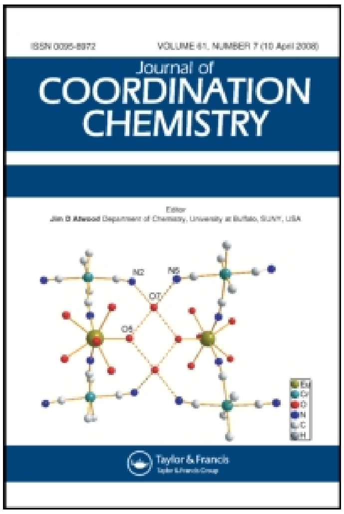

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Hydrothermal synthesis, crystal structure and luminescence properties of lanthanide fumarate coordination polymers containing 2,2'-bipyridine

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Hydrothermal synthesis, crystal structure and luminescence properties of lanthanide fumarate coordination polymers containing 2,2′-bipyridine

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Lanthanide coordination polymers with fumarate and 2,2′-bipyridine, $[Ln_2(C_4H_2O_4)_3(2,2'\text{-bpy})_2(H_2O)_2]_n$ (Ln = Sm (1), Dy (2); $C_4H_2O_4^{2-}$ = fumarate; 2,2′-bpy = 2,2′-bipyridine) have been prepared by hydrothermal reactions and characterized by X-ray diffration. Lanthanide ions are coordinated by five oxygens of fumarate groups, one oxygen of water and two nitrogens from 2,2′-bpy. Lanthanide ions bridged by fumarate groups in tridentate and tetradentate coordination modes form a 2-D layer structure. Hydrogen bonds and π–π stacking between 2-D layer result in 3-D supramolecular structure. The complexes exhibit luminescence characteristic of Sm^{3+} ion and Dy^{3+}.

Keywords: Lanthanide coordination polymers; Fumaric acid; 2,2′-Bipyridine; Crystal structure; Luminescence properties

1. Introduction

Lanthanide complexes have received attention for the various molecular structures with different potential applications [1–5]. The molecular architecture of coordination polymers can be designed and synthesized by selecting different multifunctional ligands. Polycarboxylate anions are suitable bridging ligands for constructing network coordination polymers. Recently, some one-, two- and three-dimensional lanthanide complexes with only polycarboxylate [5–14], and with polycarboxylate and other ligands [15–20] were studied. Lanthanide complexes containing mixed ligands have stable crystal packing and intense fluorescence. 1,10-phenanthroline (phen) is a good ligand for lanthanides, and polycarboxylate complexes with phen were easily synthesized [15–19]. However, relatively few lanthanide complexes containing both polycarboxylate and 2,2′-bipyridine (2,2′-bpy) have been synthesized [20]. This manuscript reports complexes $[Ln_2(C_4H_2O_4)_3(2,2'\text{-bpy})_2(H_2O)_2]_n$ (Ln = Sm, (1); Dy, (2); $C_4H_2O_4^{2-}$ = fumarate; 2,2′-bpy = 2,2′-bipyridine) from the hydrothermal method using $LnCl_3 \cdot 6H_2O$, fumaric acid and 2,2′-bpy. Although lanthanide coordination polymers with fumaric acid, such as $\{[Eu_2(C_4H_2O_4)_3 \cdot 4H_2O] \cdot 3H_2O\}_n$ [13], $[Nd_2(C_4H_2O_4)_3 \cdot 12H_2O]_n$ [14], $[Ln_2(C_4H_2O_4)_3(phen)_2(H_2O)_2]_n$ (Ln = La, Pr) and

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$[Er_2(C_4H_2O_4)_3(phen)_2]_n$ [15] have been reported, the title complexes with fumarate and 2,2′-bpy have an open channel structure. The present article reports the crystal structures and luminescence properties of the complexes.

2. Experimental

2.1. *Materials and methods*

$LnCl_3 \cdot 6H_2O$ (Ln = Sm, Dy) was prepared by dissolving the oxides in hydrochloric acid, and then drying the solution. Elemental analysis was performed on an Elementar Vario EL analyzer. Fluorescence spectra were measured on a F-4500 spectrophotometer in the solid state at room temperature.

2.2. *Synthesis of complexes*

$[Sm_2(C_4H_2O_4)_3(2,2'\text{-bpy})_2(H_2O)_2]_n$ (**1**). 0.45 mmol, fumaric acid, 0.3 mmol 2,2′-bipyridine and 0.3 mmol $SmCl_3 \cdot 6H_2O$ were dissolved in 12 mL deionized water and the pH controlled in a range 5–6 with 2 mol dm^{-3} NaOH solution. The mixture was placed in a Teflon-lined stainless-steel vessel (25 mL) and heated at 160°C for 24 h under autogenous pressure, and then slowly cooled to room temperature. The products were filtered and washed with deionized water and ethanol, then dried in air. Yellow crystals were obtained. Yield, 0.089 g, 60%. Calcd (%) for $C_{32}H_{26}N_4O_{14}Sm_2$: C, 38.77; H, 2.64, N, 5.65. Found (%): C, 38.68; H, 2.58; N, 5.63.

$[Dy_2(C_4H_2O_4)_3(2,2'\text{-bpy})_2(H_2O)_2]_n$ (**2**). The synthesis of complex **2** is similar to complex **1**. Yield, 0.090 g, 55%. Calcd (%) for $C_{32}H_{26}Dy_2N_4O_{14}$: C, 37.85; H, 2.58; N, 5.51. Found (%): C, 37.55; H, 2.37; N, 5.44.

2.3. *X-ray diffraction determination*

X-ray diffraction data for the single crystal were collected by using a Bruker Smart 1000 CCD diffractometer with monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Semi-empirical absorption corrections were applied using the SADABS program. All calculations were carried out on a computer using SHELXS-97 and SHELXL-97 programs [21, 22]. The structures were solved by direct methods and refined on F^2 using full-matrix least-squares methods. A summary of the crystallographic data and details of the structure refinements are listed in table 1.

3. Results and discussion

3.1. *Structural description of* $[Sm_2(C_4H_2O_4)_3(2,2'\text{-bpy})_2(H_2O)_2]_n$ *(1)*

Selected bond lengths and bond angles of **1** are listed in table 2. Figure 1(a) shows the asymmetric unit structure of **1**. Sm^{3+} is coordinated by five oxygens of fumarate groups, one oxygen of water and two nitrogens from 2,2′-bpy, giving coordination

Table 1. Crystal data and structure refinement for **1** and **2**.

Complex	**1**	**2**
Formula	$C_{32}H_{26}N_4O_{14}Sm_2$	$C_{32}H_{26}N_4O_{14}Dy_2$
Formula weight	991.27	1015.57
Temperature (K)	294(2)	294(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/c$	$P2(1)/c$
Unit cell dimension (Å, °)		
a	8.9520(9)	8.9448(11)
b	21.583(2)	21.577(3)
c	9.3428(9)	9.3399(12)
α	90	90
β	107.788(2)	107.789(2)
γ	90	90
Volume (Å^3)	1718.8(3)	1716.4(4)
Z	2	2
D_{Calcd} (Mg m^{-3})	1.915	1.965
μ (mm^{-1})	3.458	4.395
$F(000)$	964	980
Crystal size (mm^3)	$0.22 \times 0.08 \times 0.06$	$0.32 \times 0.08 \times 0.06$
Theta range for data collection (°)	1.89–26.35	1.89–25.01
Index ranges	$-10 \le h \le 11$, $-26 \le k \le 25$, $-11 \le l \le 6$	$-10 \le h \le 10$, $-13 \le k \le 25$, $-11 \le l \le 11$
Reflections collected	9636	8570
Independent reflections	3503 [R(int) = 0.0331]	3021 [R(int) = 0.0460]
Data/restraints/parameters	3503/3/243	3021/0/235
Goodness-of-fit on F^2	1.164	1.075
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0290$, $wR_2 = 0.0641$	$R_1 = 0.0343$, $wR_2 = 0.0929$
Largest diff. peak and hole (e Å^{-3})	0.854 and −0.736	1.006 and −1.621

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Sm(1)–O(1)	2.307(3)	Sm(1)–O(4)#1	2.310(3)
Sm(1)–O(6)#2	2.316(3)	Sm(1)–O(3)#3	2.320(3)
Sm(1)–O(5)	2.331(3)	Sm(1)–O(7)	2.411(3)
Sm(1)–N(1)	2.594(4)	Sm(1)–N(2)	2.603(4)
O(1)–Sm(1)–O(4)#1	80.87(11)	O(1)–Sm(1)–O(6)#2	142.35(11)
O(4)#1–Sm(1)–O(6)#2	77.86(11)	O(1)–Sm(1)–O(3)#3	141.19(11)
O(4)#1–Sm(1)–O(3)#3	123.37(11)	O(6)#2–Sm(1)–O(3)#3	76.14(11)
O(1)–Sm(1)–O(5)	80.09(12)	O(4)#1–Sm(1)–O(5)	76.21(11)
O(6)#2–Sm(1)–O(5)	123.46(11)	O(3)#3–Sm(1)–O(5)	77.86(11)
O(1)–Sm(1)–O(7)	70.95(10)	O(4)#1–Sm(1)–O(7)	145.97(11)
O(6)#2–Sm(1)–O(7)	136.11(11)	O(3)#3–Sm(1)–O(7)	74.15(10)
O(5)–Sm(1)–O(7)	80.42(11)	N(1)–Sm(1)–N(2)	62.19(13)

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

number of eight. The coordination environment of Sm^{3+} is a distorted square antiprism, atoms O3A, O4B, O5, O6A, and O1, O7, N1, N2 form lower and upper square planes with mean deviations of 0.0013 Å and 0.0011 Å, respectively, with a dihedral angle between them of 1.9°. The Sm1–O (carboxyl) distances range from 2.307(3) to 2.331(3) Å, with average distance of 2.317 Å; the Sm1–O(water) distance is 2.411(3) Å. The Sm1–N bond lengths are 2.594(4) and 2.603(4) Å with an average of 2.599 Å. The four C atoms of fumarate are roughly coplanar. The maximal mean

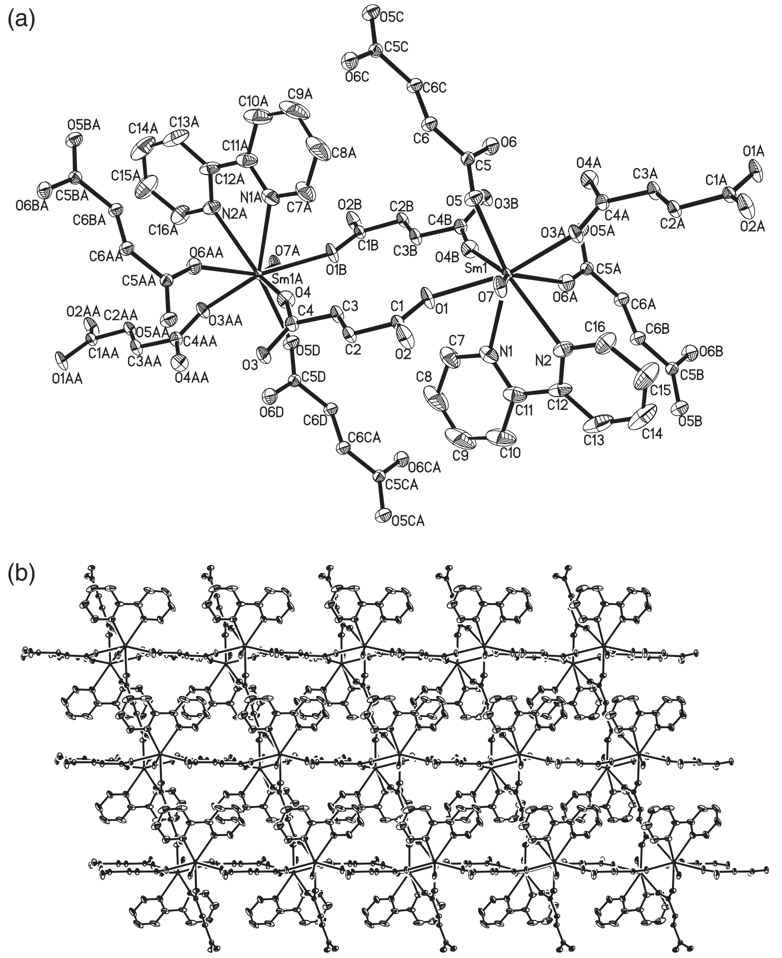


Figure 1. (a) Asymmetric unit structure of **1** with 30% probability displacement ellipsoids (all hydrogen atoms are omitted for clarity). (b) 2-D network of **1** with open channel structure viewed along the *b*-axis. (c) Space-filling model of **1** viewed along the *b*-axis (the 2,2′-bpy molecules have been omitted for clarity). (d) Packing diagram of **1** viewed along the *c*-axis.

deviation from the plane range is 0.0846 Å. The 2,2′-bpy ligand chelates Sm^{3+} with two N atoms forming a five-membered ring. The two pyridyl rings are not coplanar with a dihedral angle of 19.4°. In the crystal, the fumarate groups are tridentate and tetradentate to metal atoms. One fumarate is a tridentate (monodentate and bidentate) bridging ligand, with three oxygen atoms connecting three neighboring metal atoms (scheme 1a); Sm^{3+} ions are linked into a 1-D chain structure along the *c*-axis. Another fumarate group is a tetradentate bridging ligand with all four oxygen atoms connecting four neighboring metal atoms (scheme 1b); Sm^{3+} ions are linked into another 1-D chain structure along *a*-axis. The two types of chains are connected to a 2-D network structure like a quadrilateral channel sheet paralleling the ac plane as shown in figure 1(b). In the 2-D network structure, the dimeric unit $Sm_2(C_4H_2O_4)_3(2,2'\text{-bpy})_2(H_2O)_2$ is the building block with a $Sm \cdots Sm$ distance of 4.374(4) Å. Four dimeric units are located on the vertex of a quadrilateral, and the

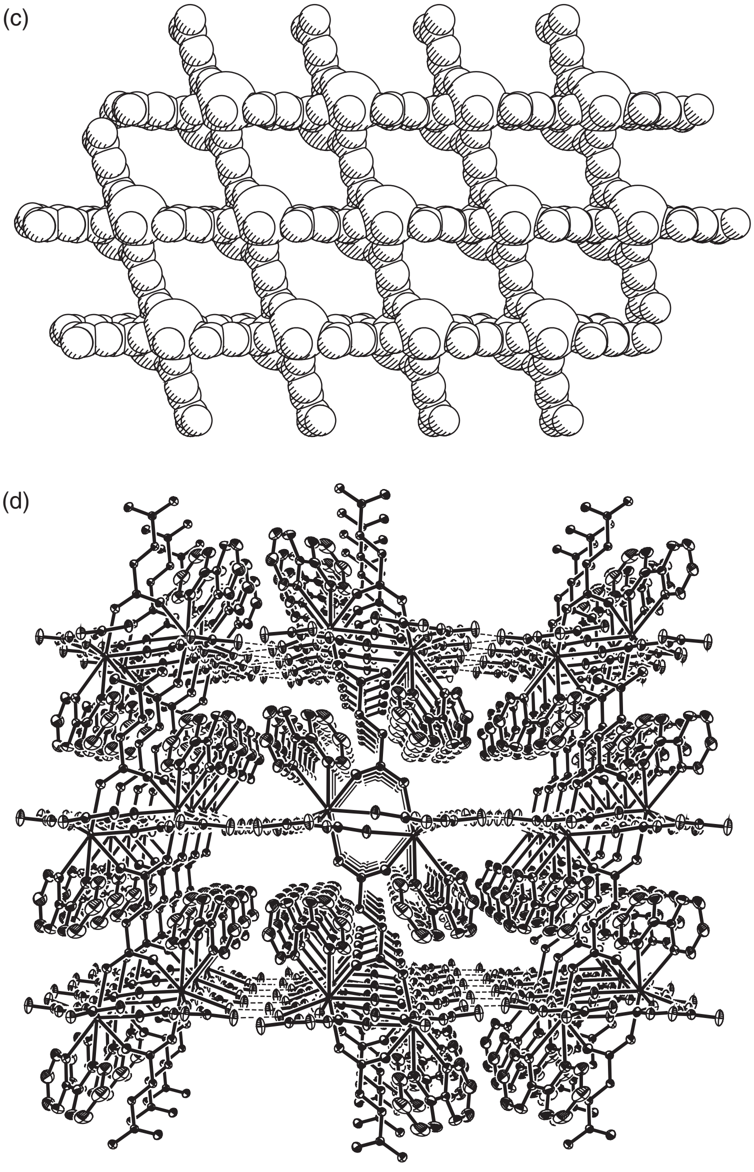
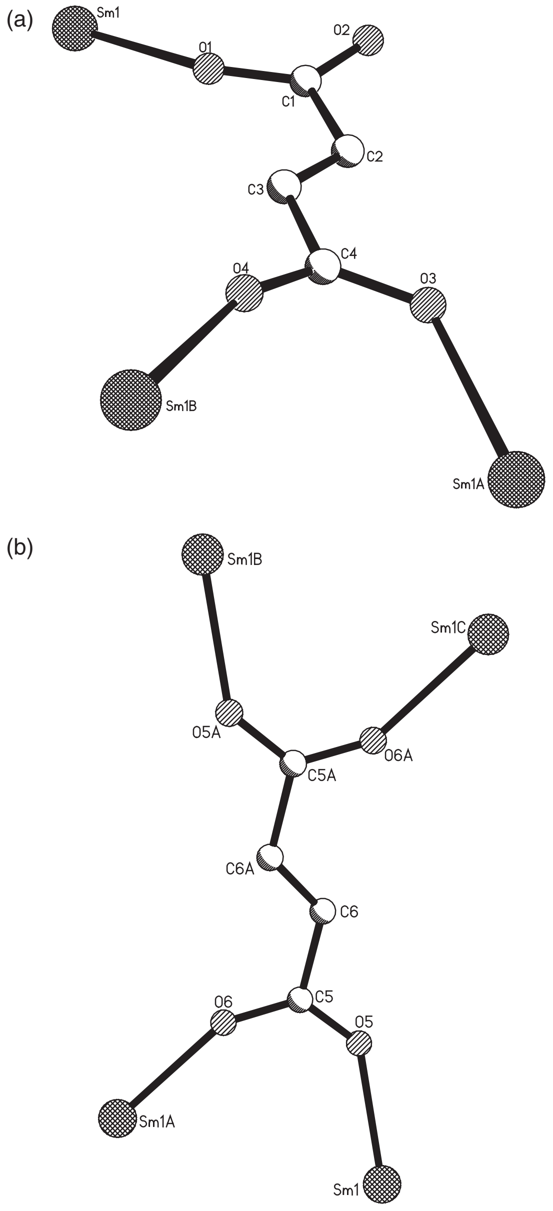


Figure 1. Continued.

eight Sm^{3+} ions are almost coplanar with a mean deviation from the plane of 1.7010 Å. The 2,2′-bpy ligands chelate Sm^{3+} in the quadrilateral channel. The channel has a diameter of $9.343 \times 8.952(4)$ Å based on the Sm ⋯ Sm distance (figure 1c).

Viewed along the *c*-axis π–π stacking interactions of pyridyl rings are observed in the 2-D structure, with an intermolecular distance between them of ca 3.83 Å, indicating that the crystal structure is stabilized by stacking interaction (figure 1d). In addition, the coordinated water molecules form hydrogen bonds with uncoordinated oxygen atoms of carboxylate groups, O(7)–H(7A) ⋯ O(2), 2.806(3) Å, 158.83°, and O(7)–H(7B) ⋯ O(2) $[X, -Y+3/2, Z-2/1]$, 2.743(3) Å, 172.46°. These hydrogen



Scheme 1. Coordination modes of fumarate in **1**.

bonds connect 2-D networks into a 3-D network, increasing the stability of the complex (figure 1d).

3.2. *Structural description of* $[Dy_2(C_4H_2O_4)_3(2,2'\text{-bpy})_2(H_2O)_2]_n$ *(2)*

The crystal structure of **2** is similar to that of **1**. The asymmetric unit of **2** is shown in figure 2 and selected bond lengths and angles are listed in table 3. The Dy^{3+} is

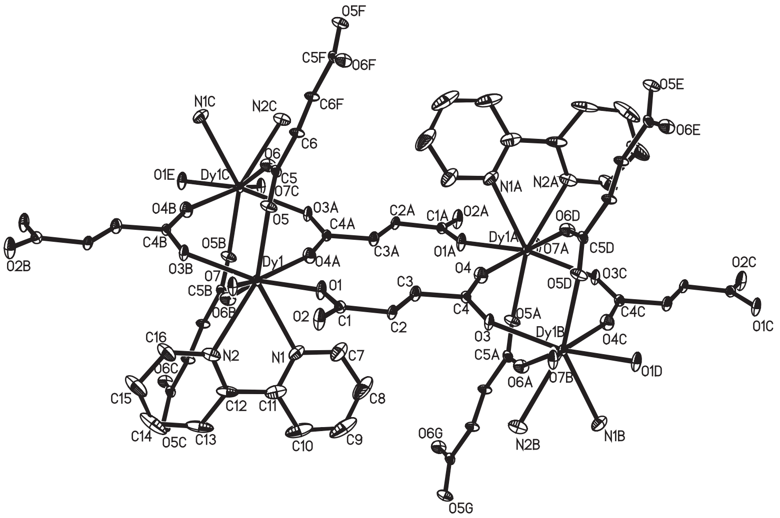


Figure 2. Asymmetric unit structure of **2** with 30% probability displacement ellipsoids (all hydrogen atoms have been omitted for clarity).

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Dy(1)–O(1)	2.306(4)	Dy(1)–O(4)#1	2.312(4)
Dy(1)–O(6)#2	2.319(4)	Dy(1)–O(3)#3	2.324(4)
Dy(1)–O(5)	2.327(4)	Dy(1)–O(7)	2.410(4)
Dy(1)–N(1)	2.595(6)	Dy(1)–N(2)	2.610(5)
O(1)–Dy(1)–O(4)#1	80.86(15)	O(1)–Dy(1)–O(6)#2	142.39(15)
O(4)#1–Dy(1)–O(6)#2	77.91(15)	O(1)–Dy(1)–O(3)#3	141.23(16)
O(4)#1–Dy(1)–O(3)#3	123.60(15)	O(6)#2–Dy(1)–O(3)#3	76.02(15)
O(1)–Dy(1)–O(5)	80.32(16)	O(4)#1–Dy(1)–O(5)	76.26(15)
O(6)#2–Dy(1)–O(5)	123.28(15)	O(3)#3–Dy(1)–O(5)	77.92(15)
O(1)–Dy(1)–O(7)	71.13(14)	O(4)#1–Dy(1)–O(7)	146.12(14)
O(6)#2–Dy(1)–O(7)	135.91(14)	O(3)#3–Dy(1)–O(7)	73.89(14)
O(5)–Dy(1)–O(7)	80.49(15)	N(1)–Dy(1)–N(2)	62.36(18)

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

eight coordinate with five O atoms of fumarate groups, one O atom of water and two N atoms from 2,2′-bpy, arranged in a distorted square antiprism with O3B, O4A, O5, O6B, and O1, O7, N1, N2 located at lower and upper square planes with mean deviations of 0.0040 Å and 0.0041 Å, respectively and a dihedral angle of 2.0° between them. The Dy1–O(carboxyl) distances range from 2.306(4) to 2.327(4) Å, with an average distance of 2.318 Å. The Dy1–O(water) distance is 2.410(4) Å. The Dy1–N bond lengths are 2.595(6) and 2.610(5) Å with an average distance of 2.602 Å. The shortest Dy···Dy distance is 4.373(6) Å. These distances in **2** are similar to corresponding distances in **1**. Hydrogen bonds were formed between coordinated water molecules and uncoordinated oxygen atoms of carboxylate groups, O(7)–H(7A)···O(2), 2.816(3) Å, 160.81°, and O(7)–H(7B)···O(2) [X, $-Y+3/2$, $Z-2/1$], 2.732(3) Å, 176.80°. Similarly, the 2-D network of **2** was constructed by dimeric units of $Dy_2(C_4H_2O_4)_3(2,2'\text{-bpy})_2(H_2O)_2$ through tridentate and tetradentate fumarate groups.

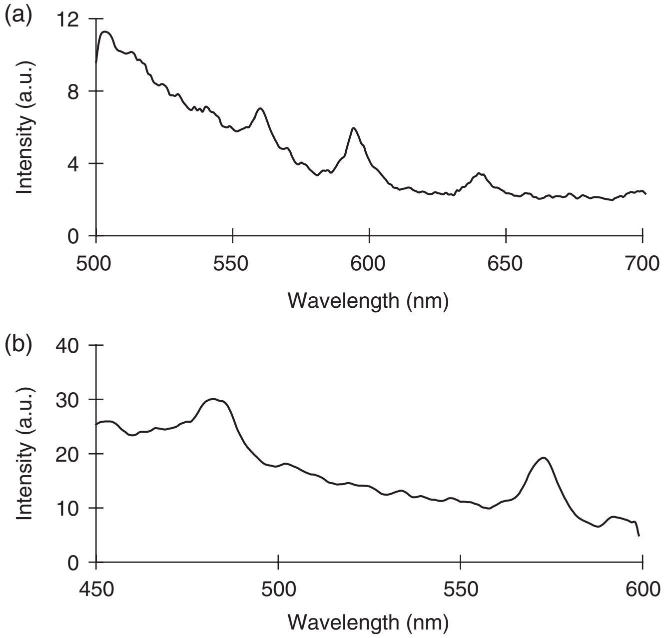


Figure 3. The emission spectra of (a) complex **1** ($\lambda = 403$ nm); (b) complex **2** ($\lambda = 309$ nm).

The 3-D supramolecular structure is formed through hydrogen bonds and π–π stacking of 2,2′-bpy molecules.

3.3. *Luminescent properties*

Emission spectra of the solid complexes were recorded at room temperature. The emission spectrum of **1** under 403 nm excitation is shown in figure 3(a). Three emission bands are at 561, 595 and 642 nm, are attributed to $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$ and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transitions of Sm^{3+} ion, respectively. The magnetic dipole transition ($^4G_{5/2} \rightarrow {}^6H_{7/2}$) is much stronger. Figure 3(b) reveals the emission spectrum of **2** under 309 nm excitation. There are two emission bands at 482 and 571 nm, corresponding to the characteristic emission transitions of Dy^{3+}, $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{5/2} \rightarrow {}^6H_{13/2}$, respectively. Samarium and dysprosium complexes usually have broad and weak emission spectra, compared to emission spectra of europium and terbium complexes [23, 24]. This may be due to the coherent characteristics and rich 4f energy levels of samarium and dysprosium.

Supplementary material

CCDC-294303 for complexes **1** and 294304 for **2** contain the supplementary crystallographic data for this article. These data can be obtained free of charge from

CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. (Fax: +44(0)1223-336033; Email: deposit@ccdc.cam.ac.uk).

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