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Synthesis, structure, and photoluminescence of a series of lanthanide coordination polymers constructed from nitrogen containing organic ligands

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We have synthesized four coordination polymers with two different nitrogen containing organic ligands and different lanthanide metal ions, under hydrothermal condition. $[\{\text{Ln}_2(\text{bpdc})_3(\text{H}_2\text{O})_2\}]_n$ (Ln = Dy (**1**), Sm (**2**)) (bpdc = 2,2-bipyridine-3,3-dicarboxylic acid) are isostructural, with 2-D supramolecular layer structure composed from 1-D chains. Like **1** and **2**, $[\{\text{Ln}(\text{pzda})_2(\text{H}_2\text{O})_2\} \cdot 4\text{H}_2\text{O}]_n$ (Ln = Dy (**3**), Nd (**4**)) (pzda = pyrazine-2,6-dicarboxylic acid) are also isostructural with 1-D chain-like structures. The photoluminescence of **2** is studied.

Keywords: Lanthanide coordination polymer; Supramolecular network; Hydrothermal reaction; Photoluminescence property

1. Introduction

The rational design and synthesis of lanthanide coordination polymers have attracted interest as a new strategy for solid functional materials with potential applications in magnetism, ion exchange, catalysis, gas absorption/separation, and conductivity [1–11]. Because of the high coordination and flexible coordination sphere of lanthanide ions, controlling the overall frameworks of lanthanide-based coordination polymers, is a challenge compared with the predictability of coordination geometry of transition metals [12, 13]. However, various coordination modes, coupled with the tendency of lanthanide ions to adopt high coordination numbers also provide opportunity for the construction of fascinating topologies and crystal packing motifs [14]. Consequently, many lanthanide polymers have been synthesized recently [15–19].

Lanthanide ions possess strong coordination tendency with oxygen donors and a ligand with carboxylate groups would be expected to be good for constructing

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lanthanide–organic coordination polymers [20]. Pyridine–carboxylic acids and pyrazine–carboxylic acids (such as bpdc and pzda) important carboxylate acid derivatives, which have attracted much interest in coordination chemistry [21–24], could provide various coordination modes to form lanthanide coordination polymers under appropriate synthetic conditions [25].

Combining the merits of lanthanide ions together with nitrogen containing organic carboxylate ligands, under hydrothermal condition, we synthesized four complexes: $[\{\text{Ln}_2(\text{bpdc})_3(\text{H}_2\text{O})_2\}]_n$ (Ln = Dy (**1**), Sm (**2**)), $[\{\text{Ln}(\text{pzda})_2(\text{H}_2\text{O})_2\} \cdot 4\text{H}_2\text{O}]_n$ (Ln = Dy (**3**), Nd (**4**)).

2. Experimental

2.1. Materials and methods

All chemicals were purchased of reagent grade and used without purification. Elemental analyses (C, H, N) were performed on a Perkin Elmer 2400 CHN elemental analyzer. FT/IR spectra were recorded from 4000 to 400 cm^{-1} on an Alpha Centaur FTIR spectrophotometer using KBr pellets. TG analyses were performed on a Perkin Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 $^\circ\text{C min}^{-1}$. Photoluminescence spectra were obtained on a SPEX FL-2T2 instrument equipped with a 450 W xenon lamp as the excitation source. All measurements were performed at room temperature.

2.2. Syntheses of complexes 1–4

2.2.1. Synthesis of $[\{\text{Dy}_2(\text{bpdc})_3(\text{H}_2\text{O})_2\}]_n$ (1**).** Crystals were prepared from the reaction of $\text{DyCl}_3 \cdot 4\text{H}_2\text{O}$ (0.136 g, 0.30 mmol), bpdc (0.147 g, 0.60 mmol) in 8 mL of water. The resulting mixture was stirred for 30 min, and then transferred into a 23 mL Teflon-lined autoclave at 180 $^\circ\text{C}$ for 4 days. After slowly cooling to room temperature, pink crystals were collected in about 52% yield by filtration and air-dried. Elemental analysis, Calcd for $\text{C}_{36}\text{H}_{22}\text{N}_6\text{O}_{14}\text{Dy}_2$: C, 39.76; H, 2.04; N, 7.73; found: C, 39.69; H, 1.99; N, 7.66 (%). Selected FTIR data (cm^{-1}): 3631 (s), 3560 (m), 3251 (s), 1569 (s), 1520 (s), 1411 (s), 1253 (w), 1129 (w), 1076 (w), 1018 (w), 987 (w), 832 (w), 771 (w), 718 (m), 622 (w), 577(w), and 519 (w).

2.2.2. Synthesis of $[\{\text{Sm}_2(\text{bpdc})_3(\text{H}_2\text{O})_2\}]_n$ (2**).** Compound **2** was prepared from the reaction of $\text{SmCl}_3 \cdot 4\text{H}_2\text{O}$ (0.104 g, 0.30 mmol), bpdc (0.147 g, 0.60 mmol) in 7 mL of water. The resulting mixture was stirred for 20 min, and then transferred into a 23 mL Teflon-lined autoclave, and reacted at 180 $^\circ\text{C}$ for 5 days. After slowly cooling to room temperature, yellow crystals were collected in about 57% yield by filtration and air-dried. To confirm the purity of **2**, the XPRD was determined (figure S1). Elemental analysis, Calcd for $\text{C}_{36}\text{H}_{22}\text{N}_6\text{O}_{14}\text{Sm}_2$: C, 40.66; H, 2.09; N, 7.90; found: C, 40.69; H, 2.15; N, 7.68 (%). Selected FTIR data (cm^{-1}): 3628 (s), 3564 (m), 3253 (s), 1568 (s), 1521 (s), 1414 (s), 1257 (w), 1132 (w), 990 (w), 829 (w), 768 (w), 720 (m), 619 (w), 575 (w), and 520 (w).

2.2.3. Synthesis of $\{[\text{Dy}(\text{pzda})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}\}_n$ (3). Crystals were prepared from the reaction of $\text{DyCl}_3 \cdot 4\text{H}_2\text{O}$ (0.136 g, 0.30 mmol), pzda (0.134 g, 0.80 mmol) in 10 mL of water. The resulting mixture was stirred for 20 min, and then transferred into a 23 mL Teflon-lined autoclave, and reacted at 160°C for 3 days. After slowly cooling to room temperature, pink crystals were collected in 61% yield by filtration and air-dried. Elemental Analysis, Calcd for $\text{C}_{12}\text{H}_{16}\text{N}_4\text{O}_{14}\text{Dy}$: C, 23.91; H, 2.68; N, 9.29; found: C, 24.04; H, 2.59; N, 9.33 (%). Selected FTIR data (cm^{-1}): 3618 (s), 3466 (s), 3162 (s), 1533 (s), 1381 (s), 1349 (s), 1184 (w), 1155 (w), 1068 (w), 1027 (w), 926 (m), 761 (w), 737 (m), and 679 (w).

2.2.4. Synthesis of $\{[\text{Nd}(\text{pzda})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}\}_n$ (4). Complex **4** was prepared from the reaction of $\text{NdCl}_3 \cdot 5\text{H}_2\text{O}$ (0.102 g, 0.30 mmol) and pzda (0.134 g, 0.80 mmol) in 8 mL of water. The resulting mixture was stirred for 30 min, and then transferred into a 23 mL Teflon-lined autoclave, and heated at 160°C for 3 days. After slowly cooling to room temperature, purple crystals were collected in about 66% yield by filtration and air-dried. Elemental analysis, Calcd for $\text{C}_{12}\text{H}_{16}\text{N}_4\text{O}_{14}\text{Nd}$: C, 24.66; H, 2.76; N, 9.59; found: C, 24.74; H, 2.64; N, 9.67 (%). Selected FTIR data (cm^{-1}): 3622 (s), 3461 (s), 3164 (s), 1531 (s), 1379 (s), 1351 (s), 1180 (w), 1152 (w), 1071 (w), 923 (m), 757 (w), and 681 (w).

2.3. X-ray crystallography

Crystallographic data for **1–4** were collected at 298 K with a Rigaku R-axis Rapid IP diffractometer using graphite monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and IP technique. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL 97 crystallographic software [26, 27]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Carbon-bound hydrogens were placed in geometrically calculated positions. Oxygen-bound hydrogens were located in the difference Fourier maps and kept in that position. Further details of the X-ray structural analysis are given in table 1. Selected bond lengths are listed in table 2 and selected bond angles are listed in table 3.

3. Results and discussion

3.1. Structure description

Single crystal structural analysis shows that the structure of **1** is a 1-D framework. The fundamental unit is shown in figure 1(a). There are two crystallographic independent Dy(III) centers in the unit which exhibit the same kind of coordination environment that are linked by bpdc ligands. The first Dy(III) is coordinated by eight oxygens, six of which come from four bpdc ligands, with Dy–O bond distances ranging from 2.296 to 2.463 Å, the other two coordination sites are occupied by water with Dy–O bond distances of 2.514 Å. The second Dy(III) also coordinates eight oxygens, from five different bpdc ligands with bond distances in the range of 2.324–2.603 Å. The bpdc ligands have two kinds of coordination modes as shown in figure S2. In the first, two

Table 1. Crystal data and structure refinement for 1–4.

	1	2	3	4
Empirical formula	C ₃₆ H ₂₂ N ₆ O ₁₄ Dy ₂	C ₃₆ H ₂₂ N ₆ O ₁₄ Sm ₂	C ₁₂ H ₁₆ N ₄ O ₁₄ Dy	C ₁₂ H ₁₆ N ₄ O ₁₄ Nd
Formula weight	1087.60	1063.30	602.79	584.53
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>
Unit cell dimensions (Å, °)				
<i>a</i>	20.917(4)	20.899(4)	13.999(3)	14.051(3)
<i>b</i>	21.346(4)	21.434(4)	11.219(2)	11.261(2)
<i>c</i>	8.2160(16)	8.2601(17)	12.887(3)	12.944(3)
β	104.04(3)	104.04(3)	102.35(3)	102.15(3)
<i>V</i> (Å ³)	3558.9(12)	3589.4(13)	1977.2(7)	2002.2(7)
<i>Z</i>	4	4	4	4
<i>D</i> _{Calcd} (g cm ^{−3})	2.030	1.968	2.025	1.939
<i>F</i> (000)	2096	2064	1176	1152
Completeness to θ	99.4%	99.1%	99.8%	99.5%
<i>R</i> (int)	0.0307	0.0431	0.0203	0.0322
<i>S</i>	1.088	1.054	1.140	1.010
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0334	0.0359	0.0311	0.0307
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.1245	0.1226	0.1241	0.1185

$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $wR_2 = \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond lengths (Å) for 1–4.

Complex 1			
Dy(1)–O(1)	2.459(2)	Dy(1)–O(3)	2.296(2)
Dy(1)–O(5)	2.463(2)	Dy(1)–O(7)	2.514(3)
Dy(2)–O(4)	2.327(2)	Dy(2)–O(6)	2.324(2)
Complex 2			
Sm(1)–O(2)	2.306(2)	Sm(1)–O(3)	2.468(2)
Sm(1)–O(7)	2.513(3)	Sm(2)–O(3)	2.609(2)
Sm(2)–O(4)	2.428(3)	Sm(2)–O(5)	2.328(2)
Complex 3			
Dy(1)–O(9)	2.431(3)	Dy(1)–O(8)	2.530(3)
Dy(1)–O(10)	2.455(3)	Dy(1)–O(2)	2.538(3)
Dy(1)–O(4)	2.464(3)	Dy(1)–N(1)	2.596(4)
Dy(1)–O(5)	2.497(2)	Dy(1)–N(3)	2.597(3)
Complex 4			
Nd(1)–O(10)	2.448(4)	Nd(1)–N(1)	2.605(4)
Nd(1)–O(2)	2.475(3)	Nd(1)–N(3)	2.609(3)
Nd(1)–O(9)	2.481(4)	Nd(1)–O(4)	2.539(3)
Nd(1)–O(5)	2.509(3)	Nd(1)–O(8)	2.544(3)

carboxylate groups are bridging-linking and in the second, one carboxylate is chelating and the other is chelating-bridging. With these coordination modes, the bpdc ligands link adjacent Dy(III)’s forming a 1-D chain-like structure. These chains are connected to form a 2-D supramolecular network through π – π interactions with neighboring phenyl rings from 3.55 to 3.61 Å as shown in figure 1(b). Other complexes have been synthesized from bpdc and lanthanide(III) ions. For example, $[\{\text{Er}_4(\mu_3\text{-OH})_4(\text{bpdc})_4(\text{H}_2\text{O})_6\}_2] \cdot (\text{H}_2\text{O})_{16.5}$, exhibits a 2-D layer structure composed by a Er₄ building unit [22]. Another interesting 1-D complex $[\text{Tb}(\mu_2\text{-bpdc})(\text{NO}_3)(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ was also reported [23]. However, **1** possesses obvious structural differences from those two complexes.

Table 3. Selected bond angles (°) for **1–4**.

Complex 1			
O(3)–Dy(1)–O(1)	71.99(8)	O(3)–Dy(1)–O(5)	91.42(9)
O(1)–Dy(1)–O(5)	132.72(8)	O(3)–Dy(1)–O(7)	93.82(11)
O(1)–Dy(1)–O(7)	70.28(9)	O(5)–Dy(1)–O(7)	67.00(9)
O(6)–Dy(2)–O(4)	87.35(9)		
Complex 2			
O(2)–Sm(1)–O(3)	72.16(8)	O(2)–Sm(1)–O(7)	93.79(11)
O(3)–Sm(1)–O(7)	70.87(9)	O(2)–Sm(1)–O(7)#1	147.24(8)
O(4)–Sm(2)–O(3)	51.46(8)	O(5)–Sm(2)–O(4)	87.39(9)
O(5)–Sm(2)–O(3)	73.64(8)		
Complex 3			
O(9)–Dy(1)–O(10)	141.52(10)	O(9)–Dy(1)–O(2)	140.53(9)
O(9)–Dy(1)–O(4)	80.00(10)	O(10)–Dy(1)–O(2)	71.61(9)
O(10)–Dy(1)–O(4)	98.17(10)	O(4)–Dy(1)–O(2)	123.86(10)
O(9)–Dy(1)–O(5)	86.24(10)	O(5)–Dy(1)–O(2)	81.30(9)
O(10)–Dy(1)–O(5)	78.08(10)	O(8)–Dy(1)–O(2)	83.28(9)
O(4)–Dy(1)–O(5)	152.45(9)	O(4)–Dy(1)–O(8)	75.15(9)
O(9)–Dy(1)–O(8)	72.64(10)	O(5)–Dy(1)–O(8)	123.18(8)
O(10)–Dy(1)–O(8)	144.54(10)	O(9)–Dy(1)–N(1)	133.42(10)
O(4)–Dy(1)–N(3)	134.99(9)	O(10)–Dy(1)–N(1)	74.08(11)
O(5)–Dy(1)–N(3)	62.09(8)	O(4)–Dy(1)–N(1)	62.25(8)
O(8)–Dy(1)–N(3)	61.73(8)	O(5)–Dy(1)–N(1)	139.13(9)
O(2)–Dy(1)–N(3)	65.39(9)	O(8)–Dy(1)–N(1)	72.08(11)
N(1)–Dy(1)–N(3)	111.87(9)	O(2)–Dy(1)–N(1)	61.89(9)
O(10)–Dy(1)–N(3)	124.19(10)	O(9)–Dy(1)–N(3)	75.65(9)
O(10)–Nd(1)–O(2)	80.30(13)	O(10)–Nd(1)–O(9)	141.24(12)
Complex 4			
O(2)–Nd(1)–O(4)	123.77(12)	O(2)–Nd(1)–O(9)	97.54(14)
O(9)–Nd(1)–O(4)	71.75(12)	O(10)–Nd(1)–O(5)	86.20(13)
O(5)–Nd(1)–O(4)	81.18(11)	O(2)–Nd(1)–O(5)	152.48(10)
O(10)–Nd(1)–O(8)	72.82(12)	O(9)–Nd(1)–O(5)	78.29(13)
O(2)–Nd(1)–O(8)	75.50(10)	O(10)–Nd(1)–O(4)	140.70(12)
O(9)–Nd(1)–O(8)	144.56(12)	O(4)–Nd(1)–O(8)	83.33(11)
O(5)–Nd(1)–O(8)	123.07(10)	O(10)–Nd(1)–N(1)	133.56(13)
O(2)–Nd(1)–N(1)	62.14(10)	O(5)–Nd(1)–N(3)	62.18(10)
O(9)–Nd(1)–N(1)	74.00(13)	O(4)–Nd(1)–N(3)	65.41(11)
O(5)–Nd(1)–N(1)	139.03(11)	O(8)–Nd(1)–N(3)	61.52(10)
O(4)–Nd(1)–N(1)	61.87(10)	N(1)–Nd(1)–N(3)	111.73(11)
O(8)–Nd(1)–N(1)	72.12(12)	O(2)–Nd(1)–N(3)	135.20(11)
O(10)–Nd(1)–N(3)	75.75(12)	O(9)–Nd(1)–N(3)	124.54(13)

When Dy(III) is replaced by Sm(III), **2** is synthesized. The crystal structure of **2** is isomorphic to **1**. As expected, because of the larger ion radius of Sm(III), all coordinative bond distances in **2** are longer than **1**.

Complex **3** is composed of 1-D layers of {Dy(pzda)₂(H₂O)₂ · 4H₂O}. The pzda adopts two coordination modes as shown in figure S3. In the first, one carboxylate is bridging and the other is monodentate. In the other type, two carboxylates both are monodentate. The fundamental unit of **3** consists of one crystallographically independent Dy(III), as shown in figure 2(a). Dy(III) connects with four oxygens and two nitrogens from two different pzda ligands; Dy–O bond distances range from 2.464 to 2.538 Å and Dy–N bond distances are from 2.596 to 2.597 Å. Two water molecules occupy the other two coordination sites with distances of 2.431–2.455 Å. There also exist four free water molecules in the fundamental unit. The pzda ligands link adjacent Dy(III) ions forming a 1-D chain-like structure. With hydrogen bonds between chains

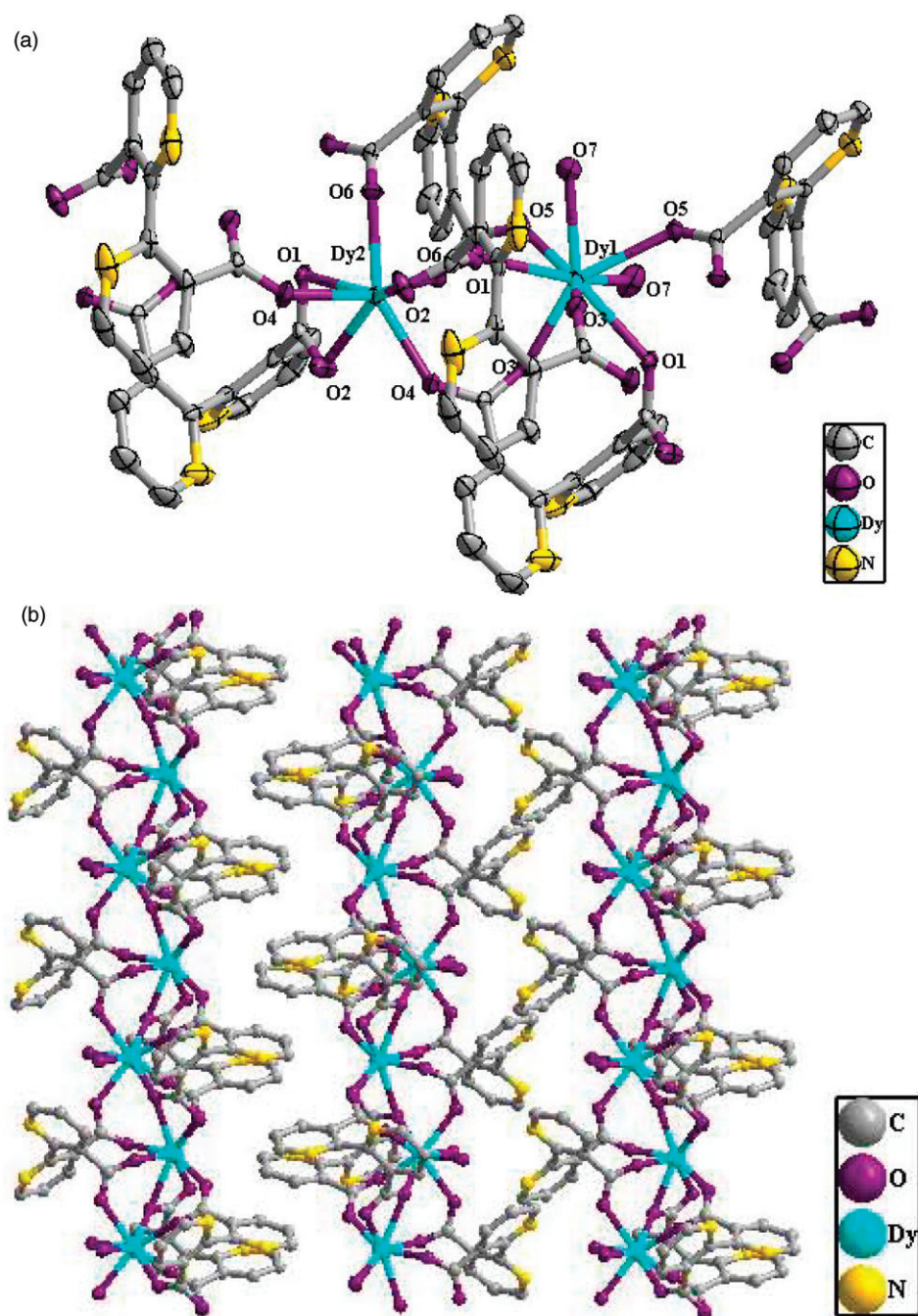


Figure 1. (a) Coordination environment of Dy(III) in **1** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity; (b) A 2-D supramolecular layer composed by 1-D $[\{Dy_2(bpdca)_3(H_2O)_2\}]_n$ chains for **1**.

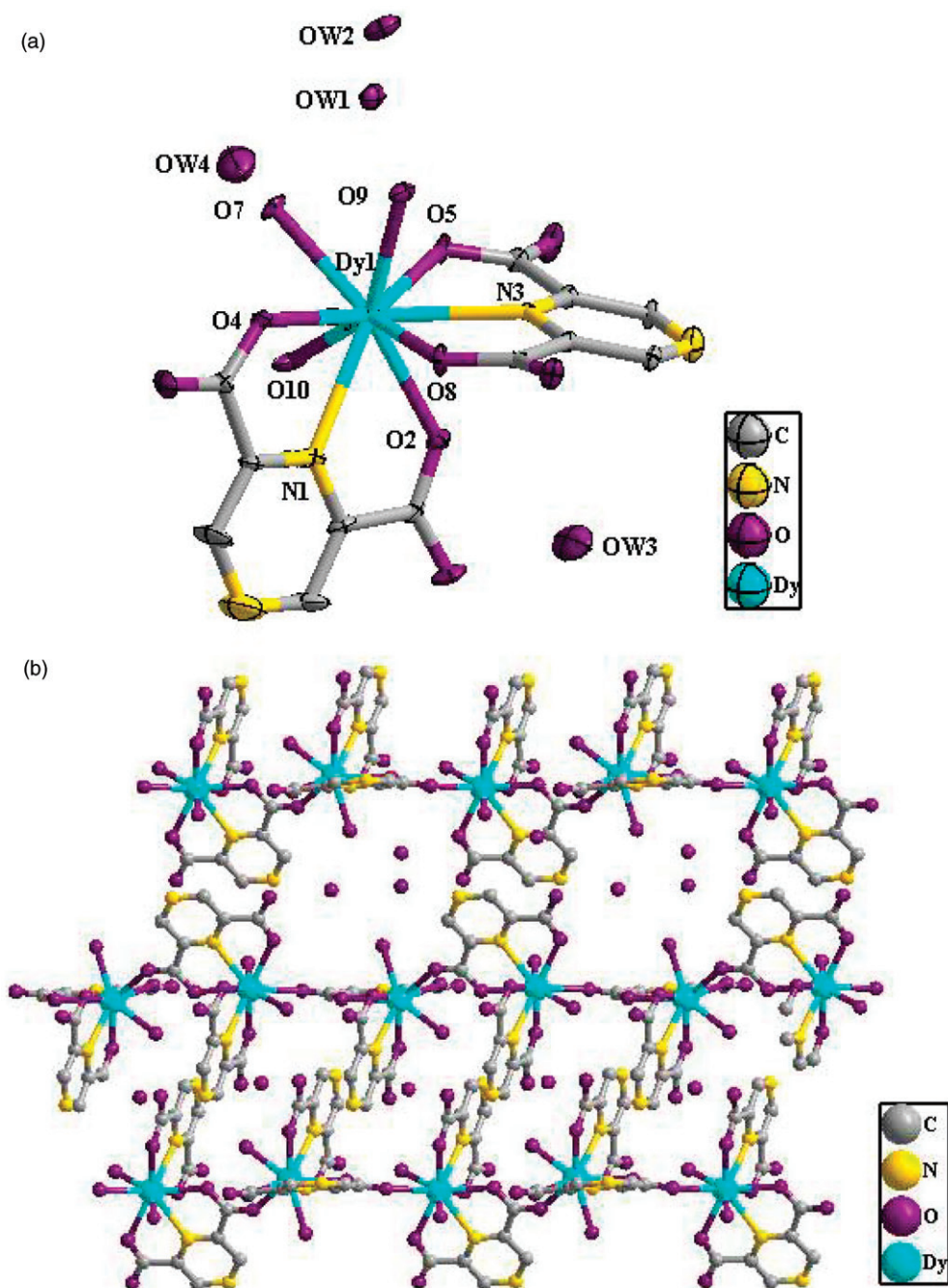


Figure 2. (a) Coordination environment of Dy(III) in **3** with thermal ellipsoids drawn at 50% probability. Hydrogens have been omitted for clarity; (b) A 2-D supramolecular layer composed by 1-D $[\{\text{Dy}(\text{pyzc})_2(\text{H}_2\text{O})_2\}]_n$ chains for **3**.

and free water molecules, neighboring chains are extended into 2-D supramolecular layers as shown in figure 2(b). Two other complexes $[\text{Ln}_2(\text{pzda})_3(\text{H}_2\text{O})_2] \cdot 2.5\text{H}_2\text{O}$ ($\text{Ln} = \text{Nd}, \text{Eu}$) have been synthesized from pzda and $\text{Ln}(\text{III})$; different from **3**, these two complexes possess 3-D structures [24].

When $\text{Dy}(\text{III})$ is replaced by $\text{Nd}(\text{III})$, **4** is synthesized. The crystal structure of **4** is isomorphic to **3**.

3.2. Thermal stability

The thermal stabilities of **1–4** have been determined on single crystal samples in a nitrogen atmosphere by thermogravimetric analysis (TGA). For **1**, TGA shows two decomposition steps starting at 115°C and ending at 492°C . The first weight loss 3.26% from 115 to 139°C represents loss of coordination water (Calcd: 3.31%). The second weight loss, 66.74%, is equivalent to loss of bpdc (Calcd: 66.80%). Complex **2** also exhibits two weight losses, the first about 3.41% from loss of water (Calcd: 3.39%), and the next of 66.42% from loss of bpdc (Calcd: 66.33%). For **3**, weight loss of 17.88% from 91 to 159°C is from loss of free and coordinated water (Calcd: 17.92%). The second weight loss of 55.24% from 400 to 533°C corresponds to loss of pzda (Calcd: 55.11%). For **4**, TGA exhibits one (18.55%) from 149 to 178°C from loss of water (Calcd: 18.48%) and another (56.68%), from 386 to 521°C , corresponding to removal of pzda (Calcd: 56.83%).

3.3. Photoluminescence property

Complex **2** yields red luminescence (figure 3) when excited at 288 nm; the emissions at 571, 589, and 644 nm are attributed to the characteristic emissions of $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$, $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$, and $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ of Sm^{3+} [28].

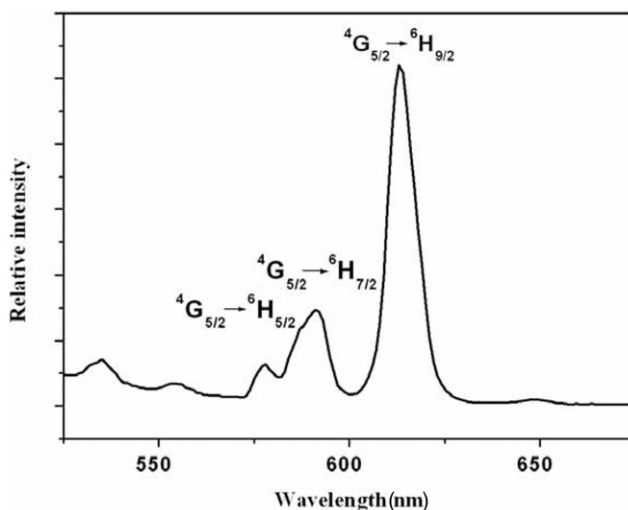


Figure 3. Emission spectra for **2**.

4. Conclusions

Four new lanthanide(III) coordination polymers with nitrogen containing organic carboxylates have been synthesized under hydrothermal condition and structurally characterized. Complex **2** exhibits photoluminescence at room temperature.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference number 710604 (**1**), 710605 (**2**), 710606 (**3**), and 710607 (**4**).

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