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Circularly polarized luminescence from chiral Eu(III) Complex with high emission quantum yield

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ABSTRACT

Luminescent Eu(III) complex with axis-chiral ligand, [Eu((*R*)-BINAPO)(hfa)$_3$] ((*R*)-BINAPO: (*R*)-2,2′-bis(diphenylphosphoryl)-1,1′-binaphthyl, hfa: 1,1,1,5,5,5-hexa-fluoropentanedione) was synthesized. Its emission quantum yield and the emission lifetime in acetone-d_6 were found to be 0.53 and 2.1 ms, respectively. The circularly polarized luminescence of the Eu(III) complex was also measured. The dissymmetry factor at the magnetic dipole transition ($|g_{lum}|$) of [Eu((*R*)-BINAPO)(hfa)$_3$] was found to be 0.03.

1. Introduction

Lanthanide(III) complexes with narrow emission bands, ideal four level transitions and long emission lifetimes have been regarded as attractive luminescent molecules for optical devices, laser materials, EL displays, and bio-sensing engineering [1]. Luminescent lanthanide(III) complexes having chiral ligands show the strong circularly polarized luminescence (CPL) [2]. Especially, the CPL properties of the magnetic dipole transition in Eu(III) complexes (λ_{em} = 595 nm) have been extensively studied because of their large dissymmetry factors (g_{lum}) [3]. In the previous literatures, Parker and Riehl have reported the CPL properties of the lanthanide(III) complexes with chiral tetraazacyclododecane (DOTA) derivatives [4]. Furthermore, Petoud has successfully synthesized Eu(III) complexes having four chiral points [5]. Previous chiral ligands in Eu(III) complexes contained the high-frequency vibrational coordination sites (at around 1600 cm^{-1}) linked with numerous C—H chemical bonds (C—H: 2950 cm^{-1}). Their chemical components might lead to increase in the radiationless transitions via vibrational relaxations of the chiral Eu(III) complexes [6]. In order to enhance the emission quantum yields of the chiral Eu(III) complexes, the chiral ligands should be composed of the low-frequency vibrational coordination sites, phosphine oxides (P═O: 1125 cm^{-1}) [7a]. Phosphine oxides with chiral structures are expected to be promising ligands for chiral Eu(III) complexes having high emission quantum yields.

Here, we report on a novel Eu(III) complex having axis-chiral phosphine oxide ligand, [Eu((*R*)-BINAPO)(hfa)$_3$] bearing (*R*)-2,2′-bis(diphenylphosphoryl)-1,1′-bi-naphthyl ((*R*)-BINAPO) and 1,1,1,5,5,5-hexafluoropentane-2,4-dione (hfa) ligands (Fig. 1). The introduction of chiral (*R*)-BINAPO ligand provides the chiral coordination structure around the Eu(III) ion center. The coordination sites of (*R*)-BINAPO are composed of the low-frequency vibrational P═O bonds which lead to increased emission quantum yield [7]. The low-frequency vibrational hfa ligand which contains C—F bonds also contributes to the suppression of the nonradiative transitions [6]. Furthermore, Eu(III) complex coordinated with three hfa ligands and one bidentate phosphine oxide ligand, [Eu((*R*)-BINAPO)(hfa)$_3$], is expected to form square antiprism (SAP) structures with no inversion center, and to show increased intensity of the electric dipole transitions related to change of odd parity[7]. A highly luminescent Eu(III) complex with achiral bidentate phosphine oxide ligand, [Eu(BIPHEPO)(hfa)$_3$] (BIPHEPO; 2,2′-bis(diphenylphosphoryl)-1,1′-biphenyl) is also prepared for the comparison of the emission and CPL properties of [Eu((*R*)-BINAPO)(hfa)$_3$]. Emission spectra, emission quantum yields, emission lifetimes and CPL spectra of the chiral [Eu((*R*)-BINAPO)(hfa)$_3$] and achiral [Eu(BIPHEPO)(hfa)$_3$] are studied. We also estimated the dissymmetry factors of the chiral Eu(III) complex by using the CPL spectrum. In present paper, chiral Eu(III) complex

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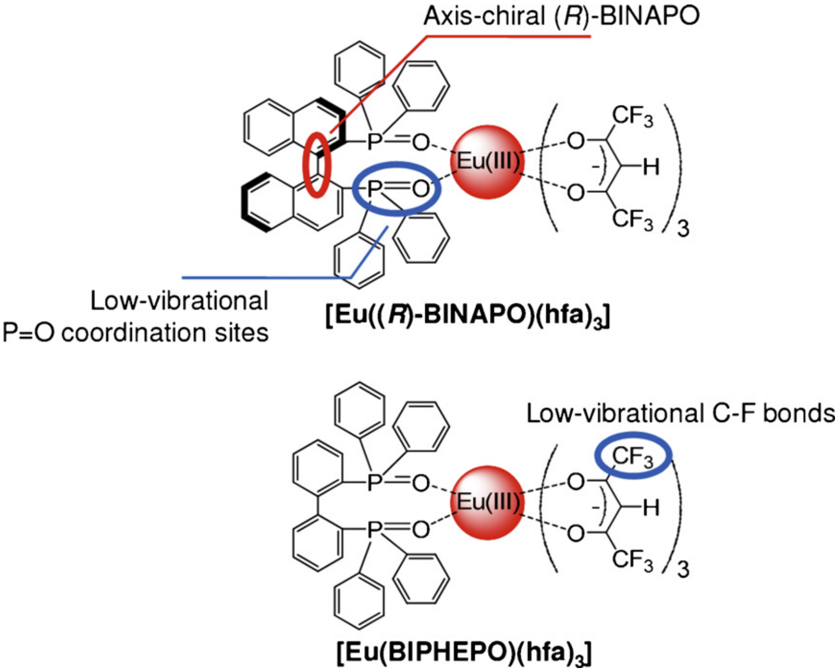

Fig. 1. Chemical structures of [Eu((*R*)-BINAPO)(hfa)$_3$] and [Eu(BIPHEPO)(hfa)$_3$].

having the high emission quantum yield is demonstrated for the first time.

2. Experimental

2.1. Apparatus

^{1}H NMR spectra were obtained with JEOL AL-300 spectrometers. Infrared spectra were recorded with a JASCO FT/IR-4200 spectrometer. Elemental analyses were performed with a Perkin Elmer, 2400 II.

2.2. Materials

(*R*)-BINAP and BIPHEP were purchased from Tokyo Chemical Industry Co., Ltd. Europium(III) acetate tetrahydrate (99.9%) and acetone-d_6 (99.9%) were obtained from Wako Pure Chemical Industries, Ltd. TPPO and hfa were purchased from Aldrich Chemical Co. Inc. All other organic compounds were reagent grade and used as received. (*R*)-BINAPO and BIPHEPO were prepared by oxidation of (*R*)-BINAP and BIPHEP, according to the literature procedure [8]. [Eu(BIPHEPO)(hfa)$_3$] was prepared according to the previous procedure [7b].

2.3. Preparation of tris(hexafluoroacetylacetonato)Europium(III)((R)-2,2′-bis-(diphenylphosphoryl)-1,1′-binaphthyl) ([Eu((R)-BINAPO)(hfa)3])

[Eu(hfa)$_3$(H$_2$O)$_2$] was prepared to the procedure described in our previous reports[7]. [Eu(hfa)$_3$(H$_2$O)$_2$] (1.3 g, 1.5 mmol) and (*R*)-BINAPO (1.0 g, 1.5 mmol) were dissolved in methanol (80 mL) and refluxed under stirring for 12 h. The solvent was removed using rotary evaporator from the reaction mixture. Obtained powder was then dissolved in toluene and insoluble residue was removed by the filtration. Powder was obtained after removal of solvent. Obtained powder was dried under vacuum and recrystallized from hot chloroform/n-hexane and gave white solids. Yield: 40%. ^{1}H NMR (acetone-d_6, 300 MHz, 298 K) δ: 8.4–6.4 (m, Aromatic), 5.9–5.7 (s) ppm. IR (ATR): 3800–3550 (w, O—H), 3060 (w, C—H), 1650 (s, C═O), 1600–1460 (m, br), 1440 (s), 1250–1050 (s, C—F), 1200 (s, P═O), 690 (s, Aromatic) cm^{-1}. Anal. Found: C, 51.08; H, 2.51%. Calcd. for $EuC_{59}H_{35}O_8F_{18}P_2$ 0.25 toluene: C, 51.11; H, 2.61%.

2.4. Optical measurements

Acetone-d_6 solutions (1.0 mM) of the Eu(III) complexes in quartz cells were treated with N$_2$ bubbling for emission spectra, emission quantum yields, emission lifetimes and CPL spectra measurements. The emission spectra were measured at room temperature using JASCO FP-6500 and ACTON Research Corporation SpectraPro 2300i system with a cooled CCD detector (Roper PIXIS 100). The spectra were corrected for detector sensitivity and lamp intensity variations. The emission quantum yield of [Eu((*R*)-BINAPO)(hfa)$_3$] excited at 465 nm was evaluated using JASCO V-660 and HITACHI F-4500. The value was corrected with [Eu(BIPHEPO)(hfa)$_3$] solution dissolved in acetone-d_6 ($\Phi = 0.60$) as a reference[9]. In the emission lifetime measurements, the samples were excited by a N$_2$ laser (Usho KEC-160, wavelength; 337 nm, pulse width; 600 ps, 10 Hz). The emission profile was recorded using a streak camera (Hamamatsu, picosecond fluorescence measurement system, C4780). The CPL spectra were measured with a JASCO CPL-200 spectrometer. Obtained emission quantum yields and emission lifetimes have uncertainness with approximately ±5.0% and ±0.02 ms, respectively.

3. Results and discussion

3.1. Emission properties

The emission spectra of [Eu((*R*)-BINAPO)(hfa)$_3$] and [Eu(BIPHEPO)(hfa)$_3$] under excitation at 365 nm (excited at π–π^* transitions of hfa ligands) are shown in Fig. 2. The emission bands were observed at 578 nm, 593 nm, 611 nm, 650 nm and 700 nm. These bands were attributed to the *f*–*f* transitions,

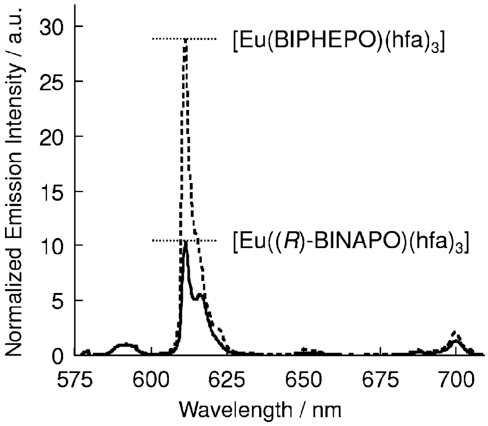

Fig. 2. Normalized emission spectra of [Eu((*R*)-BINAPO)(hfa)$_3$] (solid line) and [Eu(BIPHEPO)(hfa)$_3$] (dashed line) (excited at 365 nm, optical path: 10 mm).

$^5D_0 \rightarrow {}^7F_0$ (forbidden transition), $^5D_0 \rightarrow {}^7F_1$ (the magnetic dipole transition) and $^5D_0 \rightarrow {}^7F_J$ (J = 2,3,4, the electric dipole transitions), respectively. The emission spectra were normalized with respect to the magnetic dipole ($^5D_0 \rightarrow {}^7F_1$) transition. The strongest emission bands of those Eu(III) complexes, the $^5D_0 \rightarrow {}^7F_2$ transition corresponds to the electric dipole transitions. The probability of the electric dipole transition markedly depends on the symmetry of the coordination structure around Eu(III) ion [10]. In order to estimate the effects of the coordination structures, we calculated the relative integrated emission intensity of the $^5D_0 \rightarrow {}^7F_2$ transitions ($A_{rel} = A_{611}/A_{593}$). The A_{rel} values of [Eu((*R*)-BINAPO)(hfa)$_3$] and [Eu(BIPHEPO)(hfa)$_3$] were found to be 8.1 and 16.0, respectively. It is well known that the ligand fields with low symmetry in Eu(III) complexes enhance the probability of the electric dipole transitions and increase the A_{rel} values [11]. Relatively large A_{rel} values of these Eu(III) complexes would be associated with the low-symmetrical coordination structures and their electric dipole transitions would be sufficiently allowed. The A_{rel} value of [Eu((*R*)-BINAPO)(hfa)$_3$] was smaller than that of [Eu(BIPHEPO)(hfa)$_3$]. The smaller A_{rel} of [Eu((*R*)-BINAPO)(hfa)$_3$] might be caused by the relatively high symmetrical structure.

The emission quantum yields of [Eu((*R*)-BINAPO)(hfa)$_3$] and [Eu(BIPHEPO)(hfa)$_3$] were found to be 0.53 and 0.60, respectively. These high emission quantum yields of these Eu(III) complexes are due to the suppression of vibrational relaxations by using low-frequency vibrational hfa ligands. In our previous paper, lanthanide(III) complexes covered with low-frequency vibrational ligands ([Nd(hfa)$_3$] and [Nd(pos)$_3$]) showed strong luminescent properties [7a]. Low-frequency vibrational C—F bonds (1200 cm^{-1}) result in small Franck–Condon factors related to vibrational relaxations. In non-deuterated acetone, the emission quantum yields of [Eu((*R*)-BINAPO)(hfa)$_3$] and [Eu(BIPHEPO)(hfa)$_3$] were found to be 0.38 and 0.44, respectively. The emission decays of [Eu((*R*)-BINAPO)(hfa)$_3$] and [Eu(BIPHEPO)(hfa)$_3$] were measured, and the single-exponential decay profiles were observed. From logarithmic plots of decay profiles, the emission lifetimes of [Eu((*R*)-BINAPO)(hfa)$_3$] and [Eu(BIPHEPO)(hfa)$_3$] in acetone-d_6 were found to be 2.1 ms and 1.1 ms, respectively.

Here, we estimated the radiative and nonradiative rate constants (k_r and k_{nr}) of [Eu((*R*)-BINAPO)(hfa)$_3$] and [Eu(BIPHEPO)(hfa)$_3$] based on the emission quantum yields and the emission lifetimes. The k_r and k_{nr} of [Eu((*R*)-BINAPO)(hfa)$_3$] were found to be $4.8 \times 10^2\ \mathrm{s}^{-1}$ and $4.2 \times 10^2\ \mathrm{s}^{-1}$, respectively. These values of [Eu((*R*)-BINAPO)(hfa)$_3$] were smaller than those of [Eu(BIPHEPO)(hfa)$_3$] ($k_r = 9.1 \times 10^2\ \mathrm{s}^{-1}$, $k_{nr} = 6.1 \times 10^2\ \mathrm{s}^{-1}$). The relatively smaller k_r value of [Eu((*R*)-BINAPO)(hfa)$_3$] might be linked to the geometrical structure of this Eu(III) complex. The geometrical structure of Eu(III) complex with achiral bidentate phosphine oxide ligand, [Eu(BIPHEPO)(hfa)$_3$] has been determined to be a square antiprism structure (The symmetrical group: C_1) [7b]. According to the estimations of the radiative rates, the geometrical structure of [Eu((*R*)-BINAPO)(hfa)$_3$] might be more symmetric than that of [Eu(BIPHEPO)(hfa)$_3$]. We propose that the smaller A_{rel} of [Eu((*R*)-BINAPO)(hfa)$_3$] is due to the symmetrical coordination structures related to odd parity.

3.2. *Circularly polarized luminescence (CPL) properties*

The circularly polarized luminescence (CPL) spectrum of [Eu((*R*)-BINAPO)(hfa)$_3$] was also measured as shown in Fig. 3. CPL intensity (ΔI) is expressed by the difference between left- and right-circularly polarized luminescent intensities, I_L and I_R. We found the distinct CPL signals in the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions. On the other hand, the CPL signals of Eu(III) complex with achiral ligands, [Eu(BIPHEPO)(hfa)$_3$] were not observed.

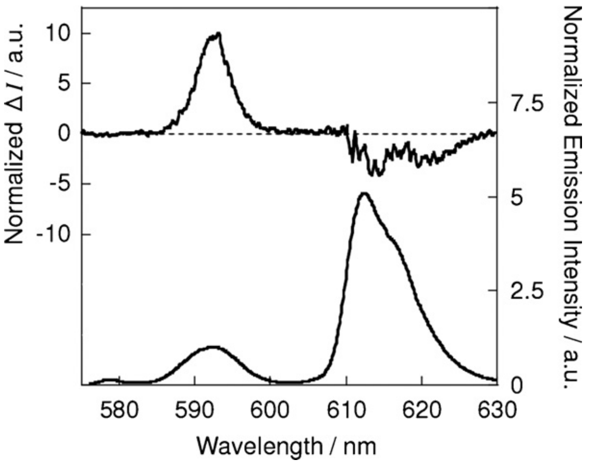

Fig. 3. Normalized emission (under) and CPL (upper) spectra of [Eu((*R*)-BINAPO)(hfa)$_3$] (excited at 350 nm, optical path: 10 mm).

We estimated the dissymmetry factor (g_{lum}) based on the CPL spectrum [12]. The g_{lum} values are given by,

$$g_{lum} = \frac{\Delta I}{1/2(I)} = \frac{I_L - I_R}{1/2(I_L + I_R)} \tag{1}$$

The g_{lum} values of [Eu((*R*)-BINAPO)(hfa)$_3$] at the magnetic and electric dipole transitions were estimated to be 0.03 and −0.003, respectively. The g_{lum} value at the magnetic dipole transition of [Eu((*R*)-BINAPO)(hfa)$_3$] was similar to that of reported Eu(III) complex with chiral 1,1′-binaphthyl-2,2′-diyl phosphate ligands (g_{lum} = ca. 0.04) [13]. CPL properties of [Eu((*R*)-BINAPO)(hfa)$_3$] seem to be induced by the coordination of the axis-chiral bidentate ligand.

4. Conclusion

We successfully synthesized a novel strong luminescent Eu(III) complex with chiral (*R*)-BINAPO and low-frequency vibrational hfa ligands. The high emission quantum yield and the CPL property of Eu(III) complex were achieved by the coordination of the axis-chiral phosphine oxide. The chiral Eu(III) complex with effectively luminescent properties would open up the novel photo-functional materials.

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