Polyhedron 49 (2013) 105–112

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

“*Facial*’ and ‘*meridional*’ coordination geometries and luminescence properties of tris(*N*-[(imidazol-4-yl)methylidene]-DL-alaninato)europium(III) and tris(*N*-[(imidazol-4-yl)methylidene]-DL-phenylalaninato)europium(III)

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ARTICLE INFO

Article history:
Received 6 June 2012
Accepted 3 October 2012
Available online 12 October 2012

Keywords:
Europium(III) complex
Tridentate ligand
Imidazole group
DL-Phenylalanine
DL-Alanine
Luminescence
Stereochemistry

ABSTRACT

Two racemic tridentate ligands, *N*-[(imidazol-4-yl)methylidene]-DL-alanine ($H_2L^{DL\text{-}ala}$) and *N*-[(imidazol-4-yl)methylidene]-DL-phenylalanine ($H_2L^{DL\text{-}phe}$), were synthesized by the 1:1 condensation reaction of 4-formylimidazole and either of DL-alanine and DL-phenylalanine, respectively. The Eu^{III} complexes ‘*fac*’-$[Eu^{III}(HL^{DL\text{-}ala})_3]$-$\cdot 8H^2O$ (**1**) and ‘*mer*’-$[Eu^{III}(HL^{DL\text{-}phe})_3]\cdot 7.75H_2O$ (**2**) were synthesized by mixing the ligand and $Eu^{III}(acetate)_3$ *n*-hydrate with 3:1 M ratio in methanol and the crystal structures were determined. Compounds **1** and **2** with three tridentate ligands have ‘*facial*’ and ‘*meridional*’ geometries, respectively, while they have a tricapped trigonal prismatic (TTP) and a capped square antiprismatic (CSAP) coordination geometry, respectively. In the crystal lattice, **1** consists of enantiomers ‘*fac*’-$[Eu^{III}(HL^{D\text{-}ala})_3]$ and ‘*fac*’-$[Eu^{III}(HL^{L\text{-}ala})_3]$, while **2** consists of ‘*mer*’-$[Eu^{III}(HL^{D\text{-}phe})_2(HL^{L\text{-}phe})]$ and ‘*mer*’-$[Eu^{III}(HL^{D\text{-}phe})(HL^{L\text{-}phe})_2]$. Compounds **1** and **2** displayed sharp emission bands based on the f–f transitions by excitation and showed a different emission pattern due to their ‘*fac*’- and ‘*mer*’-coordination geometries. The luminescence quantum yields and life times of **1** and **2** were estimated to be ($\Phi = 0.25$ and 1.40 ms) and ($\Phi = 0.30$ and 1.23 ms), respectively.

1. Introduction

Since Eu^{III} complexes have specific luminescence properties such as large Stokes shifts, sharp emission profiles corresponding to the $^5D_0 \rightarrow {}^7F_j$ ($j = 0,1,2,3,4$) transitions and long luminescence lifetimes, recently luminescent Eu^{III} complexes have attracted considerable attention aimed to the practical applications from electroluminescent devices to bio-probes for immunoassays or for imaging live cells [1–4]. Many luminescent Eu^{III} complexes have been synthesized and their physical properties have been reported [5,6]. Despite extensive attempts aimed at producing highly luminescent molecules, quantum yields above 40% are rare [7]. Eu^{III} complexes with β-diketonate have been extensively studied and high quantum yield reaching 85% is observed for [tris(thenoyltrifluoroacetonate)bis(dibenzylsulfoxide)europium(III)] [8]. On the other hand, β-diketonate is mono-anionic bidentate ligand and cannot provide neutral homoleptic lanthanide complexes with a saturated coordination sphere [9]. Optimization of the intrinsic quantum yield is achieved by the design of a tight, rigid, and fully coordinative environment. The disadvantages for the Eu^{III} complexes with β-diketonates, such as their ionic character and unsaturated coordination number, can be improved by new alternative ligand. It is anticipated that an electronic mono-negative tridentate ligand reacts with Eu^{III} ion at the 3:1 M ratio to form an electro-neutral homoleptic Eu^{III} complex with the saturated coordination number of nine. Such mono-negative tridentate ligands were used for the syntheses of neutral Eu^{III} complexes and some of the complexes give high quantum yields around ca. 60% for tris(4-phenyl-6-(2′-pyridyl)pyridine-2-carboxylate)-europium(III) [10–12] and tris(benzimidazole-substituted-pyridine-2-carboxylato)europium(III) [13].

We have reported that the metal complexes with multidentate ligand involving imidazole groups have a high-probability for enantioselective interaction. (1) Copper(II) complex $[Cu^{II}(H_2L^1)](ClO_4)_2$ with an achiral pentadentate strand-type ligand involving two imidazole groups, (H_2L^1 = bis{3-[(2-methylimidazol-4-yl)methylideneamino]propyl}methylamine), gives either Δ (clockwise) or Λ (anticlockwise) enantiomers, due to the spiral coordination arrangement of achiral ligand. The mono-deprotonated complex $[Cu^{II}(HL^1)]ClO_4$ has one imidazole and one imidazolate moiety per molecule, which functions as a chiral self-complementary building component, and aggregates into homochiral (·ΔΔΔΔ· and ·ΛΛΛΛ·) 1D zigzag chains due to the intermolecular

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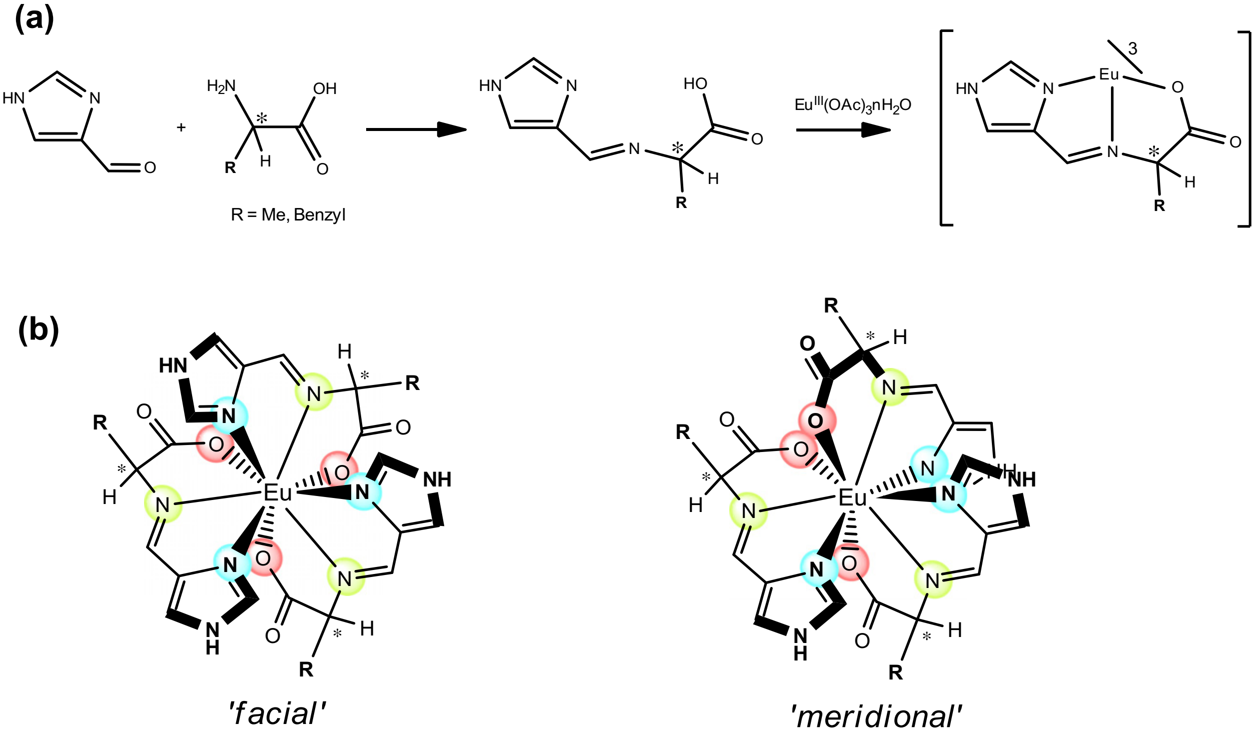
http://dx.doi.org/10.1016/j.poly.2012.10.003



Scheme 1. (a) Synthetic scheme of unsymmetric tridentate ligand H_2L^R and the Eu^{III} complex. Tridentate ligand H_2L^R is synthesized by the 1:1 condensation reactions of 4-formylimidazole and DL-alanine or DL-phenylalanine. The 3:1 reaction of the ligand and $Eu^{III}(acetate)_3$ *n*-hydrate gives $[Eu^{III}(HL^R)_3]\cdot xH_2O$. (b) '*Facial*' and '*meridional*' geometrical isomers of $[Eu^{III}(HL^R)_3]$ with N_6O_3 nine-coordinate. As strictly speaking (IUPAC) *fac* and *mer* only apply to six-coordinated octahedral complexes, '*fac*' and '*mer*' are used in this text.

imidazole···imidazolate hydrogen bond [14,15]. (2) Cobalt(III) complex with achiral tripod-type ligands involving three imidazole groups, $[Co^{III}(H_3L^2)](ClO_4)_3$ (H_3L^2 = tris{2-[(imidazol-4-yl)methylideneamino]ethyl}amine) induces the chirality of the Δ- and Λ-enantiomers due to the screw coordination arrangement. The formally hemi-deprotonated complex $[Co^{III}(H_{1.5}L^2)](ClO_4)_{1.5}$ functions as a self-complementary chiral building block to form an extended 2D homochiral layer structure due to the intermolecular imidazole···imidazolate hydrogen bonds leading to a spontaneous resolution [16–21]. (3) Copper(II) and zinc(II) complexes of tridentate ligands involving imidazole and amino acid $[M^{II}X(HL)]$ (M^{II} = Cu^{II}, Zn^{II}; X = Cl^-, Br^-) showed another enantioselective interaction [22–24]. In addition to the coordination by the imidazolate group to the adjacent molecule, the amino acid moiety is also a functional group for assembly process, in which the amino acid can coordinate and/or make hydrogen-bond to the adjacent molecule.

In this study, two racemic tridentate ligands involving imidazole and amino acid moieties, *N*-[(imidazol-4-yl)-methylidene]-DL-alanine ($H_2L^{DL\text{-}ala}$) and *N*-[(imidazol-4-yl)methylidene]-DL-phenylalanine ($H_2L^{DL\text{-}phe}$), were used for the syntheses of Eu^{III} complexes. Firstly, such mono-negative tridentate ligands H_2L^R can be useful for the synthesis of electronically neutral Eu^{III} complex with the saturated coordination number and high quantum yield. Secondly, the Eu^{III} complexes of such tridentate ligands can form enantioselective interaction, because the amino acid moiety is a functional group for assembly process and the chirality of the amino acid can give a diastereoselective effect for assembly process. The ligand (H_2L^R) was synthesized by the 1:1 condensation reactions of 4-formylimidazole derivative and various amino acids according to Scheme 1(a). As shown in Scheme 1(b) and confirmed by the X-ray analyses described later, the resulting Eu^{III} complexes with three mono-negative tridentate ligands, '*fac*'-$[Eu^{III}(HL^{DL\text{-}ala})_3]\cdot 8H_2O$ (**1**) and '*mer*'-$[Eu^{III}(HL^{DL\text{-}phe})_3]\cdot 7.75H_2O$ (**2**), are homoleptic complexes with '*facial*' and '*meridional*' coordination geometries. The crystal structures showed diastereoselective assembly manner. Here, we report the syntheses, crystal structures, and luminescent properties in the solid state of these two complexes.

2. Experimental

2.1. Materials

All reagents and solvents used in this study are commercially available from Tokyo Kasei Co. Ltd. and Wako Pure Chemical Industries Ltd. These were used without further purification.

2.2. Preparations of materials

2.2.1. Preparations of ligands $HL^{DL\text{-}ala}$ and $HL^{DL\text{-}phe}$

A tridentate ligand *N*-[(imidazol-4-yl)methylidene]-DL-alanine, which is abbreviated as $HL^{DL\text{-}ala}$, was prepared by the 1:1 condensation reaction of 4-formylimidazole and DL-alanine according to the method reported in the literature [22,23]. To a solution of 4-formylimidazole (1.5 mmol, 0.144 g) in 10 mL of methanol was added a solution of DL-alanine (1.5 mmol, 0.134 g) in 5 mL of water, and the mixture was stirred on a hot plate at 50 °C for 1 h and then cooled to room temperature. The resultant ligand solution was not isolated and used for the synthesis of Eu^{III} complex. $HL^{DL\text{-}phe}$ was prepared by a similar way of $HL^{DL\text{-}ala}$, using DL-phenylalanine instead of DL-alanine.

2.2.2. Preparation of '*fac*'-$[Eu^{III}(HL^{DL\text{-}ala})_3]\cdot 8H_2O$ (**1**)

To the resultant ligand solution of $HL^{DL\text{-}ala}$ thus obtained (1.5 mmol) was added a solution of europium(III)acetate *n*-hydrate (0.5 mmol, 0.165 g) in 5 mL of water at room temperature. The mixture was stirred for 10 min at room temperature and then filtered. For the crystallization, a diffusion method was applied. A vessel of the filtrate was left to stand for several days in an atmosphere saturated by vapor of acetone, precipitating colorless block shape crystals. Yield 64%. *Anal.* Calc. for $[\mathrm{Eu^{III}(HL^{DL\text{-}ala})_3}]\cdot 8\mathrm{H_2O}$ = $\mathrm{C_{21}H_{24}N_9O_6Eu\cdot 8H_2O}$: C, 31.74; H, 5.07; N, 15.87. Found: C, 31.99; H, 5.02; N, 15.83%. TGA; 18% weight loss was observed in the heating mode. In the cooling mode, the sample absorps the vapor to increase the weight from −18% to −2%.

2.2.3. Preparation of ‘mer’-$[\mathrm{Eu^{III}(HL^{DL\text{-}phe})_3}]\cdot 7.75\mathrm{H_2O}$ (2)

To the resultant ligand solution of $\mathrm{HL^{DL\text{-}phe}}$ (1.5 mmol) was added a solution of europium(III)acetate hydrate (0.5 mmol, 0.165 g) in 5 mL of water at room temperature. The mixture was filtered and the filtrate was left to stand for several days in an atmosphere saturated by vapor of acetone to precipitate colorless block shape crystals. Yield 55%. *Anal.* Calc. for $[\mathrm{Eu^{III}(HL^{DL\text{-}phe})_3}]\cdot 7.5\mathrm{H_2O}$ = $\mathrm{C_{39}H_{36}N_9O_6Eu\cdot 7.5H_2O}$: C, 46.20; H, 5.07; N, 12.43. Found: C, 46.51; H, 5.15; N, 12.19%.

2.3. Physical measurements

Elemental C, H, and N analyses were carried out at the Center for Instrumental Analysis of Kumamoto University. Thermogravimetric analyses (TGA) were performed on a TG/DTA6200 (Seiko Instrument Inc.). The samples of ca. 3 mg were heated from room temperature to 130 °C in the heating mode at the heating rate of 5 °C min^{-1}, kept the temperature for 1 h, and then cooled to room temperature. UV–Vis electronic spectra were measured on a Shimadzu UV-2450 UV–Vis spectrophotometer. Excitation and emission spectra were measured on a HITACHI F-7000 fluorescence spectrophotometer. The quantum yields in the solid state were obtained by an absolute method using a Hitachi F-7000 fluorescence spectrometer equipped with an integrating sphere by excitation at 302 nm.[1] The lifetimes were obtained on a HITACHI F-7000 fluorescence spectrophotometer by using the attachment program of time-domain phosphorescence lifetime measurement with optical chopping of excitation light.

2.4. X-ray crystal structure analyses

The X-ray diffraction data were collected by a Rigaku RAXIS RAPID imaging plate diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) for ‘*fac*’-$[\mathrm{Eu^{III}(HL^{DL\text{-}ala})_3}]\cdot 8\mathrm{H_2O}$ (**1**) at 103 K and ‘*mer*’-$[\mathrm{Eu^{III}(HL^{DL\text{-}phe})_3}]\cdot 7.75\mathrm{H_2O}$ (**2**) at 296 K. The temperature of the crystal was maintained at the selected value by means of a Rigaku cooling device to within an accuracy of ±2 K. The structures were solved by direct methods and expanded using the Fourier technique [25,26]. Hydrogen atoms were fixed at the calculated positions and refined using a riding model. All calculations were performed using the Crystal Structure crystallographic software package [27].

3. Results and discussion

3.1. Synthesis and characterization

Two racemic tridentate ligands, *N*-[(imidazol-4-yl) methylidene]-DL-alanine ($\mathrm{H_2L^{DL\text{-}ala}}$) and *N*-[(imidazol-4-yl)methylidene]-DL-phenylalanine ($\mathrm{H_2L^{DL\text{-}phe}}$), were synthesized by the 1:1 condensation reaction of 4-formylimidazole and either of DL-alanine and DL-phenylalanine, respectively in a mixed solution of methanol and water. The ligands were not isolated and the ligand solutions were used for the synthesis of the Eu^{III} complexes. The Eu^{III} complexes ‘*fac*’-$[\mathrm{Eu^{III}(HL^{DL\text{-}ala})_3}]\cdot 8\mathrm{H_2O}$ (**1**) and ‘*mer*’-$[\mathrm{Eu^{III}(HL^{DL\text{-}phe})_3}]\cdot 7.75\mathrm{H_2O}$ (**2**) were crystallized from the mixed solution of the ligand and Eu^{III}(acetate)$_3$ *n*-hydrate with 3:1 M ratio. The C, H, and N elemental analyses suggested the existence of the crystal water. The TGA analyses revealed the number of the crystal water. In the heating mode from room temperature to 130 °C, 18% weight loss corresponding to 8H$_2$O was observed for **1**.

Table 1
X-ray crystallographic data for ‘*fac*’-$[\mathrm{Eu^{III}(HL^{DL\text{-}ala})_3}]\cdot 8\mathrm{H_2O}$ (**1**) at 103 K and ‘*mer*’-$[\mathrm{Eu^{III}(HL^{DL\text{-}phe})_3}]\cdot 7.75\mathrm{H_2O}$ (**2**) at 296 K.

Complex	‘*fac*’-$[\mathrm{Eu^{III}(HL^{DL\text{-}ala}{}_3}]\cdot 8\mathrm{H_2O}$ (**1**)	‘*mer*’-$[\mathrm{Eu^{III}(HL^{DL\text{-}phe})_3}]\cdot 7.75\mathrm{H_2O}$ (**2**)
Formula	$\mathrm{C_{21}H_{40}N_9O_{14}Eu}$	$\mathrm{C_{39}H_{51.5}N_9O_{13.75}Eu}$
Formula weight	794.56	1018.35
Space group	$R\bar{3}$ (No. 148)	$I4_1/a$ (No. 88)
a (Å)	13.6136(7)	23.1450(6)
b (Å)	13.6136(7)	23.1450(6)
c (Å)	29.051(2)	34.8469(9)
V (Å^3)	4662.8(4)	18667.1(9)
Z	6	16
D_{calc} (g cm^{-3})	1.698	1.449
μ (cm^{-1})	20.927	14.116
R[a], R_w[b]	0.0562, 0.1580	0.0852, 0.2030

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $R_w = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$.

Table 2
Relevant coordination bond distances, angles, and hydrogen bond distances for ‘*fac*’-$[\mathrm{Eu^{III}(HL^{DL\text{-}ala})_3}]\cdot 8\mathrm{H_2O}$ (**1**) and ‘*mer*’-$[\mathrm{Eu^{III}(HL^{DL\text{-}phe})_3}]\cdot 7.75\mathrm{H_2O}$ (**2**).

Complex (**1**)		Complex (**2**)	
Eu–O(1)	2.395(4)	Eu–O(1)	2.397(9)
Eu–N(2)	2.582(6)	Eu–N(2)	2.569(9)
Eu–N(3)	2.553(7)	Eu–N(3)	2.548(9)
		Eu–O(3)	2.430(8)
		Eu–N(5)	2.589(9)
		Eu–N(6)	2.596(9)
		Eu–O(5)	2.448(8)
		Eu–N(8)	2.571(11)
		Eu–N(9)	2.577(12)
O(1)–Eu–N(2)	127.44(19)	O(1)–Eu–N(2)	126.1(3)
O(1)–Eu–N(3)	63.64(18)	O(1)–Eu–N(3)	64.2(3)
N(2)–Eu–N(3)	63.86(16)	N(2)–Eu–N(3)	64.1(3)
		O(3)–Eu–N(5)	124.1(3)
		O(3)–Eu–N(6)	62.2(3)
		N(5)–Eu–N(6)	63.8(3)
		O(5)–Eu–N(8)	121.6(3)
		O(5)–Eu–N(9)	62.5(3)
		N(8)–Eu–N(9)	64.1(4)
O(1)–Eu–O(1)^{*1}	77.35(17)	O(1)–Eu–N(5)	90.0(3)
N(2)–Eu–N(2)^{*1}	80.37(16)	N(2)–Eu–O(3)	68.5(3)
N(3)–Eu–N(3)^{*1}	120.00(15)	N(3)–Eu–N(6)	123.2(3)
		O(1)–Eu–O(5)	72.0(3)
		N(2)–Eu–N(8)	75.6(3)
		N(3)–Eu–N(9)	104.4(4)
		O(5)–Eu–N(5)	74.3(3)
		O(3)–Eu–N(8)	83.7(3)
		N(6)–Eu–N(9)	132.4(3)
Hydrogen bond (Å)			
N(1)···O(4)^{*2}	2.780(8)	N(1)···O(5)^{*4}	2.837(12)
O(2)···O(4)	2.690(10)	N(4)···O(4)^{*5}	2.694(14)
O(3)···O(4)	2.762(6)	N(7)···O(10)	2.744(16)
O(4)···O(5)	2.735(17)	O(2)···O(10)	2.637(16)
O(5)···O(2)^{*3}	2.703(18)		

Symmetry operations: (*1), $-y+1, x-y, z$; (*2), $x+1/3-1, y+2/3-1, z+2/3-1$; (*3), $-x+2/3+1, -y+1/3+1, z+1/3+1$; (*4), $y+3/4-1, -x+3/4, z+3/4-1$; (*5), $-y+3/4, x+1/4, z+1/4$.

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[1] Measurements of the amounts of fluorescence were carried out with a Hitachi F-7000 fluorescence spectrometer equipped with an integrating sphere by excitation at 302 nm.

In the cooling mode, the sample absorps the atmospheric moisture amount of $7H_2O$ to increase the 16% weight. For **2**, the weight loss corresponding to 7–8 water molecules was observed in the heating mode and the 4% weight increase corresponding to 2 water molecules was observed in the cooling mode.

3.2. Crystal structure of ‘fac’-$[Eu^{III}(HL^{DL\text{-}ala})_3]\cdot 8H_2O$ (**1**) and ‘mer’-$[Eu^{III}(HL^{DL\text{-}phe})_3]\cdot 7.75H_2O$ (**2**)

The crystal structures of ‘*fac*’-$[Eu^{III}(HL^{DL\text{-}ala})_3]\cdot 8H_2O$ (**1**) and ‘*mer*’-$[Eu^{III}(HL^{DL\text{-}phe})_3]\cdot 7.75H_2O$ (**2**) were determined by the single-crystal X-ray diffraction method at 103 and 296 K, respectively. The crystallographic data and the relevant coordination bond distances with the hydrogen bond distances are given in Tables 1 and 2, respectively.

3.2.1. Crystal structure of ‘fac’-$[Eu^{III}(HL^{DL\text{-}ala})_3]\cdot 8H_2O$ (**1**)

The complex with the formula of $[Eu^{III}(HL^{DL\text{-}ala})_3]\cdot 8H_2O$ crystallized into a centrosymmetric trigonal space group $R\bar{3}$ (No. 148) with $Z = 6$. The crystallographic unique unit is one third of ‘*fac*’-$[Eu^{III}(HL^{DL\text{-}ala})_3]\cdot 8H_2O$, consisting of one Eu^{III} ion at the special position on threefold rotation axis, one tridentate ligand $HL^{DL\text{-}ala}$ and two water molecules at the general positions, and two water molecules at the special positions. As the complex crystallized into a centrosymmetric space group and has C_3 symmetry, the crystal structure consists of two enantiomers of ‘*fac*’-$[Eu^{III}(HL^{D\text{-}ala})_3]$ and ‘*fac*’-$[Eu^{III}(HL^{L\text{-}ala})_3]$. The complex takes ‘*facial*’ geometrical configuration of two possible ‘*facial*’ and ‘*meridional*’ isomers [28].

Fig. 1(a), (a′), (b), and (b′) show the molecular structures and the space filling representations of ‘*fac*’-$[Eu^{III}(HL^{D\text{-}ala})_3]$ viewed along a C_3 axis (*c*-axis) and viewed perpendicular to the C_3 axis. The complex has a C_3 symmetry and three unsymmetrical ONN tridentate ligands are oriented parallel to each other, showing ‘*facial*’ configuration. Three methyl groups at the alanine moieties related by C_3 symmetry operations are well-packed in ‘*fac*’-$[Eu^{III}(HL^{D\text{-}ala})_3]$, demonstrating that ‘*fac*’-$[Eu^{III}(HL^{D\text{-}ala})_3]$ and ‘*fac*’-$[Eu^{III}(HL^{L\text{-}ala})_3]$ are preferable molecular geometry. The space filling representation of ‘*fac*’-$[Eu^{III}(HL^{D\text{-}ala})_3]$ also suggests that the species involving $HL^{D\text{-}ala}$ and $HL^{L\text{-}ala}$, that is, ‘*fac*’-$[Eu^{III}(HL^{D\text{-}ala})_2(HL^{L\text{-}ala})]$ and ‘*fac*’-$[Eu^{III}(HL^{L\text{-}ala})_2(HL^{D\text{-}ala})]$ are un-preferable due to the steric hindrance on the basis of the space filling consideration.

The Eu^{III} ion on threefold rotation axis is coordinated by N_6O_3 donor atoms of three unsymmetrical NNO tridentate ligands $HL^{D\text{-}ala}$ or $HL^{L\text{-}ala}$ and the Eu^{III} complex has saturated coordination number of nine, where one imidazole and one imine nitrogen atoms, and one carboxylate oxygen atom per ligand coordinate to a Eu^{III} ion to give adjacent two five-membered chelate rings. The coordination bond distances are Eu–N(2) (imidazole) = 2.582(6) Å, Eu–N(3) (imine) = 2.553(7), and Eu–O(1) (carboxylate oxygen) = 2.395(4) Å. The coordination geometry is described as a tricapped trigonal prism (TTP) [29,30], whose geometry is observed for Gd^{III} complex of three linear tridentate ligands ($[Gd(oda)_3]oda\cdot H_2O$; oda = oxydiacetate dianion) [31]. Three imidazole nitrogen atoms generated by C_3 symmetry operations to N(2) and three carboxylate oxygen atoms generated by C_3 symmetry operations to O(1) form the two outer triangular faces, and the capping positions are occupied by three imine nitrogen atoms generated by C_3 symmetry operations to N(3).

Fig. 2(a) and (b) show the manner of the hydrogen bonds around ‘*fac*’-$[Eu^{III}(HL^{D\text{-}ala})_3]$. The carboxylate oxygen atom O(2) is

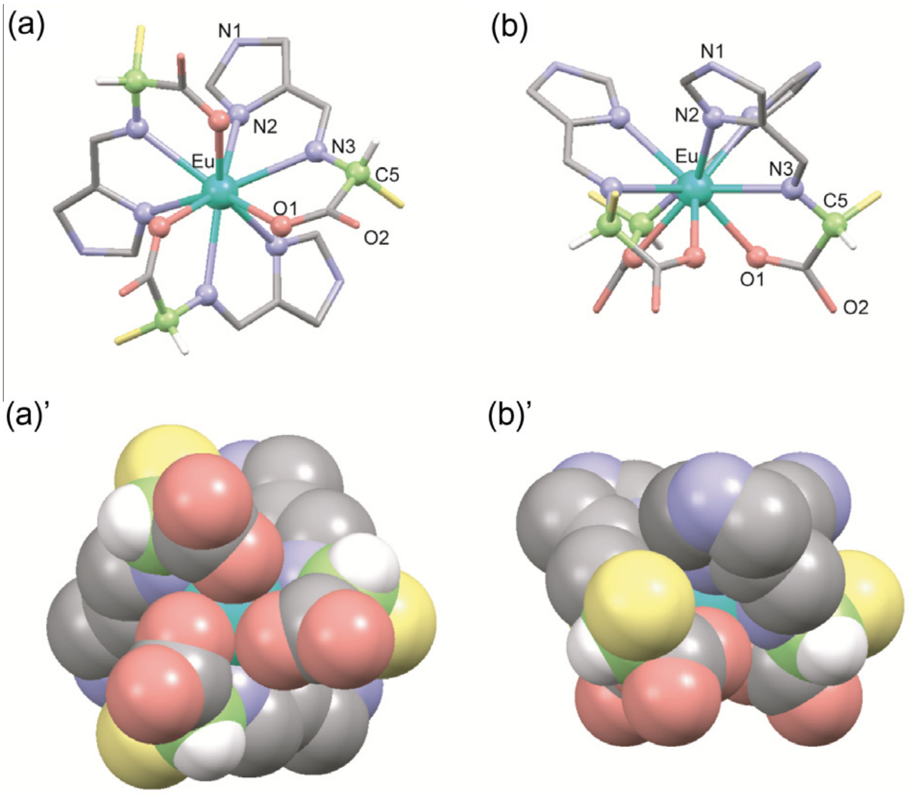

Fig. 1. (a) Molecular structure of ‘*fac*’-$[Eu^{III}(HL^{D\text{-}ala})_3]$ viewed along the C_3 axis with the selected atom numbering scheme, showing ‘*facial*’ configuration and coordination geometry of tricapped trigonal prism (TTP). Three imidazole nitrogen atoms N2 and three carboxylate oxygen atoms O1 form the two outer triangular faces, and the capping positions are occupied by three imine nitrogen atoms N3. Hydrogen atoms except for those bound for the asymmetric carbon atoms are omitted for clarity. (a′) Space filling representation. (b) Side view of ‘*fac*’-$[Eu^{III}(HL^{D\text{-}ala})_3]$. (b′) Space filling representation.

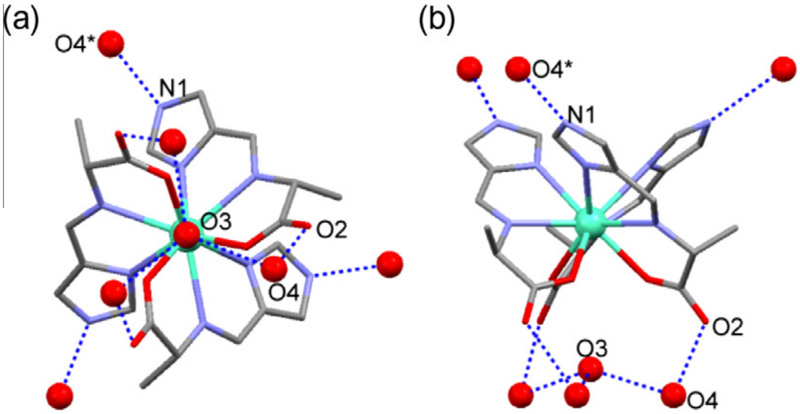

Fig. 2. (a) Hydrogen bonding manner around '*fac*'-[$Eu^{III}(HL^{D\text{-}ala})_3$] viewed along the C_3 axis. (b) Side view of the hydrogen bonding manner, showing the carboxylate side of the molecule is covered by the hydrogen bonds consisting of two water molecules O(3) and O(4) and the imidazole side is hydrogen bonded to the symmetry related water molecule O(4)*.

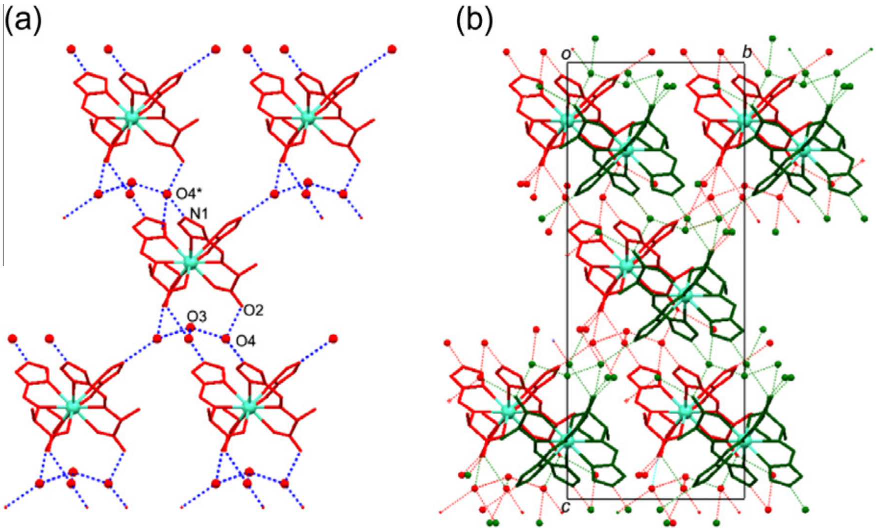

Fig. 3. (a) Homochiral 3D network structure constructed by the hydrogen bonds of O(2)···O(4) and O(4)···N(1)* viewed projected on the *bc*-plane, showing all the constituting molecules with the same chirality are arrayed in the same direction (*c*-axis). (b) Packing diagram of two 3D networks with opposite chiralities (red and green) in the crystal lattice, showing the different directions of the two 3D networks. (Color online.)

hydrogen bonded to a water molecule O(4) with O(2)···O(4) = 2.690(10) Å. Three O(4) oxygen atoms generated by C_3 symmetry operations are hydrogen bonded to a water molecule O(3) on C_3 rotation axis with O(3)···O(4) = 2.762(6) Å. As shown in Fig. 2(a) and (b), three O(3)···O(4) and three O(4)···O(2) hydrogen bonds cover or cap the carboxylate side of the complex. Three imidazole nitrogen atom N(1) of a '*fac*'-[$Eu^{III}(HL^{D\text{-}ala})_3$] at the imidazole side are hydrogen bonded to O(4)* generated by the symmetry operation with N(1)···O(4)* = 2.780(8) Å. In turn, the water oxygen atom O(4) is hydrogen bonded to the imidazole nitrogen atom N(1)* of the adjacent '*fac*'-[$Eu^{III}(HL^{D\text{-}ala})_3$], in addition to the hydrogen bonds of O(4)···O(2) and O(4)···O(3). Thus the water molecule O(4) plays a linker between adjacent complexes, where the species with same chirality are linked by the hydrogen bonds through O(4) to form a homo-chiral 3D network structure. Fig. 3(a) shows the homo-chiral 3D network structure viewed perpendicular to the *b*-axis, in which the 3D network with the opposite chirality is omitted in Fig. 3(a). In the crystal lattice, all the '*fac*'-[$Eu^{III}(HL^{D\text{-}ala})_3$] species (red color) of the 3D network are arrayed in the same direction and all the '*fac*'-[$Eu^{III}(HL^{L\text{-}ala})_3$] species (green color) are arrayed in the opposite direction. Two 3D networks with opposite chiralities are weakly linked by a water molecule O(5) through the two hydrogen bonds of O(4)···O(5) = 2.735(17) Å and O(5)···O(2)** = 2.703(18) Å to complete the crystal structure. The thermal parameters of O(5), which plays a role of linker between two 3D networks, are extremely large compared to those of O(3) and O(4), suggesting that the interaction between two 3D networks with the opposite chiralities is week.

The D-Fourier synthesis located another peak at the special position assignable to the water molecule O(6), whose thermal parameters are even larger than those of O(5). The TGA analysis detected 8 crystal waters, which were found by the X-ray analysis (O3 × 1, O4 × 3, O5 × 3, O6 × 1). In the heating mode from room temperature to 130 °C, the weight loss of $8H_2O$ was observed, but the sample absorps the amount of $7H_2O$ from the atmospheric moisture in the cooling mode to room temperature. The TGA data as well as the X-ray structural analysis demonstrate that these water molecules are essential for the formation of the crystal structure. The lost one water must be O(6).

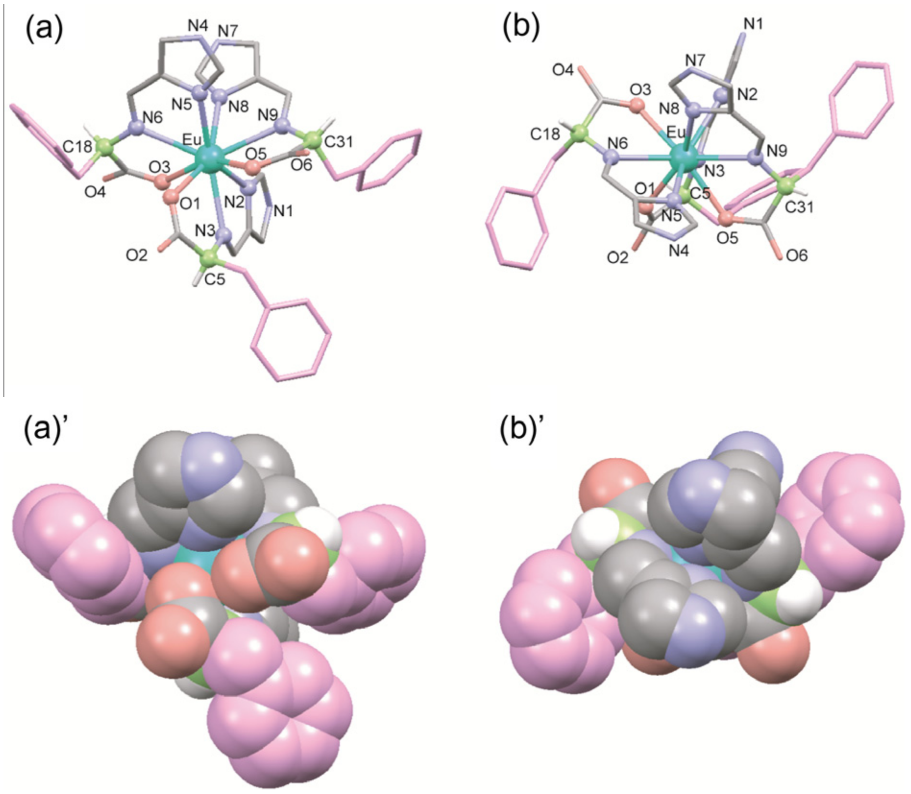

Fig. 4. (a) Molecular structure of '*mer*'-[Eu^{III}(HL$^{D\text{-}phe}$)$_2$(HL$^{L\text{-}phe}$)] with the selected atom numbering scheme, showing '*meridional*' configuration and coordination geometry of capped square antiprism (CSAP). Two imidazole nitrogen atoms of two tridentate ligands and one carboxylate oxygen atom of one ligand (N2, N8, O3) form the one outer triangular face, two carboxylate oxygen atoms and one imidazole nitrogen atom (O1, O5, N5) form the another outer triangular face, and the capping positions are occupied by three imine nitrogen atoms (N3, N6, N9). Hydrogen atoms except for those bound for the asymmetric carbon atoms are omitted for clarity. (a′) Space filling representation of '*mer*'-[Eu^{III}(HL$^{D\text{-}phe}$)$_2$(HL$^{L\text{-}phe}$)]. (b) Side view of '*mer*'-[Eu^{III}(HL$^{D\text{-}phe}$)$_2$(HL$^{L\text{-}phe}$)]. (b′) Space filling representation.

3.2.2. Crystal structure of '*mer*'-[Eu^{III}(HL$^{DL\text{-}phe}$)$_3$]·7.75H$_2$O (**2**)

The complex **2** crystallized into a centrosymmetric tetragonal space group $I4_1/a$ (No. 88) with $Z = 16$. The crystallographic unique unit consists of one '*mer*'-[Eu^{III}(HL$^{DL\text{-}phe}$)$_3$] and several water molecules as the crystal solvents. In the crystal lattice two enantiomers related by an inversion center, '*mer*'-[Eu^{III}(HL$^{D\text{-}phe}$)$_2$(HL$^{L\text{-}phe}$)] and '*mer*'-[Eu^{III}(HL$^{D\text{-}phe}$)(HL$^{L\text{-}phe}$)$_2$], exist. Fig. 4 shows the molecular structure of '*mer*'-[Eu^{III}(HL$^{D\text{-}phe}$)$_2$(HL$^{L\text{-}phe}$)] involving two HL$^{D\text{-}phe}$ and one HL$^{L\text{-}phe}$, in which two of three ligands with NNO donor set array in the same direction and one ligand arrays in the opposite direction forming '*meridional*' configuration. The Eu^{III} ion is coordinated by N$_6$O$_3$ donor atoms of three tridentate ligands and the coordination geometry is approximately described as a capped square antiprism (CSAP). In the CSAP geometry with the '*meridional*' configuration, two imidazole nitrogen atoms of two tridentate ligands and one carboxylate oxygen atom of one ligand (N2, N8, O3) form the one outer triangular face, two carboxylate oxygen atoms and one imidazole nitrogen atom (O1, O5, N5) form the another outer triangular face, and the capping positions are occupied by three imine nitrogen atoms (N3, N6, N9). Three Eu–O distances are 2.397(9)–2.448(8) Å, and three Eu–N(imine) distances are 2.548(9)–2.596(9) Å, and three Eu–N(imidazole) distances are 2.569(9)–2.589(9) Å.

Two intermolecular imidazole···carboxylate hydrogen bonds of N(1)···O(5)* = 2.837(12) Å and O(4)···N(4)* = 2.694(14) Å are repeated to gives a one-dimensional chain structure, where the chain consists of two enantiomers (DDL)$_{1\infty}$ (above) or (DLL)$_{1\infty}$ (below). The chain structure of (DDL)$_{1\infty}$ is shown in Fig. 5(a). As shown in Fig. 5(b), the adjacent chains with (DDL)$_{1\infty}$ and (DLL)$_{1\infty}$ were hydrogen-bonded through a crystal water O(10) (gray) with N(7)···O(10) = 2.744(16) Å and O(2)···O(10) = 2.637(16) Å. Another two crystal waters O(7) and O(4) are hydrogen bonded to the carboxylate

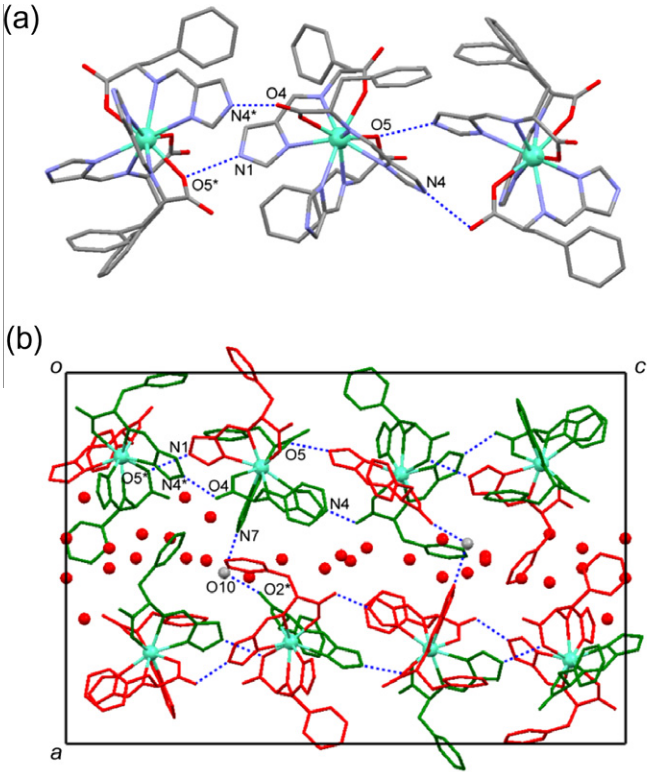

Fig. 5. (a) One-dimensional structure of '*mer*'-[Eu^{III}(HL$^{L\text{-}phe}$)$_2$(HL$^{D\text{-}phe}$)] running along the *c*-axis constructed by intermolecular imidazole···carboxylate hydrogen bonds. (b) The adjacent chains with (DDL)$_{1\infty}$ and (DLL)$_{1\infty}$ are lined by hydrogen-bonds through a crystal water O(10).

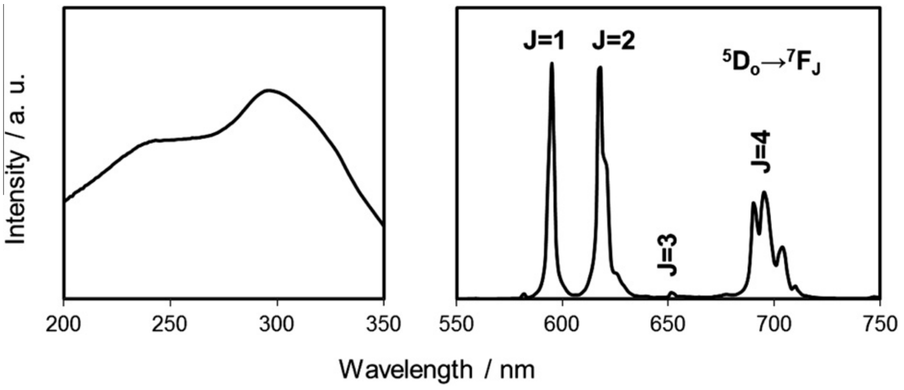

Fig. 6. Excitation and emission spectra of '*fac*'-$[\mathrm{Eu^{III}(HL^{DL\text{-}ala})_3}]\cdot 8H_2O$ (**1**) in the solid state at room temperature. The emission spectrum was measured by excitation at 296 nm.

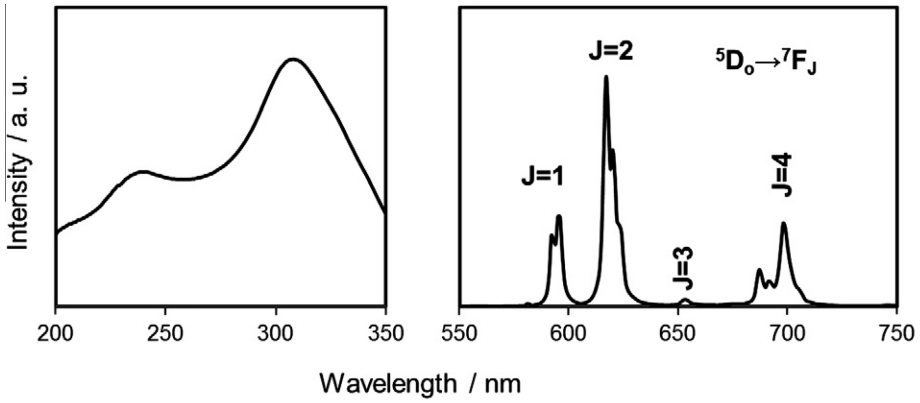

Fig. 7. Excitation and emission spectra of '*mer*'-$[\mathrm{Eu^{III}(HL^{DL\text{-}phe})_3}]\cdot 7.75H_2O$ (**2**) in the solid state at room temperature. The emission spectrum was measured by excitation at 309 nm.

oxygen atoms of '*mer*'-$[\mathrm{Eu^{III}(HL^{L\text{-}phe})_2(HL^{D\text{-}phe})}]$ with O(7)$\cdots$O(4) = 2.67(4) Å and O(14)$\cdots$O(6) = 2.99(4) Å. The several other peaks assignable to the crystal waters were located on the D-Fourier but the thermal parameters were extremely large. Three crystal waters of O(7), O(10), and O(14) are bound by the hydrogen bonds, but the other crystal waters can easily eliminate, being consistent with the TGA result.

3.3. Luminescence properties

Bright red luminescence based on the f–f transitions is visibly observed for '*fac*'-$[\mathrm{Eu^{III}(HL^{DL\text{-}ala})_3}]\cdot 8H_2O$ (**1**) and '*mer*'-$[\mathrm{Eu^{III}(HL^{DL\text{-}phe})_3}]\cdot 7.75H^2O$ (**2**) when the samples in the solid state were irradiated by UV light. The excitation and emission spectra of **1** and **2** in the solid state are shown in Figs. 6 and 7. Broad bands in the range of 200–350 nm at the maximum around 300 nm were observed in the excitation spectra of both **1** and **2**. On the other hand, the emission spectra of **1** and **2** show a different pattern. The emission spectrum of **1** displays emission bands at 582 nm ($^5D_0 \rightarrow {}^7F_0$), 595 nm ($^5D_0 \rightarrow {}^7F_1$), 618 nm ($^5D_0 \rightarrow {}^7F_2$), 651 nm ($^5D_0 \rightarrow {}^7F_3$), and 690, 695, 704, 710 nm ($^5D_0 \rightarrow {}^7F_4$). The emission spectrum of **2** displays emission bands at 581 nm ($^5D_0 \rightarrow {}^7F_0$), 592, 595 nm ($^5D_0 \rightarrow {}^7F_1$), 617, 620 nm ($^5D_0 \rightarrow {}^7F_2$), 653 nm ($^5D_0 \rightarrow {}^7F_3$), and 687, 692, 698 nm ($^5D_0 \rightarrow {}^7F_4$). A single peak is observed for the $^5D_0 \rightarrow {}^7F_1$ transition of **1**, whereas splitting two peaks are observed for that of **2**, although the amounts of fluorescence (total area of the emission bands) of the emission bands for the $^5D_0 \rightarrow {}^7F_1$ transition are almost the same [32]. Moreover, the amount of fluorescence of the emission bands for the $^5D_0 \rightarrow {}^7F_2$ transition of **2** is 1.7 times larger than those of **1**. The $^5D_0 \rightarrow {}^7F_1$ transition is magnetic-dipolar in character, and the emission intensity of the transition is relatively independent of the coordination environment around the europium(III) ion. On the other hand, the $^5D_0 \rightarrow {}^7F_2$ transition is predominantly electric-dipolar in character, and the emission intensity of the transition is very sensitive to the coordination environment around the europium(III) ion [33–35]. These different emission spectra of **1** and **2** may be caused by the different coordination environment around the europium ion: the '*fac*'-coordination environment for **1**, and the '*mer*'-coordination environment for **2** with lower symmetry.

The luminescence quantum yields in the solid state obtained by an absolute method at room temperature (λ_{ex} = 302 nm) is 0.25 for **1**, and 0.30 for **2**, respectively. The luminescence life times in the solid state obtained at room temperature (λ_{ex} = 302 nm) is 1.40 ms for **1**, and 1.23 ms for **2**, respectively.

Acknowledgements

H. Hagiwara was supported by the Research Fellowship for young scientists of the Japan Society for the Promotion of Science.

Appendix A. Supplementary data

CCDC 885087 and 885088 contain the supplementary crystallographic data for $[\mathrm{Eu^{III}(HL^{DL\text{-}ala})_3}]\cdot 8H_2O$ (**1**) and $[\mathrm{Eu^{III}(HL^{DL\text{-}phe})_3}]\text{-}\cdot 7.75H^2O$ (**2**). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge

Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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