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Structural diversity and fluorescence properties of three 2-sulfoterephthalate Cd^{II}/Zn^{II} coordination polymers employing 1,4-bisbenzimidazole

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ABSTRACT

Three novel coordination polymers, namely, $[Cd(2\text{-}Hstp)(1,4\text{-}bbi)(H_2O)_2]\cdot 3H_2O$ (**1**), $[Cd_{1.5}(2\text{-}stp)(1,4\text{-}bbi)(H_2O)_2]\cdot H_2O$ (**2**) and $[Zn_2(2\text{-}stp)(\mu_2\text{-}OH)(1,4\text{-}bbi)_{1.5}(H_2O)]\cdot 6H_2O$ (**3**) (2-H_3stp is equal to 2-sulfoterephthalate and 1,4-bisbenzimidazole is equal to 1,4-bbi), have been synthesized by hydrothermal reaction. The structural analyses show that **1** and **2** possess different structural features despite the same raw materials, which are 1D chain structure featuring 6-member-water H-bonds cluster and 3D bbi-pillared wavy-like layer framework, respectively. As changing the metal ion to zinc ion, **3** exhibits 3D stp-pillared layer architecture, which discovers the effect of the central metal ions on the formation of metal–organic frameworks. The fluorescence studies show that the emissions of the coordination polymers are attributed to the ligand π–π^* transition, which means they could be potential fluorescence materials.

1. Introduction

The design and synthesis of metal–organic coordination polymers have attracted the attention of many researchers in the past two decades, not only for their diversified structural features, but also for their potential applications of gas storage, catalysis, magnetic, luminescent and so on [1–3]. Changing the organic ligands, metal ions, reaction solvents or other reaction conditions is a main strategy to investigate the influencing factors and mechanism of the formation of the metal–organic material. On one hand, the effects of organic ligands to the self-assembling of metal complexes have been reported widely. In the used organic ligands, the multidentate organic ligands including carboxyl groups have been used widely in the formation of transitional metal coordination polymers due to the versatile coordination modes of carboxyl group, such as monodentate, bidentate, chelated and their combinations [4–6]. Differed from the evergreen terephthalic acid ligand, 2-sulfoterephthalic acid (2-H_3stp) possesses three functional groups which exhibit stronger coordination ability and more flexible coordination fashions as a linker in assembling of coordination polymers [7–9]. On the other hand, the central metal ion is also important for the formation of these coordination polymers. Several complexes based on 2-H_3stp have been reported involving p-block (Pb^{2+}), d-block (Mn^{2+}, Ag^{+}, Cu^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+}) and f-block (Eu^{3+}, Tb^{3+} and Dy^{3+}), which have the helical, stranded or interpenetrated structural characteristics [10–12]. To introduce N-donor organic ligands is an important strategy of constructing novel coordination polymers, for their abilities of coordinating to metal ions, forming H-bonds or π–π stacking interactions, and altering the coordination environment of central ions and the dimension of the frameworks [13–15]. 1,4-bisbenzimidazole (1,4-bbi) is a long linear N-donor organic ligand and apt to be a spacer in high-dimensional networks or frameworks [16]. In the course of ongoing studies on 2-sulfoterephthalic acid (2-H_3stp), we prepared three cadmium (II) or zinc (II) coordination polymers combining 2-H_3stp and 1,4-bbi ligands, and studied their crystal structures depending on the metal ions and reaction conditions. The d^{10} metal compounds have been shown to exhibit interesting photoluminescent properties, such as structure-, metal-dependent or an intraligand transition emission [17]. The metal–organic frameworks (MOFs) have high thermal stability due to their structure features in general. So the fluorescence properties in solid state of these coordination polymers are investigated, as well as their thermal stabilities.

2. Experimental

2.1. Materials and measurements

All chemicals were commercially available and used as received without further purification. Elemental analyses (CHN) were

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performed using an Vario EL elemental analyzer. FT-IR spectra were recorded from KBr pellets in the range of 4000–400 cm^{-1} on a Nicolet Avatar 360 FT-IR spectrometer. Thermogravimetric curves were measured on a Netzsch STA449 F3 at a heating rate of 10 °C/min from room temperature to 900 °C in nitrogen. Fluorescence measurements were carried out with a SHIMADZU RT5301PC spectrofluorophotometer.

2.2. Synthesis of $[Cd(2\text{-}Hstp)(1,4\text{-}bbi)(H_2O)_2]\cdot 3H_2O$ (1)

A mixture of $Cd(NO_3)_2\cdot 4H_2O$ (0.015 g, 0.05 mmol), NaH_2stp (0.013 g, 0.05 mmol) and 1,4-bbi (0.011 g, 0.05 mmol) was added to 3 mL H_2O. The mixture was stirred for 10 min and was placed in a 23 mL Teflon-lined stainless steel autoclave and heated at 140 °C for 72 h. The autoclave was cooled over a period of 16 h in air. The colorless lath-like crystals of **1** were collected by filtration, washed with ethanol, and dried in air (yield 42% based on Cd). Elemental analyses: calcd for $C_{20}H_{24}CdN_4O_{12}S$ (**1**): C:36.57, H:3.68, N:8.53%; found for C:36.83, H: 3.21, N:8.09%. IR (cm^{-1}): 3447 (m), 2365(w), 1589 (s), 1526 (s), 1390 (m), 1305 (m), 1206 (s), 1067 (s), 1025(m), 831(w), 625(m).

2.3. Synthesis of $[Cd_{1.5}(2\text{-}stp)(1,4\text{-}bbi)(H_2O)_2]\cdot H_2O$ (2)

A mixture of $Cd(NO_3)_2\cdot 4H_2O$ (0.015 g, 0.05 mmol), NaH_2stp (0.013 g, 0.05 mmol), NaOH (0.12 mL, 0.65 $mol\cdot L^{-1}$) and 1,4-bbi (0.011 g, 0.05 mmol) was added to 3 mL H_2O. The mixture was stirred for 10 min and was placed in a 23 mL Teflon-lined stainless steel autoclave and heated at 140 °C for 72 h. The autoclave was cooled over a period of 16 h in air. The colorless block-like crystals of **2** were collected by filtration, washed with ethanol, and dried in air (yield 58% based on Cd). Elemental analyses: calcd for $C_{20}H_{19}Cd_{1.5}N_4O_{10}S$ (**2**): C: 35.53, H: 2.83, N:8.29%; found for C:35.25, H: 3.06, N:8.11%. IR (cm^{-1}): 3455 (m), 2368(w), 1586(s), 1557(s), 1400(s),1307(m), 1230 (s), 1176(s), 1068(s), 1021(m), 851 (w), 770(w).

2.4. Synthesis of $[Zn_2(2\text{-}stp)\ (\mu_2\text{-}OH)\ (1,4\text{-}bbi)_{1.5}(H_2O)]\ (H_2O)_6$ (3)

A mixture of $Zn(OAc)_2$ (0.013 g, 0.05 mmol), NaH_2stp (0.026 g, 0.1 mmol) and 1,4-bbi (0.011 g, 0.05 mmol) was added to a mixed solvent of 5 mL and 1 mL isopropanol containing 0.2 mmol NaOH solution. The mixture was stirred for five minutes and was placed in a 23 mL Teflon-lined stainless steel autoclave and heated at 160 °C for 72 h. The autoclave was cooled over a period of 16 h in air. The colorless stick-like crystals of **3** were collected by filtration, washed with ethanol, and dried in air (yield 38% based on Zn). Elemental analyses: calcd for $C_{26}H_{23}Zn_2N_6O_{15}S$ (3): C: 37.98, H:2.82, N:10.22%; found for C:38.05, H: 3.01, N:10.31%. IR (cm^{-1}): 3426 (w), 1632 (s), 1592 (s), 1530 (s), 1418 (m), 1349 (m), 1219 (m), 1189 (m), 1071 (s), 833 (w), 650 (w).

2.5. Crystal structure determination

Single crystal X-ray diffraction analyses of three coordination polymers were carried out on a Bruker SMART APEX CCD diffractometer equipped with a graphite monochromated Mo-Kα radiation (λ=0.71073 Å). Raw data were integrated with the SAINT program [18]. The structures were solved by direct methods with SHELXS-97 and refined by full-matrix least-squares on F^2 using SHELXS-97 [19]. An empirical absorption correction was applied with the program SADABS [20]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set in calculated positions and refined by a riding mode. The crystallographic details of **1–3** are provided in Table 1, while the selected bond distances and angles are listed in Table S1.

3. Results and discussion

3.1. Crystal structures

X-ray single-crystal diffraction analysis shows **1** is one-dimensional chain structure based on Cd^{2+} ions linked by $2\text{-}Hstp^{2-}$ anions. Each Cd^{2+} ion lies in a hexa-coordinated octahedron (Fig. S1) surrounded by three oxygen atoms (O1, O2A and O5B) from 1-site carboxyl and 2-site sulfonate of three $2\text{-}Hstp^{2-}$ ligands, one nitrogen atom (N1) from one 1,4-bbi ligand, and two oxygen atoms (O8 and O9) from two lattice water molecules (Fig. 1). The bond lengths of Cd–O range from 2.243(4) to 2.385(3) Å, and the Cd–N bond length is 2.258(4) Å. The $Hstp^{2-}$ anion adopts a $\eta_1{:}\eta_1{:}\eta_1{:}\mu_3$ coordination mode (Scheme 1a) bridging three Cd^{2+} ions into

Table 1
Crystallographic data for complexes 1–3.

Empirical formula	$C_{20}H_{24}CdN_4O_{12}S$	$C_{20}H_{19}Cd_{1.5}N_4O_{10}S$	$C_{26}H_{23}Zn_2N_6O_{15}S$
Formula weight	656.89	676.05	820.29
Temperature (K)	296 (2)	296 (2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	Triclinic, *P*-1	orthorhomibic,Aba2	Monoclinic, $P2_1/n$
a/ Å	7.8741(11)	14.373(2)	1.00991(6)
b/ Å	9.0834(13)	38.220(5)	1.59353(9)
c/ Å	19.283(3)	9.0099(12)	2.01512(11)
α (deg)	101.181(2)	90	90
β (deg)	92.501(2)	90	93.981
γ (deg)	111.959(2)	90	90
Volume ($Å^3$)	1244.6(3)	4949.3(12)	3.2352(3)
Z	2	8	4
Calculated density (mg/m^3)	1.753	1.815	1.684
Absorption coefficient (mm^{-1})	1.033	1.446	1.628
F(000)	664		
	2680	1660	
Theta range for data collection (deg)	2.1–25.00	1.77–25.00	3.04–27.59
Reflections collected	4350	4177	66741
Reflections unique	3687	3955	7470
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.054	1.127	1.032
Final *R* indices [I > 2sigma(I)]	R_1=0.0428, wR_2=0.1056	R_1=0.0184, wR_2=0.0208	R_1=0.0377, wR_2=0.0973
R indices (all data)	R_1=0.0553, wR_2=0.1172	R_1=0.0470, wR_2=0.0573	R_1=0.0512, wR_2=0.1044