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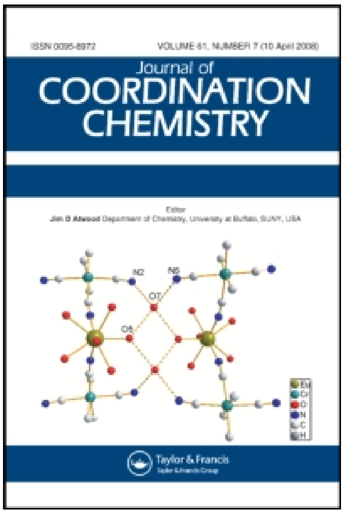

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Two binuclear lanthanide complexes with 4-quinoline carboxylic acid: crystal structures and luminescent properties

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Two binuclear lanthanide complexes with 4-quinoline carboxylic acid: crystal structures and luminescent properties

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Two isomorphic lanthanide complexes $[Eu_2(\mathbf{L})_6(H_2O)_4] \cdot 2H_2O$ (**1**) and $[Tb_2(\mathbf{L})_6(H_2O)_4] \cdot 2H_2O$ (**2**), (H**L** = 4-quinoline carboxylic acid) have been synthesized and structurally characterized by single-crystal X-ray diffraction. Both complexes are binuclear and each metal center adopts nine-coordination with nine oxygens from two H_2O molecules and carboxylates of three ligands; **L** exhibits three different coordination modes. Luminescent properties of **1** and **2** at room temperature indicate that the triplet-state level of this ligand matches better with the lowest excited state level of Eu(III) than with Tb(III).

Keywords: 4-Quinoline carboxylic acid; Lanthanide complex; Crystal structure; Luminescent properties

1. Introduction

Proposed as light conversion molecular devices (LCMDs) [1], organic complexes of lanthanides such as Eu(III) and Tb(III) have found several applications as luminescence probes of biomedical assays [2, 3], luminescence sensors for chemical species [4], electroluminescent devices [5], and UV dosimeters [6]. Although lanthanide ions exhibit broad emission spectral range from infrared to blue light [7, 8], the radial absorption ability of lanthanides is very weak. When lanthanides are coordinated to organic ligands, the ‘‘Antenna effect’’ of ligands improves the absorption of radiation and possesses an excited-state capable of sensitizing the emission of lanthanide ions [9].

By choosing suitable ligands [10, 11], the distance between metal centers could be controlled, and the dimensions of complexes could be predicted. Structures of complexes are closely related to properties [12–14], so design of lanthanide coordination polymers is important. Due to strong coordination and diverse coordination modes, organic carboxylates are often used to synthesize lanthanide complexes [15, 16]. Although transition metal complexes of 4-quinoline carboxylic acid have been investigated [17–19], lanthanide complexes of 4-quinoline carboxylic have been rarely

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reported. Herein we report the synthesis, structures, and luminescent properties of two isostructural binuclear lanthanide complexes with 4-quinoline carboxylic acid (**HL**).

2. Experimental

2.1. *Materials and general methods*

$Ln(NO_3)_3 \cdot 6H_2O$ (Ln = Eu, Tb) was prepared by dissolving oxides in concentrated nitric acid and evaporating to dryness. All other reagents for syntheses and analyses were of analytical grade and used without purification. 4-Quinoline carboxylate acid was purchased from Aldrich Chem. Co. FT-IR spectra (KBr pellet) were obtained on a FT-IR 170 SX (Nicolet) spectrometer. Elemental analyses were taken using a Perkin-Elmer 240C analyzer. Thermal stability was carried out on a NETZSCH TG 209 thermal analyzer from room temperature to 800°C. The luminescence study was carried out on powdered samples in the solid state at room temperature using a VARIAN Cary Eclipse spectrometer.

2.2. *Synthesis of [$Eu_2(L)_6(H_2O)_4$] • $2H_2O$ and [$Tb_2(L)_6(H_2O)_4$] • $2H_2O$*

[$Eu_2(\mathbf{L})_6(H_2O)_4$] $\cdot$ $2H_2O$ (**1**) was synthesized using the following method: $Eu(NO_3)_3$ (0.1 mmol) and **HL** (0.3 mmol) were mixed in $MeOH/H_2O$ (20 mL). The pH of this solution was adjusted with dilute KOH aqueous solution to *ca* 7. Colorless block single crystals of **1** suitable for X-ray analysis were obtained by slow evaporation of the solvent for several days (yield: 55%). Anal. Found: C, 50.03; H, 3.48; N, 6.02. Calcd for $C_{30}H_{24}EuN_3O_9$: C, 49.87; H, 3.35; N, 5.82. FT-IR (KBr pellet, cm^{-1}): 3415s, 3036s, 3005s, 1938w, 1629vs, 1598m, 1549m, 1508m, 1432m, 1412sv, 1378vs, 1295w, 804m, 786m, 765m, and 655sv.

Colorless block single crystals of [$Tb_2(\mathbf{L})_6(H_2O)_4$] $\cdot$ $2H_2O$ (**2**) were obtained by adopting the same procedure (yield: 47%). Anal. Found: C, 49.31; H, 3.43; N, 5.67. Calcd for $C_{30}H_{24}TbN_3O_9$: C, 49.40; H, 3.32; N, 5.76. FT–IR (KBr pellet, cm^{-1}): 3405s, 3036s, 1938w, 1632vs, 1599m, 1550m, 1509m, 1463m, 1413sv, 1378vs, 1296w, 804m, 783m, 765m, and 655sv.

2.3. *Crystal structure determination*

Single crystal X-ray diffraction data were collected on a Bruker Smart 1000 diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The total of 11,399 including 6360 independent reflections ($R_{\text{int}} = 0.0171$) and 15,937 including 5787 independent reflections ($R_{\text{int}} = 0.0291$) were collected in the range of $3.03° < \theta < 27.48°$ and $2.31° < \theta < 26.39°$ for **1** and **2**. Unit cell dimensions were obtained with least-squares refinements and multi-scan absorption corrections were applied using SADABS [20]. The structures were solved by direct methods [21] and non-hydrogen atoms were obtained in successive difference Fourier syntheses. Hydrogens on carbons were included in calculated positions and refined with fixed thermal parameters riding on their parent atoms. Hydrogens of water were located on

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

Structure parameter	**1**	**2**
Empirical formula	$C_{60}H_{48}Eu_2N_6O_{18}$	$C_{60}H_{48}Tb_2N_6O_{18}$
Formula weight ($g\,mol^{-1}$)	1444.96	1458.88
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P21/n$	$P21/n$
Units cell dimensions (Å, °)		
a	11.620(2)	11.680(4)
b	16.357(3)	16.477(5)
c	15.335(3)	15.360(5)
β	105.95(3)	106.251(4)
V ($Å^3$)	2802.4(10)	2838.0(15)
Z	2	2
μ (mm^{-1})	2.300	2.553
$F(000)$	1440	1448
Reflections collected/unique	11399/6360	15937/5787
R	0.0256	0.0227
Rw	0.0673	0.0496

difference Fourier maps and refined isotropically with $U_{iso}(H) = 1.2U_{eq}$. Further details of the X-ray structural analysis are given in table 1.

3. Results and discussion

3.1. *Syntheses and general methods*

Complexes **1** and **2** were prepared by reactions of $Ln(NO_3)_3$ (Ln = Eu, Td) and H**L** in neutral water at room temperature. Complexes **1** and **2** have 1 : 3 metal : **L** composition; **1** and **2** can also be isolated using 1 : 1, 1 : 2, and even 1 : 6, metal : **L** stoichiometries in $MeOH/H_2O$ at room temperature or even by hydrothermal reaction, which was confirmed by X-ray diffraction, IR spectra, and elemental analyses, indicating the reaction is independent of metal : **L** ratio and reaction conditions. In the IR spectrum of **1**, the strong broad peak at $3415\,cm^{-1}$ indicates O–H stretch of aqua molecules. Skeletal vibrations of aromatic rings appear at $1550 \sim 1580\,cm^{-1}$. Deacon–Philips rule is helpful to determine the coordination of carboxylate and metal by calculating the frequency separation ($\Delta\nu$) between the asymmetric (ν_{as}) and symmetric stretching (ν_s) modes of carboxylate [22]. The $\Delta\nu$ for **1** indicates bridging coordination ($\Delta\nu = 197\,cm^{-1} < 200\,cm^{-1}, \nu_{as}(COO^-) = 1629\,cm^{-1}$, $\nu_s(COO^-) = 1432\,cm^{-1}$) and bidentate chelating coordination ($\Delta\nu = 166\,cm^{-1}, \nu_{as}(COO^-) = 1598\,cm^{-1}$, $\nu_s(COO^-) = 1432\,cm^{-1}$) and both chelating and bridging coordination ($\Delta\nu = 117\,cm^{-1}$, $\nu_{as}(COO^-) = 1549\,cm^{-1}$, $\nu_s(COO^-) = 1432\,cm^{-1}$) of coordinated carboxylate. Similar character is also observed in **2**. Both complexes are air-stable. To further study thermal stability, samples were carried out on a NETZSCH TG 209 thermal analyzer from room temperature to 800°C (figure 1). Weight loss of 7.00% corresponds to loss of uncoordinated and coordinated H_2O in the temperature range of $22 \sim 192.6$°C; further decomposition occurs at *ca* 520°C.

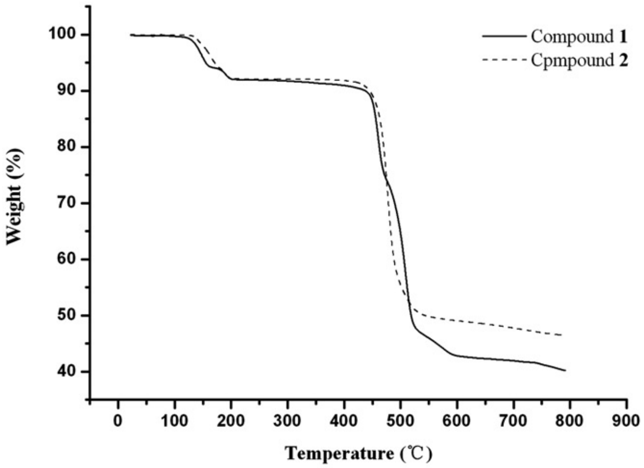

Figure 1. TGA trace for **1** and **2**.

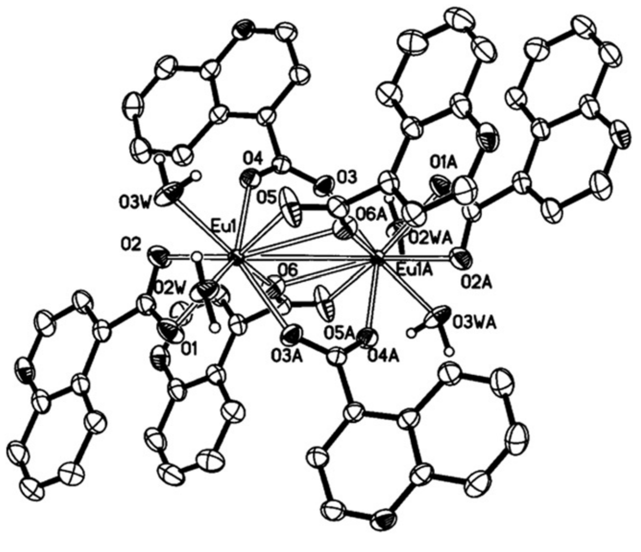

Figure 2. ORTEP view of the crystal structure of $[Eu_2(\mathbf{L})_6(H_2O)_4]$ in **1**.

3.2. *Description of the crystal structure*

Complexes **1** and **2** have isomorphic structures, and **1** is chosen for the description of structure. Complex **1** consists of binuclear neutral $[Eu_2(\mathbf{L})_6(H_2O)_4]$ and uncoordinated water. In the binuclear structure, a crystallographic inversion center is located in the midpoint of the two symmetrical metal centers. Figure 2 shows a perspective view of the structure with atom labeling; selected bond lengths and angles are listed in table 2. In each binuclear unit, there are six ligands performing three kinds of coordination, chelating, bridging, and both chelating and bridging, in agreement with the results of IR. Bidentate bridging was performed by O3 and O4, with Eu1A–O3 length of 2.322(2) Å, Eu1–O4 length of 2.3220(19) Å, and O4–Eu1–O3A angle of 134.29(7)°; the chelating mode is O1 and O2, with Eu1–O1 length of 2.393(2) Å, Eu1–O2 length of

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

1			
Eu(1)–O(6)	2.305(2)	Eu(1)–O(4)	2.3220(19)
Eu(1)–O(3)^{1a}	2.322(2)	Eu(1)–O(3W)	2.341(2)
Eu(1)–O(2W)	2.369(2)	Eu(1)–O(1)	2.393(2)
Eu(1)–O(5)	2.407(2)	Eu(1)–O(2)	2.459(2)
Eu(1)–O(6)^{1a}	2.720(2)	Eu(1)–Eu(1)^{1a}	4.0264(8)
O(6)–Eu(1)–O(4)	75.44(8)	O(6)–Eu(1)–O(3W)	142.59(9)
O(6)–Eu(1)–O(3)^{1a}	74.15(8)	O(3)^{1a}–Eu(1)–O(3W)	142.67(8)
O(4)–Eu(1)–O(3W)	76.64(8)	O(4)–Eu(1)–O(2W)	142.23(8)
O(6)–Eu(1)–O(2W)	142.15(8)	O(3W)–Eu(1)–O(2W)	70.43(9)
O(3)^{1a}–Eu(1)–O(2W)	72.82(8)	O(4)–Eu(1)–O(1)	129.58(8)
O(6)–Eu(1)–O(1)	84.78(9)	O(3W)–Eu(1)–O(1)	94.32(11)
O(3)^{1a}–Eu(1)–O(1)	80.26(9)	O(6)–Eu(1)–O(5)	122.83(8)
O(2W)–Eu(1)–O(1)	71.93(10)	O(3)^{1a}–Eu(1)–O(5)	85.12(11)
O(4)–Eu(1)–O(5)	83.57(10)	O(2W)–Eu(1)–O(5)	71.95(10)
O(3W)–Eu(1)–O(5)	77.66(11)	O(6)–Eu(1)–O(2)	76.64(9)
O(1)–Eu(1)–O(5)	143.61(9)	O(3)^{1a}–Eu(1)–O(2)	126.54(8)
O(4)–Eu(1)–O(2)	77.04(7)	O(2W)–Eu(1)–O(2)	109.50(9)
O(3W)–Eu(1)–O(2)	73.20(10)	O(5)–Eu(1)–O(2)	147.94(11)
O(1)–Eu(1)–O(2)	53.20(8)	O(4)–Eu(1)–O(6)^{1a}	69.56(7)
O(6)–Eu(1)–O(6)^{1a}	73.79(8)	O(3W)–Eu(1)–O(6)^{1a}	118.19(10)
O(3)^{1a}–Eu(1)–O(6)^{1a}	69.67(7)	O(1)–Eu(1)–O(6)^{1a}	146.72(9)
O(2W)–Eu(1)–O(6)^{1a}	110.64(9)	O(2)–Eu(1)–O(6)^{1a}	139.74(7)
O(5)–Eu(1)–O(6)^{1a}	49.04(7)	O(4)–Eu(1)–Eu(1)^{1a}	67.68(5)
O(6)–Eu(1)–Eu(1)^{1a}	40.44(6)	O(3W)–Eu(1)–Eu(1)^{1a}	140.70(7)
O(3)^{1a}–Eu(1)–Eu(1)^{1a}	66.98(5)	O(1)–Eu(1)–Eu(1)^{1a}	120.84(8)
O(2W)–Eu(1)–Eu(1)^{1a}	133.64(7)	O(2)–Eu(1)–Eu(1)^{1a}	112.53(6)
O(5)–Eu(1)–Eu(1)^{1a}	82.39(6)	Eu(1)–O(6)–Eu(1)^{1a}	106.21(8)
O(6)^{1a}–Eu(1)–Eu(1)^{1a}	33.35(4)		
2			
Tb(1)–O(6)	2.3516(19)	Tb(1)–O(3)	2.3543(17)
Tb(1)–O(4)^{2a}	2.3649(19)	Tb(1)–O(3W)	2.369(2)
Tb(1)–O(2W)	2.402(2)	Tb(1)–O(1)	2.426(2)
Tb(1)–O(5)	2.463(2)	Tb(1)–O(2)	2.485(2)
Tb(1)–O(6)^{2a}	2.7023(19)	Tb(1)–Tb(1)^{2a}	4.035(7)
O(6)–Tb(1)–O(3)	75.21(7)	O(6)–Tb(1)–O(4)^{2a}	73.94(7)
O(3)–Tb(1)–O(4)^{2a}	135.01(6)	O(6)–Tb(1)–O(3W)	142.60(7)
O(3)–Tb(1)–O(3W)	77.00(7)	O(4)^{2a}–Tb(1)–O(3W)	142.60(7)
O(6)–Tb(1)–O(2W)	142.39(7)	O(3)–Tb(1)–O(2W)	142.14(7)
O(4)^{2a}–Tb(1)–O(2W)	72.52(7)	O(3W)–Tb(1)–O(2W)	70.36(7)
O(6)–Tb(1)–O(1)	85.70(8)	O(3)–Tb(1)–O(1)	129.04(7)
O(4)^{2a}–Tb(1)–O(1)	80.02(7)	O(3W)–Tb(1)–O(1)	92.84(9)
O(2W)–Tb(1)–O(1)	72.25(8)	O(6)–Tb(1)–O(5)	123.26(7)
O(3)–Tb(1)–O(5)	83.29(9)	O(4)^{2a}–Tb(1)–O(5)	87.07(10)
O(3W)–Tb(1)–O(5)	77.10(9)	O(2W)–Tb(1)–O(5)	71.35(9)
O(1)–Tb(1)–O(5)	143.53(8)	O(6)–Tb(1)–O(2)	76.75(7)
O(3)–Tb(1)–O(2)	77.02(7)	O(4)^{2a}–Tb(1)–O(2)	125.33(7)
O(3W)–Tb(1)–O(2)	72.98(8)	O(2W)–Tb(1)–O(2)	110.01(8)
O(1)–Tb(1)–O(2)	52.52(7)	O(5)–Tb(1)–O(2)	147.11(9)
O(6)–Tb(1)–O(6)^{2a}	74.25(7)	O(3)–Tb(1)–O(6)^{2a}	70.48(6)
O(4)^{2a}–Tb(1)–O(6)^{2a}	70.15(6)	O(3W)–Tb(1)–O(6)^{2a}	118.59(8)
O(2W)–Tb(1)–O(6)^{2a}	109.09(7)	O(1)–Tb(1)–O(6)^{2a}	147.55(7)
O(5)–Tb(1)–O(6)^{2a}	49.05(6)	O(2)–Tb(1)–O(6)^{2a}	140.79(6)

Symmetry code: for **1** (a) $-x+1, -y+2, -z$; for **2** (a) $-x+2, -y+1, -z-1$.

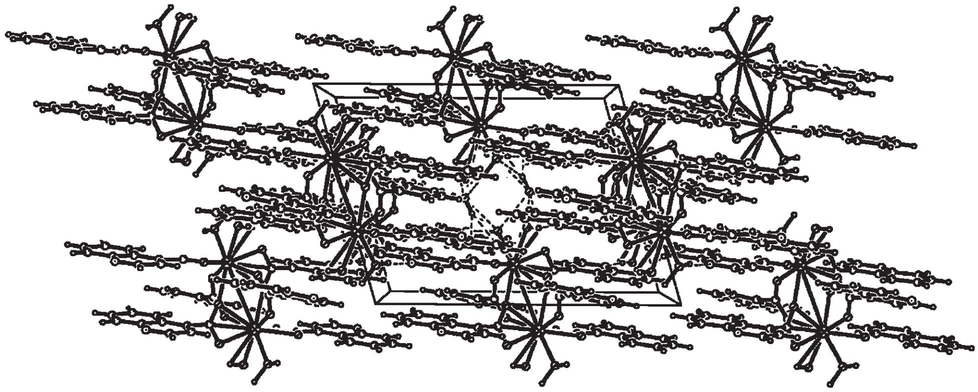

Figure 3. The 3-D supramolecular structure of **1** formed by hydrogen bonds.

Table 3. O–H···O and O–H···N hydrogen-bond parameters in **1**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠D–H···A(°)
O1W–H1WA–O2W	0.87	2.18	2.851(3)	134
O1W–H1WA–O1	0.87	2.53	3.309(4)	150
O1W–H1WB–N2$^{\#1}$	0.84	1.88	2.710(3)	169
O2W–H2WA–N1$^{\#2}$	0.85	1.91	2.746(3)	171
O3W–H3WA–O5	0.85	1.88	2.730(3)	173
O3W–H3WB–N3$^{\#3}$	0.85	1.95	2.742(4)	154
O2W–H2WB–O1W$^{\#4}$	0.85	1.92	2.734(3)	160

Symmetry codes: 1: $x-1/2, -y+3/2, z+1/2$; #2: $-x+1/2, y+1/2, -z+1/2$; #3: $-x+1/2, y-1/2, -z-1/2$; #4: $-x, -y+2, -z$.

2.459(2) Å, and O1–Eu1–O2 angle of 53.20(8)°; chelating and bridging could be regarded as O5 and O6A, with Eu1–O5 length of 2.407(2) Å, Eu1–O6 length of 2.305(2) Å, Eu1–O6A length of 2.720(2) Å, and O1–Eu1–O6A angle of 49.04(7)°, less than that of the pure chelating mode. The angle of Eu1–O6A–Eu1A is 106.21(8)°. The ligands perform homologous coordination in **2** with Tb1–O lengths from 2.3516(19) Å to 2.7023(19) Å, and angles around Tb1 ranging from 49.05(6)° to 147.55(7)°. Each Eu(III) is nine-coordinate, and in addition to carboxylates there are two molecules of water, with bond lengths of 2.369(2) and 2.341(2) Å. In the binuclear structure, the lanthanide distances are 4.0264(8) Å for **1** and 4.035(7) Å for **2**.

A 3-D structure is formed through hydrogen bond interactions (figure 3); hydrogen bond parameters are listed in table 3. There are two kinds of hydrogen bonds, one is O–H···O observed between coordinated water and uncoordinated water. The other is O–H···N between hydrogen of coordinated water and nitrogen of ligand. The two kinds of hydrogen bonds are almost perpendicular to each other and link the binuclear structure into a 3-D network.

3.3. *Solid-state emission*

Solid-state emission spectra of **1** and **2** were studied at room temperature (figure 4). As expected, 4-quinoline carboxylate acid activates both Eu(III) and Tb(III) to

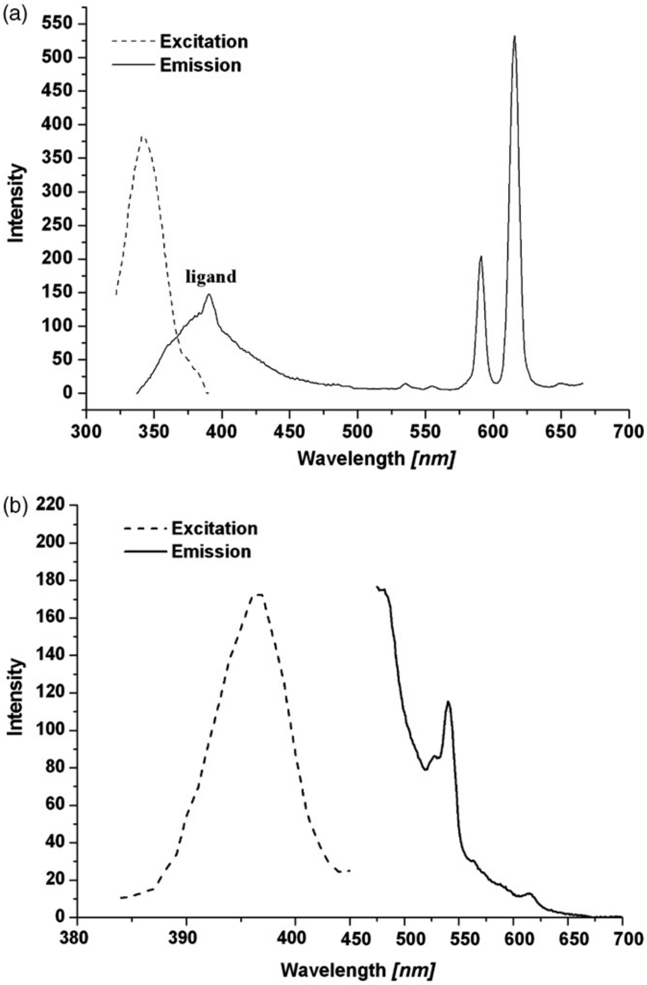

Figure 4. Excitation and emission spectra of **1** (a) and **2** (b).

emit their characteristic wavelengths. The luminescence spectrum of **1** corresponds to $^5D_0 \rightarrow {}^7F_J$ ($J = 0 \sim 4$) [23]; two weak emission bands at 535 and 555 nm correspond to $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_1$ transitions, while the two intense bands at 592 and 618 nm originate from $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_3$ transitions, and the last weaker one at 653 nm is from $^5D_0 \rightarrow {}^7F_4$. The luminescence spectrum of **2** has two intense peaks at 490 and 545 nm corresponding to $^5D_4 \rightarrow {}^7F_6$ and $^5D_4 \rightarrow {}^7F_5$ transitions and two weaker bands at 587 and 624 nm arising from $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$ transitions, respectively [11]. The excitation spectra of $^5D_0$ and $^5D_4$ emission of Eu(III) and Tb(III) indicate an efficient ligand-to-metal energy transfer, since the most intense feature in the spectrum is a broad band corresponding to transitions populating ligand-centered excited states. The luminescence intensity of **1** (figure 4a) is much stronger than that of **2** (figure 4b). The better the triplet-state level of ligand matches with the lowest excited state level of metal, the more effective energy transfer will occur. Thus, the luminescence emission will be more completely quenched [24]. Their luminescence spectra indicate that the triplet-state level of this ligand matches better with the lowest excited state level of Eu(III) than with Tb(III).

Supplementary material

Crystallographic data for **1** and **2** in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC-671913, 671914. Copies of this information may be obtained free from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk

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