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## 3-D frameworks assembled by lanthanide dimers with 1,4-cyclohexanedicarboxylic acid and 1,10-phenanthroline via hydrogen bonds and $\pi$ – $\pi$ stacking interactions

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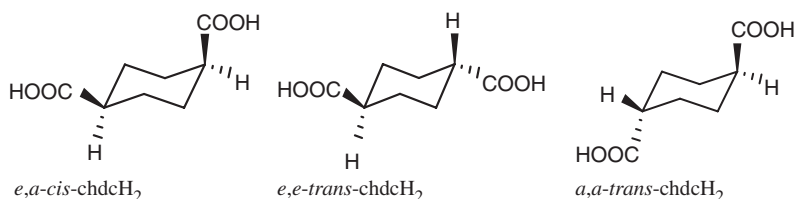
Two complexes  $[\text{Ln}(\text{e},\text{a}-\text{cis}-1,4\text{-chdc})(\text{e},\text{a}-\text{cis}-1,4\text{-Hchdc})(\text{phen})(\text{H}_2\text{O})_2]\cdot 10\text{H}_2\text{O}$  (Ln = Eu, **1**; Tb, **2**, 1,4-H<sub>2</sub>chdc = 1,4-cyclohexanedicarboxylic acid; phen = 1,10-phenanthroline) have been synthesized and structurally characterized by single-crystal X-ray diffraction. Both complexes are doubly e,a-cis-1,4-chdc-bridged dimers. The e,a-cis-1,4-Hchdc, phen, and water molecules bond to Ln<sup>3+</sup>, forming nine-coordinate complexes. 3-D supramolecular frameworks are constructed by hydrogen bonds and  $\pi$ – $\pi$  stacking interactions. Luminescence spectra exhibit the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>J</sub> (*J* = 0–4) and <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>J</sub> (*J* = 6–3) transitions of Eu<sup>3+</sup> for **1** and Tb<sup>3+</sup> ion for **2**, respectively.

**Keywords:** Lanthanide complex; 1,4-Cyclohexanedicarboxylic acid; Crystal structure; Luminescence

### 1. Introduction

Design and synthesis of metal–organic supramolecular frameworks have attracted considerable attention because of their structural diversities and potential applications in catalysis, magnetism, fluorescent materials, etc. [1–10]. Polycarboxylic acids are good ligands for construction of metal coordination polymers and supramolecular frameworks [11–23]. Multidentate organic ligands connect metal ions to give metal–organic frameworks (MOFs) through coordination bonds [11–20]. However, noncovalent interactions, such as hydrogen bonds and  $\pi$ – $\pi$  stacking can link discrete molecular building blocks or low-dimensional structures into high-dimensional supramolecular frameworks [5, 24–27]. Polycarboxylic acids can be completely or partly deprotonated to coordinate metal ions. Moreover, COO<sup>−</sup> and COOH groups can act as hydrogen bond acceptors and/or hydrogen bond donors resulting in supramolecular frameworks by intermolecular hydrogen bond interactions. Free water molecules in the crystals often affect assembly of supramolecular structures through hydrogen bonds. Introduction of 1,10-phenanthroline (phen) as an auxiliary ligand in complexes is helpful for formation of supramolecular frameworks.

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Scheme 1. Conformations of 1,4-H<sub>2</sub>chdc.

1,4-Cyclohexanedicarboxylic acid (1,4-H<sub>2</sub>chdc) is a flexible ligand with three predominant conformations, *a,a-trans*-, *e,e-trans*-, and *e,a-cis*-H<sub>2</sub>chdc (scheme 1). Conformational flexibility makes versatile structures of complexes [16–19]. Two luminescent lanthanide complexes, [Ln(*e,a-cis*-1,4-chdc)(*e,a-cis*-1,4-Hchdc)(phen)(H<sub>2</sub>O)]<sub>2</sub> · 10H<sub>2</sub>O (Ln = Eu, **1**; Tb, **2**) are binuclear molecules, different from the reported lanthanide complexes with 1,4-H<sub>2</sub>chdc [16–19]. The dimers self-assemble *via* hydrogen bonds and  $\pi$ – $\pi$  stacking interactions into supramolecular frameworks. The synthesis, crystal structure, and luminescent properties of the two complexes are reported.

## 2. Experimental

### 2.1. Materials

LnCl<sub>3</sub> · 6H<sub>2</sub>O (Ln = Eu, Tb) were prepared by the corresponding oxide with hydrochloric acid. Other analytical grade chemicals and solvents were purchased and used without purification.

### 2.2. Synthesis of the complexes

1,4-H<sub>2</sub>chdc (mixture of *cis* and *trans* 99%; 1.2 mmol) and phen (0.4 mmol) were dissolved in 25 mL ethanol. The pH of the solution was controlled in a range of 5–6 with 2 mol L<sup>-1</sup> NaOH solution. Then 5 mL ethanol solution of LnCl<sub>3</sub> · 6H<sub>2</sub>O (0.4 mmol) was dropped into the mixed solution. The mixture was heated with stirring for 2 h. Colorless square single crystals of the complexes were obtained from the mother liquor after a week at room temperature. For **1**, Yield: 43%. Anal. Calcd (%) for C<sub>56</sub>H<sub>82</sub>N<sub>4</sub>O<sub>28</sub>Eu<sub>2</sub>: C, 43.02; H, 5.25; N, 3.59. Found (%): C, 43.22; H, 5.46; N, 3.13. Selected IR (KBr pellet,  $\nu$  cm<sup>-1</sup>): 3406w, 2951w, 1721w, 1693w, 1535vs, 1453vs, 1429vs, 1349m, 1310m, 1202s, 1146m, 1106w, 939m, 847s, 730s, 592w, 416w. For **2**, Yield: 39%. Anal. Calcd (%) for C<sub>56</sub>H<sub>82</sub>N<sub>4</sub>O<sub>28</sub>Tb<sub>2</sub>: C, 42.64; H, 5.20; N, 3.55. Found (%): C, 42.68; H, 5.35; N, 3.26. Selected IR (KBr pellet,  $\nu$  cm<sup>-1</sup>): 3406w, 2949w, 1720w, 1533vs, 1452vs, 1428vs, 1348m, 1309m, 1202m, 1149m, 1106w, 935m, 847s, 730s, 591w, 419w.

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

Complex	<b>1</b>	<b>2</b>
Empirical formula	C <sub>56</sub> H <sub>82</sub> N <sub>4</sub> O <sub>28</sub> Eu <sub>2</sub>	C <sub>56</sub> H <sub>82</sub> N <sub>4</sub> O <sub>28</sub> Tb <sub>2</sub>
Formula weight	1561.93	1575.85
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Unit cell dimensions (Å, °)		
<i>a</i>	9.9066(3)	9.9105(3)
<i>b</i>	11.1275(3)	11.1270(4)
<i>c</i>	14.9146(4)	14.8523(5)
$\alpha$	80.4150(10)	80.7210(10)
$\beta$	86.5030(10)	86.807(2)
$\gamma$	84.7450(10)	84.695(2)
Volume (Å <sup>3</sup> ), <i>Z</i>	1612.60(8), 2	1608.08(9), 1
Calculated density (mg m <sup>-3</sup> )	1.601	1.602
Absorption coefficient (mm <sup>-1</sup> )	2.014	2.268
<i>F</i> (000)	788	792
Crystal size (mm <sup>3</sup> )	0.35 × 0.30 × 0.18	0.18 × 0.14 × 0.10
$\theta$ range for data collection (°)	1.86–27.94	2.07–27.96
Limiting indices	–13 ≤ <i>h</i> ≤ 12; –14 ≤ <i>k</i> ≤ 14; –19 ≤ <i>l</i> ≤ 19	–13 ≤ <i>h</i> ≤ 12; –14 ≤ <i>k</i> ≤ 14; –19 ≤ <i>l</i> ≤ 19
Reflections collected	15,688	13,412
Independent reflection	6904 [ <i>R</i> (int) = 0.0172]	4425 [ <i>R</i> (int) = 0.0259]
Data/restraints/parameters	6904/0/442	4425/7/351
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.932	1.034
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0224, <i>wR</i> <sub>2</sub> = 0.0596	<i>R</i> <sub>1</sub> = 0.0232, <i>wR</i> <sub>2</sub> = 0.0620
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0241, <i>wR</i> <sub>2</sub> = 0.0604	<i>R</i> <sub>1</sub> = 0.0253, <i>wR</i> <sub>2</sub> = 0.0635
Largest difference peak and hole (e Å <sup>-3</sup> )	0.754 and –0.437	1.229 and –0.567

### 2.3. Single-crystal X-ray diffraction

X-ray single crystal data collection for the two complexes were performed on a Bruker Smart Apex II CCD diffractometer equipped with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293(2) K. Semiempirical absorption corrections were applied. The structures were solved by direct methods and refined by full-matrix least-squares on *F*<sup>2</sup> using the SHELXTL-97 software package [28, 29]. All non-hydrogen atoms in the two complexes were refined anisotropically. The hydrogens were generated geometrically and treated by a mixture of independent and constrained refinement. The summary of crystal data and selected bond lengths and angles for **1** and **2** are listed in tables 1–3.

### 2.4. Physical measurement

Elemental analyses (C, H, N) were performed using an Elementar Vario EL analyzer. IR spectra were recorded with a Bruker EQUINOX-55 spectrometer using KBr pellets from 400 to 4000 cm<sup>-1</sup>. Excitation and emission spectra of solid samples were recorded on an F-4500 Fluorescence Spectrophotometer at room temperature. Thermogravimetric analyses were carried out on a WCT-1A Thermal Analyzer at a heating rate of 10°C min<sup>-1</sup> from room temperature to 1000°C in air atmosphere.

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

Eu(1)–O1W	2.398(2)	Eu(1)–O(4)	2.4367(17)
Eu(1)–O(3)	2.4376(19)	Eu(1)–O(6)	2.4543(19)
Eu(1)–O(2)	2.468(2)	Eu(1)–O(1)	2.4727(18)
Eu(1)–O(5)	2.5138(17)	Eu(1)–N(2)	2.571(2)
Eu(1)–N(1)	2.574(2)		
O1W–Eu(1)–O(3)	136.30(9)	O(4)–Eu(1)–O(3)	53.42(6)
O1W–Eu(1)–O(6)	82.73(9)	O(4)–Eu(1)–O(6)	77.23(7)
O(3)–Eu(1)–O(6)	73.32(7)	O1W–Eu(1)–O(2)	69.08(8)
O(4)–Eu(1)–O(2)	79.19(7)	O(3)–Eu(1)–O(2)	112.39(7)
O(6)–Eu(1)–O(2)	144.14(8)	O1W–Eu(1)–O(1)	121.47(8)
O(4)–Eu(1)–O(1)	83.49(7)	O(3)–Eu(1)–O(1)	74.73(7)
O(6)–Eu(1)–O(1)	148.04(7)	O(2)–Eu(1)–O(1)	52.39(6)
O1W–Eu(1)–O(5)	71.79(8)	O(4)–Eu(1)–O(5)	125.74(6)
O(3)–Eu(1)–O(5)	115.74(6)	O(6)–Eu(1)–O(5)	51.74(6)
O(2)–Eu(1)–O(5)	131.36(6)	O(1)–Eu(1)–O(5)	150.15(6)
O1W–Eu(1)–O(4)	86.26(9)	N(1)–Eu(1)–N(2)	64.15(7)

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

Tb(1)–O1W	2.363(2)	Tb(1)–O(1)	2.5012(16)
Tb(1)–O(2)	2.4376(19)	Tb(1)–O(5)	2.4216(19)
Tb(1)–O(6)	2.4095(18)	Tb(1)–O(7)	2.444(2)
Tb(1)–O(8)	2.4509(18)	Tb(1)–N(1)	2.546(2)
Tb(1)–N(2)	2.539(2)		
O1W–Tb(1)–O(5)	135.69(9)	O(6)–Tb(1)–O(5)	53.85(6)
O1W–Tb(1)–O(2)	82.75(9)	O(6)–Tb(1)–O(2)	77.44(7)
O(5)–Tb(1)–O(2)	73.28(7)	O1W–Tb(1)–O(7)	69.21(8)
O(6)–Tb(1)–O(7)	78.93(7)	O(5)–Tb(1)–O(7)	112.20(7)
O(2)–Tb(1)–O(7)	144.53(8)	O1W–Tb(1)–O(8)	122.14(8)
O(6)–Tb(1)–O(8)	84.09(7)	O(5)–Tb(1)–O(8)	74.41(7)
O(2)–Tb(1)–O(8)	147.69(7)	O(7)–Tb(1)–O(8)	52.97(7)
O1W–Tb(1)–O(1)	71.65(7)	O(6)–Tb(1)–O(1)	125.91(6)
O(5)–Tb(1)–O(1)	116.47(7)	O(2)–Tb(1)–O(1)	52.17(6)
O(7)–Tb(1)–O(1)	130.84(7)	O(8)–Tb(1)–O(1)	149.46(7)
O1W–Tb(1)–O(6)	85.19(9)	N(1)–Tb(1)–N(2)	64.83(7)

### 3. Results and discussion

#### 3.1. Crystal structure

The molecular structure of **1**, shown in figure 1, consists of a binuclear molecule [Eu(*e,a-cis*-1,4-chdc)(*e,a-cis*-1,4-Hchdc)(phen)(H<sub>2</sub>O)]<sub>2</sub> and 10 free water molecules (figure 1a). The 1,4-H<sub>2</sub>chdc possesses *e,a-cis*-conformation and two types of coordination of *e,a-cis*-1,4-chdc and *e,a-cis*-1,4-Hchdc. The former is completely deprotonated using two bidentate-chelating carboxylates to coordinate Eu<sup>3+</sup>. The partly deprotonated ligand uses one bidentate-chelating carboxylate to coordinate Eu<sup>3+</sup>; its other carboxyl group is not deprotonated and is free. Two *e,a-cis*-1,4-chdc ligands act as a bridge, linking two Eu<sup>3+</sup> ions and the other two *e,a-cis*-1,4-Hchdc terminal ligands coordinate Eu<sup>3+</sup>, which are linked by the *e,a-cis*-1,4-chdc ligand, forming a Eu–[*e,a-cis*-1,4-chdc]–Eu linkage. The distance between the two Eu<sup>3+</sup> ions, 9.149(5) Å, is significantly larger than that in other europium carboxylate complexes [30, 31].

Eu<sup>3+</sup> forms a nine-coordinate complex with four oxygens of *e,a-cis*-1,4-chdc ligands, two oxygens of *e,a-cis*-1,4-Hchdc, one water molecule, and two nitrogens of phen.

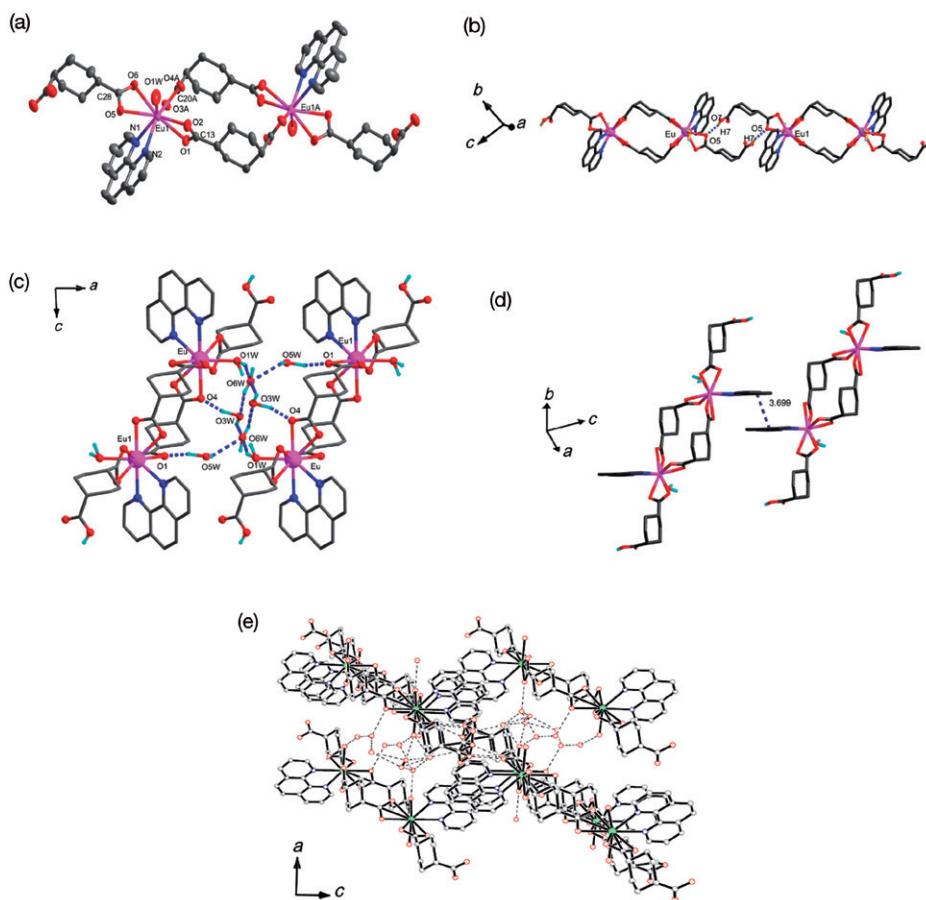


Figure 1. View of the structure of **1**: (a) Molecular structure. Free water molecules and all hydrogen atoms are omitted for clarity, (b) 1-D chain, (c) H-bonds, (d)  $\pi$ - $\pi$  stacking, and (e) 3-D network.

The coordination environment of  $\text{Eu}^{3+}$  can be best described as distorted monocapped square antiprism. The upper and lower planes of the square antiprism are composed of O2, O4A, O5, O6 and O1, O3A, N1, N2, respectively, with the mean deviation from the upper and lower planes of 0.0110 and 0.4647 Å, respectively. The dihedral angle between the upper and lower planes is 14.9°. O1W caps the monocapped square antiprism. The bond lengths of Eu1–O range from 2.398(2) to 2.5138(17) Å, with average of 2.4550 Å. The Eu1–N bond lengths are 2.574(2) and 2.571(2) Å, respectively, with average bond length of 2.5725 Å. The O–Eu1–O bond angles vary in the range of 51.74(6)°–148.04(7)° and the bond angle of N1–Eu1–N2 is 64.15(7)°.

The uncoordinated carboxyl of *e,a-cis*-1,4-Hchdc forms a hydrogen bond with the coordinated carboxylate oxygen of *e,a-cis*-1,4-chdc from the adjacent binuclear molecules, O7–H7 $\cdots$ O5 [ $-x+2, -y+1, z+1$ ], 2.684 Å, 155.31°. Adjacent binuclear molecules are connected “hand in hand” to form a 1-D chain by hydrogen bonds (figure 1b). Free water molecules present in the crystal participate in hydrogen bond formation. Hydrogen bonds form between free water molecules, O6W–H6W $\cdots$ O3W,

2.786 Å, 113.50°; O5W–H5W...O6W, 2.837 Å, 125.57° and free water molecules form hydrogen bonds with coordinated carboxylate oxygens, O5W–H5W...O1, 2.785 Å, 165.87°; O3–H3W...O4, 2.802 Å, 164.09°. In addition, coordinated water molecules form hydrogen bonds with free water molecules, O1W–H1W...O6W [ $x+1, y, z$ ], 2.839 Å, 153.71° (figure 1c). The molecular packing diagram indicates  $\pi$ – $\pi$  stacking interactions between phen ligands from adjacent molecules with an interplanar distance of 3.699 Å (figure 1d). Therefore, binuclear molecules interact with each other through strong hydrogen bonds and  $\pi$ – $\pi$  stacking interactions to form a 3-D supramolecular framework (figure 1e).

The structure of **2** is similar to that of **1**. In **2**, the average bond distances of Tb–O, Tb–N, and Tb...Tb are 2.4325, 2.5425, and 9.114 Å, respectively, which are shorter than the corresponding distances in **1**, due to the radius of Tb<sup>3+</sup> being less than the radius of the Eu<sup>3+</sup>.

Lanthanide carboxylate complexes show varieties of crystal structures due to various coordination motifs of carboxylate. Dimeric forms with Ln–O–C–O–Ln or Ln–O–Ln linkages are most frequently observed for dimeric compounds [30–32]. Such lanthanide dimeric complexes are commonly obtained from the reaction of Ln<sup>3+</sup> with monoacid in the presence of ancillary ligands, such as 2,2'-bipyridine or phen [30–32]. A large number of lanthanide polycarboxylates reported are polymeric structures due to the presence of more coordinate sites of polycarboxylates [11–23]. Dimers are relatively less reported [26, 33]. For example, the binuclear molecules [Ln<sub>2</sub>(pdoa)<sub>3</sub>-(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O (Ln = Eu (**1**), Tb (**2**), and Dy (**3**); H<sub>2</sub>pdoa = 1,2-phenylenedioxydiacetic acid) are formed through one pdoa spacer with its two bidentate-chelating carboxylates linking the two Ln(III) centers [26]. [Tb<sub>2</sub>(1,2-pdoa)<sub>3</sub>·6H<sub>2</sub>O]·H<sub>2</sub>O is also formed through one 1,2-pdoa spacer *via* two bidentate-chelating carboxylates linking Tb<sup>3+</sup> ions [33]. However, the dimeric structures of **1** and **2** are different from the above dimeric structures of lanthanide carboxylates. In **1** and **2**, two metal centers are linked by the two complete *e,a-cis*-1,4-chdc ligands as a bridge, showing new types of structures of lanthanide carboxylates.

Some lanthanide complexes with 1,4-H<sub>2</sub>chdc have been reported, La(*cis*-chdc)(DMF)<sub>2</sub>(NO<sub>3</sub>) (DMF, dimethylformamide) and La<sub>2</sub>(*trans*-chdc)<sub>3</sub>(DMSO)<sub>4</sub> (DMSO, dimethyl sulfoxide) [16], [Nd<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(*cis*-chdc)<sub>2</sub>(*trans*-chdc)]·2H<sub>2</sub>O, Nd<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>(*trans*-chdc)<sub>3</sub>, and [Sm<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(*cis*-chdc)(*trans*-chdc)<sub>2</sub>]·4H<sub>2</sub>O [17], [La<sub>2</sub>(1,4-chdc)<sub>3</sub>(H<sub>2</sub>O)<sub>4</sub>], [La<sub>3</sub>(1,4-Hchdc)<sub>2</sub>(1,4-chdc)<sub>5</sub>(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O and [La<sub>2</sub>(1,4-chdc)<sub>3</sub>-(H<sub>2</sub>O)]·2.5H<sub>2</sub>O [18], and La<sub>2</sub>(1,10-phen)<sub>2</sub>(*e,a-cis*-1,4-chdc)<sub>3</sub>·2.5H<sub>2</sub>O [19], which are 1-D–3-D coordination polymers constructed by coordination bonds. The present structures differ from the above-reported lanthanide complexes as 3-D supramolecular structures of **1** and **2** are based on discrete molecules are constructed by noncovalent interactions including hydrogen bonds and  $\pi$ – $\pi$  stacking. We use *cis*- and *trans*-mixture of 1,4-H<sub>2</sub>chdc during the reaction, but in the product complexes, the ligand only possesses *e,a-cis*-conformation, providing an example of separating *e,a-cis*-conformation H<sub>2</sub>chdc from the mixed conformation.

### 3.2. Luminescence properties

Complexes **1** and **2** emit bright red and green light in the solid state under UV irradiation, respectively. Excitation spectra under 616 nm for **1** and 545 nm for **2** show a

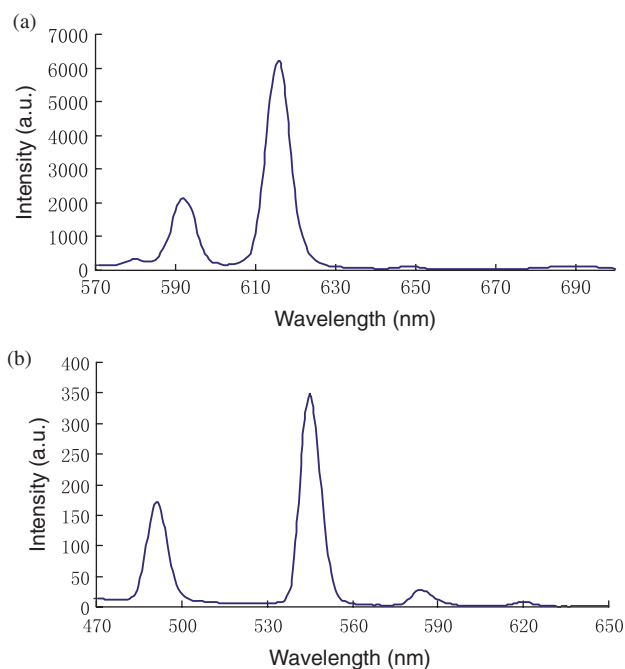


Figure 2. Luminescence spectra of **1** (a)  $\lambda_{\text{ex}} = 395$  nm and **2** (b)  $\lambda_{\text{ex}} = 346$  nm.

wide excitation band between 200 and 380 nm, attributed to the  $\pi-\pi^*$  transition of the ligand. Emission spectra of the two complexes were obtained under excitation wavelength of 395 nm for **1** and 346 nm for **2**. The ligands do not show emission bands under excitation at 395 and 346 nm. The spectra exhibit luminescence characteristics of  $\text{Eu}^{3+}$  for **1** and  $\text{Tb}^{3+}$  for **2** (figure 2). For **1**, emission peaks at 580, 592, and 616 nm correspond to  $^5\text{D}_0 \rightarrow ^7\text{F}_0$ ,  $^5\text{D}_0 \rightarrow ^7\text{F}_1$ , and  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transitions of  $\text{Eu}^{3+}$ . Weak peaks at 648 and 693 nm correspond to  $^5\text{D}_0 \rightarrow ^7\text{F}_3$  and  $^5\text{D}_0 \rightarrow ^7\text{F}_4$  transitions (figure 2a). The strongest band,  $^5\text{D}_0 \rightarrow ^7\text{F}_2$ , results in red luminescence. For **2**, the strongest emission at 545 nm corresponds to the  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  transition of  $\text{Tb}^{3+}$ , resulting in green luminescence. The second largest peak at 492 nm corresponds to  $^5\text{D}_4 \rightarrow ^7\text{F}_6$ ; weak emission peaks at 584 and 621 nm correspond to the  $^5\text{D}_4 \rightarrow ^7\text{F}_4$  and  $^5\text{D}_4 \rightarrow ^7\text{F}_3$  transitions, respectively (figure 2b).

### 3.3. Thermogravimetric analysis

The DTA-TGA analyses performed between room temperature and 1000°C are similar. The first weight loss starts at 103°C for **1** and 114°C for **2**, loss of water molecules. The corresponding weight losses are 13.76% (Calcd 13.83%) for **1** and 14.04% (Calcd 13.70%) for **2**. Decomposition of organic ligands takes place in the region 273–418°C for **1** and 293–448°C for **2**. The total weight losses of 75.9% for **1** and 76.58% for **2** suggest decomposition leaving  $\text{Eu}_2\text{O}_3$  for **1** and  $\text{Tb}_4\text{O}_7$  for **2** as the final products (Calcd 77.5% for **1** and 76.39% for **2**).



#### 4. Conclusion

We obtained Eu(III) and Tb(III) binuclear molecules using the 1,4-H<sub>2</sub>chdc and phen. The dimeric structures are different from many reported lanthanide complexes containing carboxylate ligands. The most remarkable feature of **1** and **2** is the molecular self organization of the neutral [Ln(e,a-*cis*-1,4-chdc)(e,a-*cis*-1,4-Hchdc)(phen)(H<sub>2</sub>O)]<sub>2</sub>·10H<sub>2</sub>O (Ln = Eu, **1**; Tb, **2**) building blocks into a 3-D open framework *via* intermolecular hydrogen bonds and  $\pi$ - $\pi$  stacking interactions.

#### Supplementary material

The crystallographic data of **1** (CCDC 763078) and **2** (CCDC 763077) can be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB21EZ, UK; Fax: +44(0)1223-336033; E-mail: deposit@ccdc.cam.ac.uk.

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