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Hydrothermal synthesis, crystal structures and photoluminescent properties of four cadmium(II) coordination polymers derived from diphenic acid and auxiliary ligands

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ABSTRACT

Four novel metal coordination polymers, $[Cd(dpa)(H_2O)]_n$ (**1**), $[Cd(dpa)(2,2'\text{-bipy})]_n$ (**2**), $\{[Cd_2(dpa)_2(4,4'\text{-bipy})_3](4,4'\text{-bipy})(H_2O)_2\}_n$ (**3**) and $[Cd(dpa)(bim)_2(H_2O)]\}_n$ (**4**) (H_2dpa = 2,4′-biphenyl-dicarboxylic acid, 2,2′-bipy = 2,2′-bipyridine, 4,4′-bipy = 4,4′-bipyridine, bim = benzimidazole), have been synthesized and structurally characterized by elemental analysis, IR and X-ray diffraction. Single-crystal X-ray analyses reveal that the 2,4′-diphenic acids acts as bridging ligands, exhibiting rich coordination modes to link metal ions: bis-monodentate, bidentate chelating, chelating/bridging, monoatomic bridging and monodentate modes. In addition, the luminescent properties for compound **1–4** are also investigated in this work.

1. Introduction

The interest in the construction of metal–organic frameworks (MOFs) is rapidly increasing due to their diverse structures and potential applications such as gas storage, catalysis, nonlinear optics, molecular magnetism and luminescence [1–10]. It is well-known that carboxylate-metal compounds exhibit various network topologies and remarkable prospect, therefore the construction of novel coordination polymers using metal ions and anionic O-donor ligands is a hotspot in the field [11–15]. On the other hand, the introduction of neutral N-donor building block ligands into MOFs provides further impetus for research on metal–organic supramolecular frameworks. Recently, a number of structurally defined new MOFs have been rationally and successfully constructed by using mixed-ligand method [16–18].

Diphenic acid (H_2dpa) as O-donor ligand has received much attention in the designed synthesis of coordination polymers [19–26], but the MOFs constructed from unsymmetric diphenic acid are less reported [27–29]. In this paper, we select 2,4′-dpa as the first ligand based on the following considerations: (a) in H_2dpa, the two functional groups may have different coordination modes (monodentate, chelating and/or bridging) which allows a wide variety of structures; (b) in deprotonated H_2dpa, two phenyl rings are not coplanar with each other owing to the steric hindrance of carboxylate groups in coordination process. The distortion of diphenyl spacer about the central bond allows dpa^{2-} to link metal ions or metal clusters into macrocycles, helical chains and one dimensional chains. Herein, we report the synthesis, crystal structure and luminescent properties of four cadmium coordination polymers based on the 2,4′-diphenic acid or/and auxiliary ligands.

2. Experimental

2.1. General materials and method

All reagents and solvents employed were commercially available and used as received without further purification. 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 as a dry KBr pellet in the 400–4000 cm^{-1} range. Solid-state fluorescence spectra were recorded on a F-4600 equipped with a xenon lamp and a quartz carrier at room temperature.

2.2. Synthesis of complexes *1–4*

2.2.1. $[Cd(dpa)(H_2O)]_n$ (*1*)

A mixture of $Cd(OAc)_2\cdot 2H_2O$ (0.267 g, 1 mmol), H_2dpa (0.242 g, 1 mmol), NaOH (0.08 g, 2 mmol) and deionized water (18 mL) was sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 160 °C for 96 h. After cooling to room temperature, the colorless block crystals were obtained and washed with alcohol for several

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Table 1
Crystallographic data and structure refinement summary for complexes **1**–**4**.

Empirical formula	$C_{14}H_{10}CdO_5$	$C_{24}H_{16}CdN_2O_4$	$C_{34}H_{26}CdN_4O_5$	$C_{28}H_{24}CdN_4O_6$
Formula weight	370.62	508.79	683.00	624.91
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group	*Pbca*	$P2_1/n$	$P\bar{1}$	$P2_1/c$
Unit cell dimensions				
a (Å)	7.449(4)	10.194(6)	9.730(5)	18.533(10)
b (Å)	15.357(8)	10.384(7)	11.911(7)	8.434(5)
c (Å)	23.297(11)	18.518(10)	14.245(8)	17.692(10)
α (°)	90.00	90.00	107.36(10)	90.00
β (°)	90.00	93.30(5)	104.28(10)	108.60(10)
γ (°)	90.00	90.00	101.92(10)	90.00
V (Å^3)	2664.9(2)	1957.0(14)	1455.08(14)	2621.2(3)
Z	8	4	2	4
D_{calc} (mg m^3)	1.847	1.727	1.559	1.584
F(0 0 0)	1456	1016	692	1264
Reflections collected	3302	4863	5206	5243
Independent reflections ($I > 2\sigma(I)$)	2349	4191	4838	4823
θ Range for data collection	2.65–28.34	2.25–28.53	1.88–25.20	2.43–30.88
Limiting indices	$-9 \leqslant h \leqslant 9$	$-13 \leqslant h \leqslant 12$	$-11 \leqslant h \leqslant 11$	$-20 \leqslant h \leqslant 23$
	$-19 \leqslant k \leqslant 19$	$-13 \leqslant k \leqslant 13$	$-14 \leqslant k \leqslant 13$	$-10 \leqslant k \leqslant 7$
	$-13 \leqslant l \leqslant 31$	$-16 \leqslant l \leqslant 24$	$-10 \leqslant l \leqslant 17$	$-20 \leqslant l \leqslant 21$
Goodness-of-fit on F^2	1.024	1.022	1.022	1.047
R_1[a], wR_2[b] [$I > 2\sigma(I)$]	R_1 = 0.0253	R_1 = 0.0227	R_1 = 0.0244	R_1 = 0.0217
	wR_2 = 0.0567	wR_2 = 0.0512	wR_2 = 0.0601	wR_2 = 0.0565
R_1, wR_2 (all data)	R_1 = 0.0434	R_1 = 0.0288	R_1 = 0.0272	R_1 = 0.0242
	wR_2 = 0.0641	wR_2 = 0.0535	wR_2 = 0.0620	wR_2 = 0.0580
Largest difference in peak and hole (e Å^3)	0.076 and −0.591	0.056 and −0.345	0.058 and −0.340	0.054 and −0.277

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$.
[b] $wR = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(F_o^2)]^{1/2}$.

times (yield: 56% based on Cd). Elemental *Anal.* Calc. (%) for $C_{14}H_{10}CdO_5$: C, 45.37; H, 2.72. Found: C, 45.20; H, 2.73%. IR: 3320 b, 3012 w, 1616 s, 1586 s, 1577 s, 1420 s, 1365 w, 1228 w, 864 m, 621 m.

2.2.2. [Cd(dpa)(2,2′-bipy)]$_n$ (**2**)

Compound **2** was synthesized in a procedure similar to that of compound **1**, except the 2,2′-bipy (0.156 g, 1 mmol) was used. Colorless block crystals of **2** were obtained with 62% yield on Cd basis. Elemental *Anal.* Calc. (%) for $C_{24}H_{16}CdN_2O_4$: C, 56.66; H, 3.17; N, 5.51. Found: C, 57.22; H, 3.16; N, 5.56%. IR: 3010 b, 1608 s, 1542 s, 1428 m, 1390 s, 1281 m, 1098 m, 1064 m, 984 m, 860 m, 751 s, 697 m, 654 m.

2.2.3. {[Cd$_2$(dpa)$_2$(4,4′-bipy)$_3$](4,4′-bipy)(H$_2$O)$_2$}$_n$ (**3**)

The compound **3** was prepared in a similar manner as compound **2** by using of 4,4′-bipy (0.156 g, 1 mmol) in place of 2,2′-bipy. Colorless block crystals of **3** were obtained with 60% yield on Cd basis. Elemental *Anal.* Calc. (%) for $C_{34}H_{26}CdN_4O_5$: C, 59.79; H, 3.84; N, 8.20. Found: C, 59.92; H, 4.03; N, 8.14%. IR: 3442 br, 3025 w, 1605 s, 1587 s, 1500 w, 1435 m, 1410 m, 1022 m, 927 w, 845 w, 821 w, 753 s, 684 m, 612 m, 537 w, 496 w.

2.2.4. [Cd(dpa)(bim)$_2$(H$_2$O)]}$_n$ (**4**)

The compound **4** was prepared in a similar manner as compound **2** by using of bim (0.236 g, 2 mmol) in place of 2,2′-bipy. Colorless block crystals of **4** were obtained with 42% yield on Cd basis. Elemental *Anal.* Calc. (%) for $C_{28}H_{24}CdN_4O_6$: C, 53.82; H, 3.87; N, 8.97. Found: C, 53.70; H, 3.94; N, 9.05%. IR: 3406 br, 3007 w, 1625 s, 1589 s, 1521 w, 1452 m, 1423 m, 1248 w, 1094 w, 1060 m, 1015 w, 826 m, 804 s, 715 w, 647 w, 563 m.

2.3. X-ray crystallography

Diffraction intensity data of the single crystal of the four compounds were collected on a Bruker Smart Apex II CCD diffractometer equipped with a graphite monochromated Mo Kα radiation (λ = 0.71073 Å) by using a ω-scan mode. Empirical absorption correction was applied using the SADABS programs [30]. All the structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 using the program SHEXL-97 [31]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by geometrically calculations, and their positions and thermal parameters were fixed during the structure refinement. In compound **3**, little crystallographic disorder can be observed for the C_{33} and C_{34} of the free 4,4′-bipy molecule. In compound **4**, the lattice water molecule is disordered in two positions (O6A and O6B). The hydrogen atoms attached to the disordered water molecule were located from the difference Fourier maps but their positional and thermal parameters were not refined. The crystallographic data and experimental details of structural analyses for cadmium coordination polymers are summarized in Table 1. Selected bond and angle parameters for cadmium are listed in Table 2.

3. Results and discussion

3.1. Structural descriptions of **1**–**4**

3.1.1. [Cd(dpa)(H$_2$O)]$_n$ (**1**)

The structure of complex **1** is determined by X-ray single-crystal diffraction. As shown in Fig. 1a, each Cd(II) ion is surrounded by five oxygen atoms from different dpa^{2-} ligands and one oxygen atom from coordinated water molecule in a octahedral coordination geometry. The Cd(1)–O bond lengths vary from 2.214(17) Å to 2.399(16) Å and the O–Cd(1)–O bond angles range from 55.09(6)° to 162.50(7)°. The equatorial plane is defined by four oxygen atoms (the equation of plane is $9.945x + 2.558y + 5.889z = 2.9249$, the maximal and the mean deviation are 0.0457 Å and 0.0182 Å, respectively). Two carboxylate groups of 2,4′-dpa adopt chelating/bridging and bis-monodentate coordination modes (Scheme 1a). In the first mode, one of the carboxylate group [O(3) and O(4)] bridges between two Cd(II) atoms through chelating with Cd(1) and coordinating to Cd(1A) in a chelating/