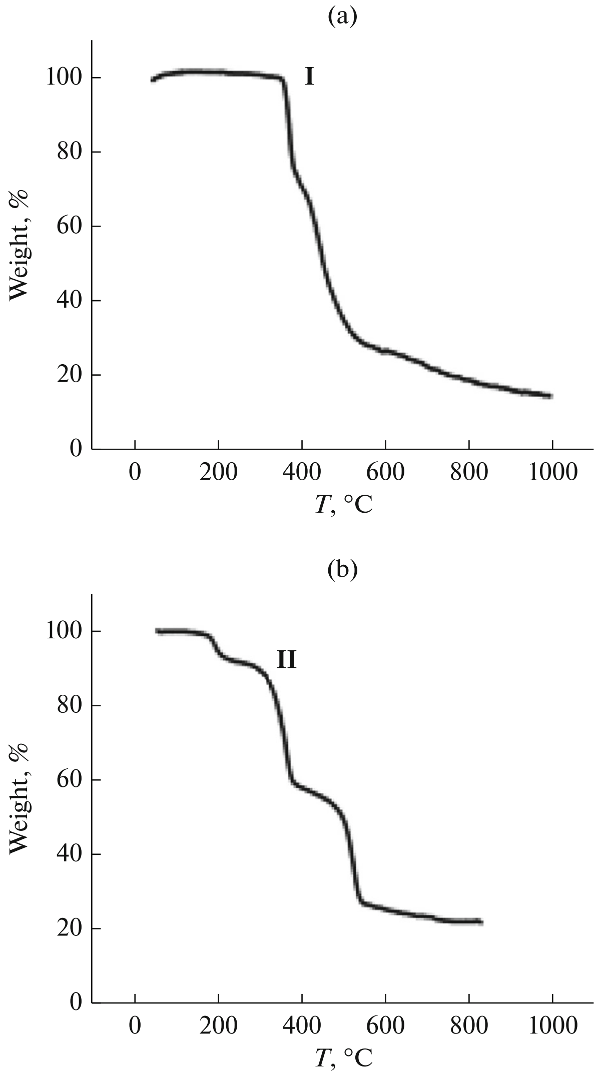

Fig. 4. TGA curves of complexes **I** (a) and **II** (b).

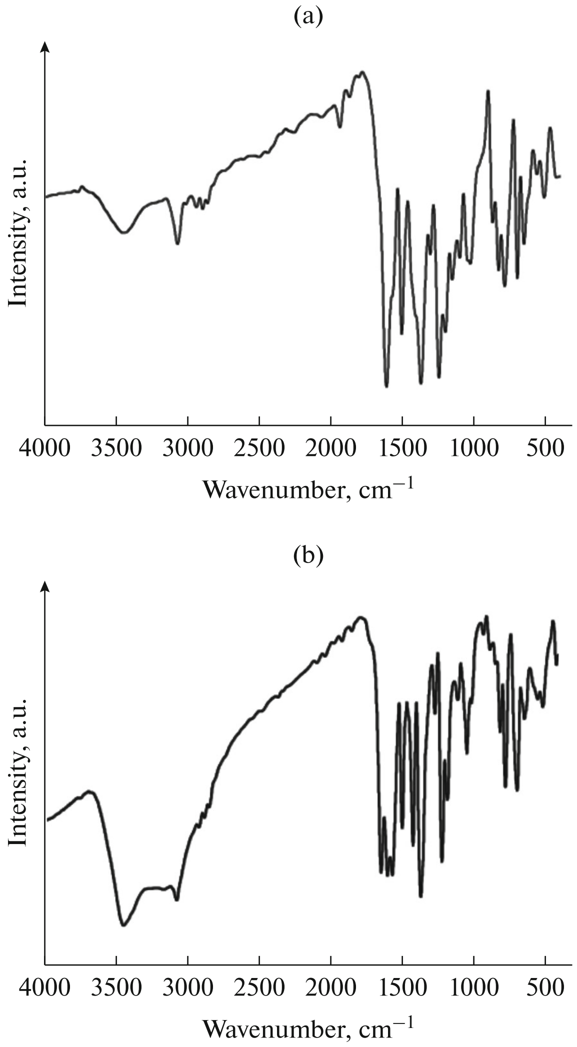

Fig. 5. FT-IR spectrum of complexes **I** (a) and **II** (b).

ylate groups coordinate to the Cd^{2+} ions in monodentate coordination mode [20]. These IR spectra are in good agreement with the results of X-ray structural analysis.

Thus, two new compounds have been synthesized by combining long flexible N-bridging ligands and carboxylic group ancillary ligands under hydrothermal conditions. The solid-state fluorescent analyses show that compounds **I** and **II** exhibit luminescence properties. Further systematic work toward fabricating more MOFs with interesting structure and functionalities using Dpb ligand is in progress.

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REFERENCES

1. Sawano, T., Lin, Z., Boures, D., An, B., et al., *J. Am. Chem. Soc.*, 2016, vol. 138, p. 9783.
2. Zheng, N.F., Bu, X.H., and Feng, P.Y., *J. Am. Chem. Soc.*, 2002, vol. 124, p. 9688.
3. Lu, J.F., Shi. J., Zheng, N., and Guo, X.H., *Chin. J. Struct. Chem.*, 2016, vol. 35, p. 319.
4. Paul, A., Ribeiro, P.C., Karmakar, A., et al., *Dalton Trans.*, 2016, vol. 45, p. 12779.
5. Brana, M.F., Gradillas, A., Ovalles, A.G., et al., *Bioorg. Med. Chem.*, 2006, vol. 14, p. 9.
6. Yu, Z.G., Li, J.Z., and Liu, S.Q., *Chin. J. Appl. Chem.*, 2004, vol. 21, p. 1300.
7. Liu, J.W., Chen, L.F., Cui, H., et al., *Chem. Soc. Rev.*, 2014, vol. 43, p. 6011.

8. Lu, J.F., Liu, J., and Jiang Min. *Chin. J. Struct. Chem.*, 2015, vol. 34, p. 248.
9. Yuan, F., Xie, J., Hu, H.M., et al., *CrystEngComm*, 2013, vol. 15, p. 1460.
10. Wang, Z.Q., Xu, G.F., Bi, Y.F., and Wang, C., *CrystEngComm*, 2010, vol. 12, p. 3703.
11. Yue, C.Y., Lei, X.W., Yin, L., et al., *CrystEngComm*, 2015, vol. 17, p. 814.
12. Gou, L., Han, Z.X., Hu, H.M., et al., *Inorg. Chim. Acta*, 2010, vol. 363, p. 2590.
13. Swiegers, G.F. and Malefetse, T.J., *Chem. Rev.*, 2000, vol. 100, p. 3483.
14. Leininger, S., Olenyuk, B., and Stang, P.J., *Chem. Rev.*, 2000, vol. 100, p. 853.
15. Cui, G.H., Li, J.R., Tian, J.L., et al., *Cryst. Growth. Des.*, 2005, vol. 5, p. 1775.
16. Sheldrick, G.M., *SHELXS-97, Program for the Solution of Crystal Structures*, Göttingen: Univ. of Göttingen, 1997.
17. Sheldrick, G.M., *SHELXS-97, Program for the Refinement of Crystal Structures*, Göttingen: Univ. of Göttingen, 1997.
18. Zhang, X., Huang, Y.Y., Cheng, J.K., et al., *CrystEngComm*, 2012, vol. 14, p. 4843.
19. Sun, Y.Q., Zhang, J., Ju, Z.F., and Yang, G.Y., *Cryst. Growth Des.*, 2005, vol. 5, p. 1939.
20. Chen, X.L., Gou, L., Hu, H.M., et al., *Eur. J. Inorg. Chem.*, 2008, p. 239.