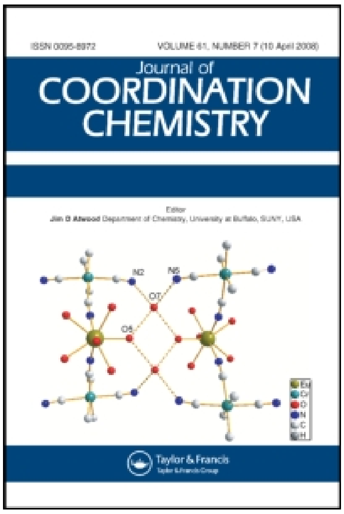

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Two lanthanide coordination polymers with one-dimensional chain structure constructed from 2,2'-diphenyldicarboxylate

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Two lanthanide coordination polymers with one-dimensional chain structure constructed from 2,2′-diphenyldicarboxylate

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Two lanthanide coordination polymers, $[Ln_2(dpdc)_3(H_2O)_2]_n$ (Ln = Sm **1**, Dy **2**; dpdc = 2,2′-diphenyldicarboxylate) were prepared by hydrothermal reaction and characterized by elemental analyses, IR spectroscopy, thermogravimetry, fluorescence spectrometry, and single-crystal X-ray diffraction. X-ray studies indicate that the two complexes are isostructural, with two different lanthanide ion nodes linked by dpdc ligands into an infinite one-dimensional chain structure, in which dpdc ligands are bidentate-bridging/bidentate-bridging and bidentate-bridging/chelate-bridging. Complexes **1** and **2** exhibit luminescent characteristics of Sm(III) and Dy(III) ions, respectively.

Keywords: Lanthanide; Coordination polymer; 2,2′-Diphenyldicarboxylate; Crystal structure

1. Introduction

The design and synthesis of luminescent lanthanide complexes has potential applications in biochemistry and materials science [1–8]. Lanthanide ions, especially Eu(III), Tb(III), Sm(III), and Dy(III), are good luminescent centers and their luminescent properties depend on organic ligands. Carboxylic acid ligands have been used for preparation of such complexes, and lanthanide carboxylates also have potential applications in magnetism, extraction, separation and catalysis [9–19]. Polycarboxylic acid ligands with metal ions construct fascinating structures from versatile coordination modes of carboxylate. The carboxylate groups can bridge metal ions through M–O–M and M–O–C–O–M bridges to generate one-dimensional chain, two-dimensional layer, and three-dimensional framework structures. Lanthanide complexes with aromatic acids show high thermal stability and intense fluorescence because of a large conjugated π-electron system. Benzene-polycarboxylate ligands are widely employed in construction of lanthanide coordination polymers [12–19]. Several transition and lanthanide complexes with 2,2′-diphenyldicarboxylic acid (H_2dpdc) have

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been reported [19–21]. Herein, the H_2dpdc with samarium and dysprosium gave two new lanthanide coordination polymers, $[Ln_2(dpdc)_3(H_2O)_2]_n$ (Ln = Sm **1**, Dy **2**). The crystal structures and properties of the two complexes are reported.

2. Experimental

2.1. *Materials and methods*

$Sm(NO_3)_3 \cdot 6H_2O$ and $Dy(NO_3)_3 \cdot 6H_2O$ were prepared from the corresponding oxide with nitric acid. Other analytical grade chemicals and solvents were purchased and used without further purification.

Elemental analyses (C, H, N) were determined on an Elementar Vario EL elemental analyzer. IR spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer using KBr pellets from 400–4000 cm^{-1}. Thermogravimetric analyses were performed on a WCT-1A thermal analyzer with a heating rate of 10°C min^{-1} from 20 to 1000°C. Excitation and emission spectra of solid samples were recorded on an F-4500 fluorescence spectrophotometer at room temperature.

2.2. *Synthesis of complexes, $[Ln_2(dpdc)_3(H_2O)_2]_n$ (Ln = Sm 1, Dy 2)*

Mixture of $Ln(NO_3)_3 \cdot 6H_2O$ (0.1333 g, 0.3 mmol), 2,2′-diphenyldicarboxylic acid (0.1090 g, 0.45 mmol), 2,2′-bipyridine (0.0312 g, 0.2 mmol), potassium oxalate (0.0360 g, 0.2 mmol), H_2O (10 mL), and aqueous solution of NaOH (0.5 mL, 0.3 mmol) was heated in a 25 mL stainless-steel reactor with Teflon liner at 170°C for 3 days and then slowly cooled to room temperature. The colorless crystals were collected by filtration and washed with ethanol. Yield: 58% for **1** and 54% for **2**. For **1**, $C_{42}H_{28}O_{14}Sm_2$ (1057.34), Calcd (%): C, 47.71; H, 2.67. Found (%): C, 47.49; H, 2.56. Selected IR (KBr pellet, ν/cm^{-1}): 3424 br, 1621 vs, 1554 vs, 1525 vs, 1442 s, 1406 s, 1086 m, 860 m, 765 s, 717 m, 657 m, 534 w, 426 w. For **2**, $C_{42}H_{28}O_{14}Dy_2$ (1081.64), Calcd (%): C, 46.64; H, 2.61. Found (%): C, 46.45; H, 2.43. Selected IR (KBr pellet, ν/cm^{-1}): 3434 br, 1625 vs, 1562 vs, 1529 vs, 1446 s, 1405 s, 1087 m, 865 m, 763 s, 717 m, 663 m, 534 w, 430 w.

2.3. *Crystal structure determination*

X-ray single crystal data collections for **1** and **2** were performed on a Bruker Smart 1000 CCD diffractometer using graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å). Semiempirical absorption corrections were applied using SADABS. The structures were solved by direct methods and refined by full matrix least squares on F^2 using SHELXS-97 and SHELXL-97, respectively [22, 23]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement. Summary of the crystallographic data and details of the structure refinements are listed in table 1. Selected bond lengths of **1** and **2** are listed in tables 2 and 3, respectively.

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

Complex	**1**	**2**
Empirical formula	$C_{42}H_{28}O_{14}Sm_2$	$C_{42}H_{28}O_{14}Dy_2$
Formula weight	1057.34	1081.64
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
Unitcells and dimensions (Å, °)		
a	20.960(2)	20.9169(6)
b	21.450(2)	21.3300(6)
c	8.2778(8)	8.1871(2)
α	90	90
β	103.818(5)	104.0920(10)
γ	90	90
Volume (Å^3)	3613.9(6)	3542.81(17)
Z	4	4
Calculated density (Mg m^{-3})	1.943	2.028
Absorption coefficient (mm^{-1})	3.293	4.263
$F(000)$	2064	2096
Crystal size (mm^3)	$0.28 \times 0.24 \times 0.22$	$0.26 \times 0.22 \times 0.20$
θ range for data collection	1.38 to 28.50	3.04 to 28.30
Limiting indices	$-28 \le h \le 26$	$-27 \le h \le 27$
	$-28 \le k \le 28$	$-28 \le k \le 28$
	$-11 \le l \le 11$	$-10 \le l \le 10$
Reflections collected/unique	14679/4433	15190/4360
	[R(int) = 0.0238]	[R(int) = 0.0187]
Data/restraints/parameters	4433/2/271	4360/0/271
Goodness-of-fit on F^2	1.045	1.033
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0225$, $wR_2 = 0.0540$	$R_1 = 0.0167$, $wR_2 = 0.0413$
R indices (all data)	$R_1 = 0.0293$, $wR_2 = 0.0572$	$R_1 = 0.0209$, $wR_2 = 0.0435$
Largest diff. peak and hole (e Å^{-3})	0.534 and −0.709	0.496 and −0.629

Table 2. Bond lengths (Å) for **1**.

Sm(1)–O(6)#3	2.3305(17)	Sm(1)–O(6)#2	2.3305(17)
Sm(1)–O(4)#3	2.3359(18)	Sm(1)–O(4)#2	2.3359(18)
Sm(1)–O(1)#4	2.436(2)	Sm(1)–O(1)	2.436(2)
Sm(1)–O(2)	2.6197(18)	Sm(1)–O(2)#4	2.6197(18)
Sm(5)–O(2)	2.4828(18)	Sm(2)–O(3)#2	2.3105(18)
Sm(2)–O(3)	2.3105(18)	Sm(2)–O(2)	2.4716(16)
Sm(2)–O(2)#2	2.4716(16)	Sm(2)–O(5)#2	2.4828(18)
Sm(2)–O(7)	2.520(2)	Sm(2)–O(7)#2	2.520(2)

Symmetry transformations used to generate equivalent atoms: #2: $-x, y, -z+1/2$; #3: $x, y, z-1$; #4: $-x, y, -z-1/2$.

Table 3. Bond lengths (Å) for **2**.

Dy(1)–O(3)	2.2597(14)	Dy(1)–O(3)#1	2.2597(14)
Dy(1)–O(1)	2.4258(14)	Dy(1)–O(1)#1	2.4259(14)
Dy(1)–O(5)#1	2.4313(14)	Dy(1)–O(5)	2.4314(14)
Dy(1)–O(7)#1	2.4553(19)	Dy(1)–O(7)	2.4553(19)
Dy(2)–O(6)#1	2.2757(14)	Dy(2)–O(6)#2	2.2757(14)
Dy(2)–O(4)#1	2.2818(15)	Dy(2)–O(4)#2	2.2818(15)
Dy(2)–O(2)#3	2.3771(15)	Dy(2)–O(2)	2.3771(15)
Dy(2)–O(1)#3	2.5771(14)	Dy(2)–O(1)	2.5771(14)

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

3. Results and discussion

3.1. *Structural description of complexes*

Complexes **1** and **2** are isostructural; only **1** will be discussed in detail as representative. The structure of **1** consists of a 1-D chain, as shown in figure 1(a). All H_2dpdc molecules are completely deprotonated and all oxygen atoms from the carboxylate groups of dpdc anions take part in coordination with Sm(III). The dpdc anions adopt two coordination modes: (i) two carboxylate groups of dpdc ligand coordinate three Sm(III) ions through bidentate bridging coordination as a tetradentate ligand [scheme 1(a)]; (ii) two carboxylate groups of dpdc coordinate three Sm(III) ions through bidentate bridging and chelate-bridging coordination as a pentadentate ligand [scheme 1(b)]. The asymmetric unit of **1** consists of two Sm(III) ions, three dpdc ligands and two water molecules; as shown in figure 1(b), there are two environments for Sm(III) ions.

Sm1 is coordinated to eight oxygens, O6A, O6B from a tetradentate dpdc ligand, O1, O2 and O1AA, O2AA from two different pentadentate dpdc ligands and O4A, O4B from two other pentadentate dpdc ligands. The Sm1 is located in the center of a distorted square-antiprism formed by these eight O atoms. Atoms O2, O6A, O6B, O2AA and O1, O4A, O1AA, O4B form the upper and lower squares with mean deviations of 0.1706 and 0.4645 Å, respectively; the dihedral angle between the two planes is 0.0°. The Sm1–O bond lengths range from 2.3305(17) to 2.6197(18) Å, with mean distance of 2.4305 Å, while O–Sm1–O bond angles are in the range 51.32(6) – 150.65(7)°. The Sm2 is eight-coordinate also, surrounded by O3, O2 from a pentadentae dpdc, O2A, O3A from another pentadentae dpdc, O5, O5A from two tetradentate dpdc and O7, O7A from two waters. The coordination environment of Sm2 can be described as a distorted square-antiprism also, the upper and lower planes structured by atoms O5, O5A, O7, O7A and O2, O2A, O3, O3A with mean deviation from the upper and lower planes of 0.0585 and 0.4036 Å, respectively; the dihedral angle between the two planes is 0.0°. The Sm2–O(carboxylate) bond lengths range from 2.3105(18) to 2.4828(18) Å, with mean distance of 2.4216 Å, while O–Sm2–O bond angles are in the range 72.04(6)–146.15(6)°. Two Sm2–O(water) bond lengths are 2.520(2) Å. Sm1 and Sm2 ions are interconnected by three $-COO^-$ groups from three dpdc anions, through Sm–O–Sm and Sm–O–C–O–Sm bridges to generate an infinite 1-D chain. The repeating unit can be described as a binuclear unit containing Sm1 and Sm2 ions, $[Sm_2(dpdc)_3(H_2O)_2]$, with the distance between adjacent Sm(III) ions of 4.485(2) Å. All Sm(III) ions are coplanar. When viewed along the *c* axis, the phenyl rings of the 1-D chain are parallel to each other and adjacent 1-D chains are interdigitated to form channels with cavities [figure 1(c)].

The structure of **2** also shows a 1-D chain and the asymmetric unit of **2** is shown in figure 2. The coordination environments of Dy1 and Dy2 of **2** are similar to that of Sm2 and Sm1 of **1**, respectively, with Dy1–O(carboxylate) bond lengths from 2.2597(14) to 2.4314(14) Å, with mean distance of 2.3723 Å and O–Dy1–O bond angles are in the range 72.61(5)–146.29(6)°. Two Dy1–O(water) bond lengths are 2.4553(19) Å. The Dy2–O bond lengths range from 2.2757(14) to 2.5771(14) Å, with mean distance of 2.378 Å, while O–Dy2–O bond angles are in the range 51.37(5)–150.20(6)°. The distance of two adjacent Dy(III) ions is 4.428(2) Å.

A comparison of crystal data between **1** and **2** shows that the mean distances of Sm–O(carboxylate) and Sm–O(water) are longer than Dy–O(carboxylate) and

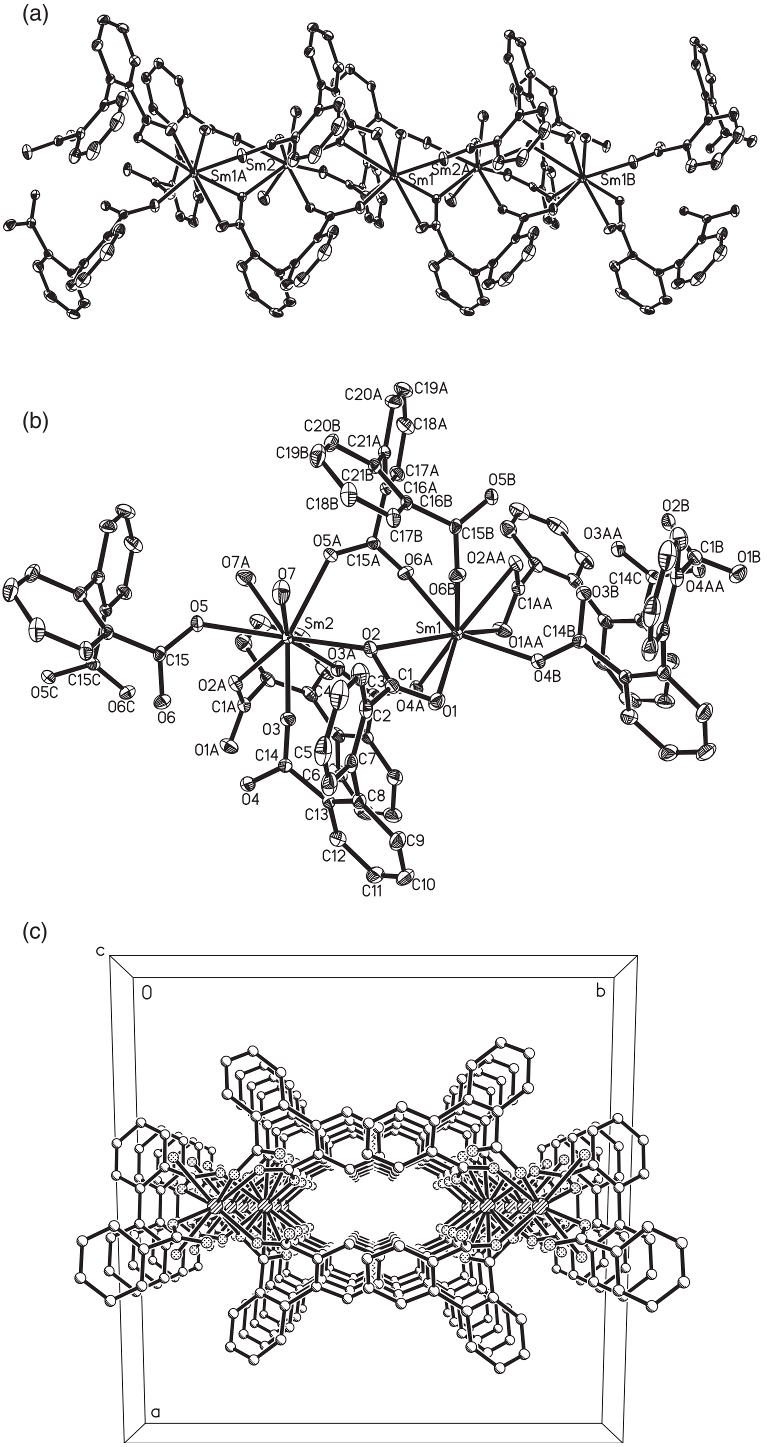
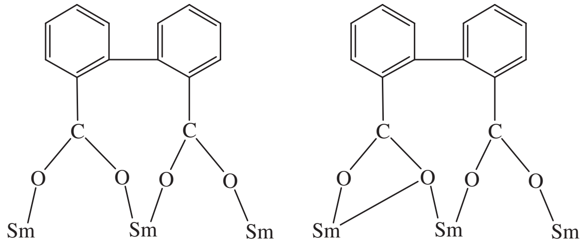


Figure 1. (a) 1-D chain of **1** viewed along the *a* axis. (b) Asymmetric unit of **1** at the 15% probability displacement ellipsoids. (c) Packing diagram of **1** showing channels with cavities. All hydrogen atoms are omitted for clarity.



(a) (b)

Scheme 1. Coordination modes of dpdc ligands in **1**.

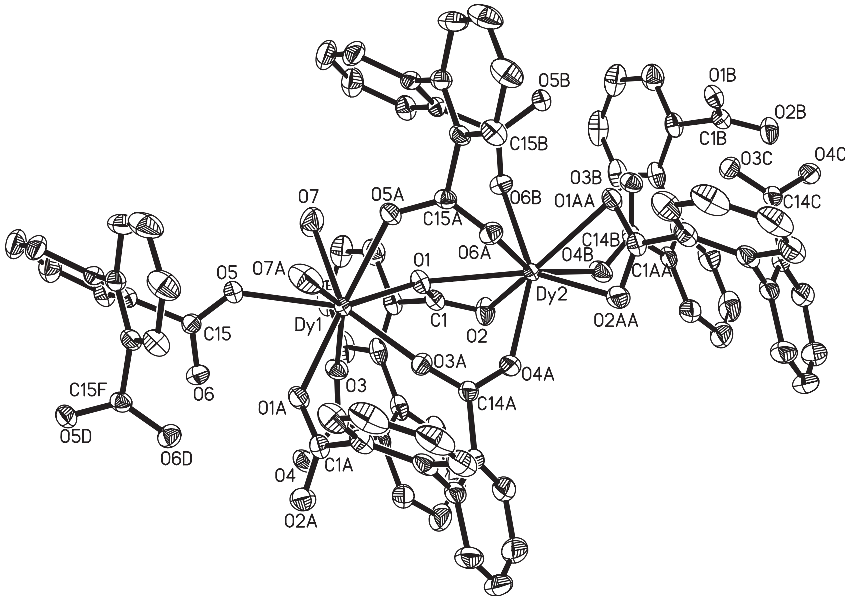


Figure 2. Asymmetric unit of **2** at the 30% probability displacement ellipsoids. All hydrogen atoms are omitted for clarity.

Dy–O(water), respectively. The Sm ··· Sm distance is also longer than that of Dy ··· Dy. These differences are caused by decrease of ion radius from Sm(III) to Dy(III), in accord with the lanthanide contraction.

3.2. *Thermogravimetric analyses*

The DTA-TG analyses studied in air with a heating rate of $10^{\circ}\mathrm{C\,min^{-1}}$ from 20 to 1000°C show similar behavior of complexes **1** and **2**. At 184°C for **1** and at 194°C for **2**, the complexes begin to decompose, with first weight losses of 3.5% for **1** and 3.6% for **2**, corresponding to loss of coordinated water (calculated 3.4% for **1** and 3.3% for **2**). At 496°C for **1** and 504°C for **2**, the complexes are completely degraded into Sm_2O_3 and Dy_2O_3. The total weight losses of 66% for **1** and 60% for **2** are close to the calculated value 67% for **1** and 66% for **2**, respectively.

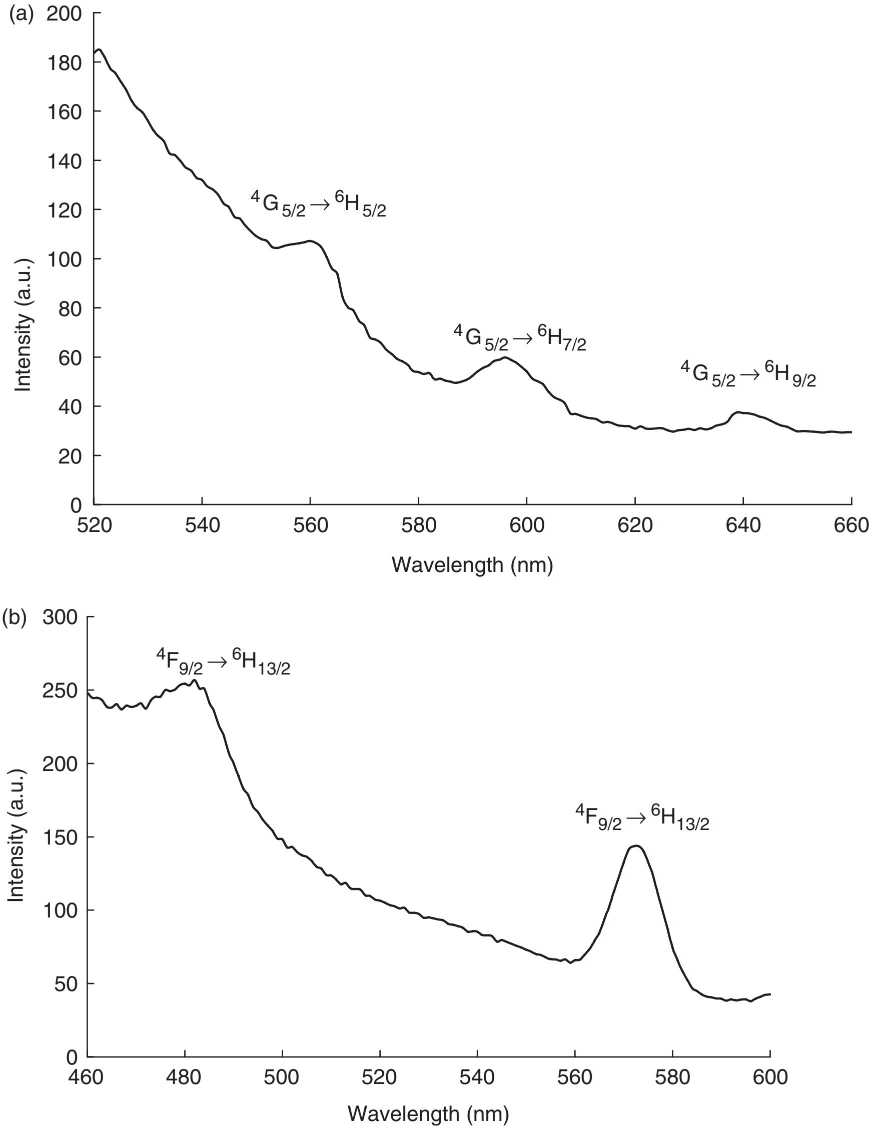


Figure 3. Fluorescence spectra of **1** (a) ($\lambda_{ex} = 346$ nm) and **2** (b) ($\lambda_{ex} = 309$ nm).

3.3. *Fluorescence properties*

The solid-state luminescent spectra of **1** and **2** were investigated at room temperature. Emission spectra of **1** and **2** were recorded under excitation at 346 and 309 nm, respectively, as shown in figure 3. In the emission spectrum of **1**, the peaks at 559, 592 and 642 nm are assigned 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(III) ion, respectively. In the emission spectrum of **2**, there are emission bands at 482 and 573 nm, which correspond to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions of Dy(III) ion, respectively. The characteristic emissions of Sm(III) and Dy(III) ions indicate that energy absorbed by dpdc transfers to Sm(III) and Dy(III) ions, resulting in the emission. The energy transfer and energy emission processes in the different complexes are dissimilar.

Supplementary material

CCDC-662920 for **1** and 662921 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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References

[1] B.D. Chandler, D.T. Cramb, G.K.H. Shimizu. *J. Am. Chem. Soc.*, **128**, 10403 (2006).
[2] D.T. de Lill, A. de Bettencourt-Dias, C.L. Cahill. *Inorg. Chem.*, **46**, 3960 (2007).
[3] D.A. Voss Jr, E.R. Farquhar, W. De, W. Horrocks Jr, J.R. Morrow. *Inorg. Chim. Acta*, **357**, 859 (2004).
[4] M. Kawa, J.M.J. Fréchet. *Chem. Mater.*, **10**, 286 (1998).
[5] R.A. Campos, I.P. Kovalev, Y. Guo, N. Wakli, T. Skotheim. *J. Appl. Phys.*, **80**, 7144 (1996).
[6] J. Kiao, K. Nagai. *J. Alloys Comp.*, **192**, 30 (1993).
[7] A. Mortellaro, D.G. Nocera. *J. Am. Chem. Soc.*, **118**, 7414 (1996).
[8] P.H. Smith, J.R. Brainard, D.E. Morris, G.D. Jarvinen, R.R. Ryan. *J. Am. Chem. Soc.*, **111**, 6437 (1989).
[9] C. Seward, N.X. Hu, S. Wang. *J. Am. Soc. Dalton Trans.*, 134 (2001).
[10] X. Li, Y.L. Ju, Y.Q. Zou. *J. Coord. Chem.*, **60**, 1513 (2007).
[11] X. Li, T.T. Zhang, Y.L. Ju, C.Y. Wang, Y.Q. Li, L. Zhang, Q. Zhang. *J. Coord. Chem.*, **60**, 2121 (2007).
[12] T.M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley, O.M. Yaghi. *J. Am. Chem. Soc.*, **121**, 1651 (1999).
[13] Z.H. Zhang, T. Okamura, Y. Hasuchika, H. Kawaguchi, L.Y. Kong, W.Y. Sun, N. Ueyama. *Inorg. Chem.*, **44**, 6219 (2005).
[14] C. Daiquebonne, N. Kerbellec, K. Bernot, Y. Gérault, A. Deluzet, O. Guillou. *Inorg. Chem.*, **45**, 5399 (2006).
[15] Y.H. Wan, L.P. Zhang, L.P. Jin, S. Gao, S.Z. Lu. *Inorg. Chem.*, **42**, 4985 (2003).
[16] X.J. Zheng, L.P. Jin, S. Gao, S.Z. Lu. *Inorg. Chem. Commun.*, **8**, 72 (2005).
[17] L. Pan, K.M. Adams, H.E. Hernandez, X. Wang, C. Zheng, Y. Hattori, K. Kaneko. *J. Am. Chem. Soc.*, **125**, 3062 (2003).
[18] S. Si, C. Li, R. Wang, Y. Li. *J. Coord. Chem.*, **59**, 215 (2007).
[19] Y.B. Wang, X.J. Zheng, W.J. Zhuang, L.P. Jin. *Eur. J. Inorg. Chem.*, **19**, 3572 (2003).
[20] H. Kumagai, K. Inoue, M. Kurmoo. *Bull. Chem. Soc. Jpn*, **75**, 1283 (2002).
[21] J.M. Rueff, S. Pillet, N. Claiser, G. Bonaventure, M. Souhassou, P. Rabu. *Eur. J. Inorg. Chem.*, **4**, 895 (2002).
[22] G.M. Sheldrick. *Phase Annealing in SHELX-97: Direct Methods for Larger Structures*, Acta Cryst., **A46**, 467 (1990).
[23] G.M. Sheldrick. *SHELXL-97, Program for X-ray Crystal Structure Solution*, University of Göttingen, Germany (1997).