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High lasing oscillation efficiency of Eu(III) complexes having remarkably sharp emission band

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Abstract

Luminescent Eu(III) complexes with bis-phosphine oxide ligands were synthesized. Geometric structures of novel Eu(III) complexes were determined by single-crystal X-ray diffraction. One of the Eu(III) complexes showed remarkably sharp red emission and large stimulated emission cross-section (full width at half maximum (FWHM) = 2.1 nm, stimulated emission cross-section = 1.80×10^{-20} cm^2). The sharpness of the emission bands of the Eu(III) complexes was discussed in terms of the symmetry of the geometrical structure.

Keywords: Chemical synthesis; Crystal structure and symmetry; Luminescence; X-ray diffraction

1. Introduction

Lanthanide(III) ions have been regarded as attractive luminescent centers for optical devices, luminescence sensors of chemical species and biomedical assays [1–5]. The photophysical properties depending on the geometrical structure of the Eu(III) complexes was reported by Richardson, Horrocks and co-workers [6,7]. These reports mainly discussed the transition probability or the emission quantum yields of the Eu(III) complexes. However, the full width at half maximum (FWHM) of the emission bands was not directly linked to the geometrical structures of the Eu(III) complexes, though the control of the sharpness of the emission bands is one of the most important factors for laser application [8].

Here, we report the series of novel strong-luminescent Eu(III) complexes which have anti-symmetrical and low vibrational structures (Fig. 1). In order to discuss the relation between the FWHM and structure in liquid media, the *o*,*m*-phenylene and alkyl chains with different length were introduced as linker moieties between bis-phosphine oxide groups. In this work, we have successfully synthesized a Eu(III) complex having remarkably sharp red emission band. The lasing oscillation efficiencies of the Eu(III) complexes were estimated by the calculation of stimulated emission cross-sections. The symmetry of Eu(III) complexes was discussed in terms of the geometrical structures, related to the emission spectra and the stimulated emission cross-sections.

2. Experimental

2.1. Apparatus

^{1}H NMR and ^{19}F NMR data were obtained with a JEOL EX-270 spectrometer. ^{19}F NMR chemical shifts were

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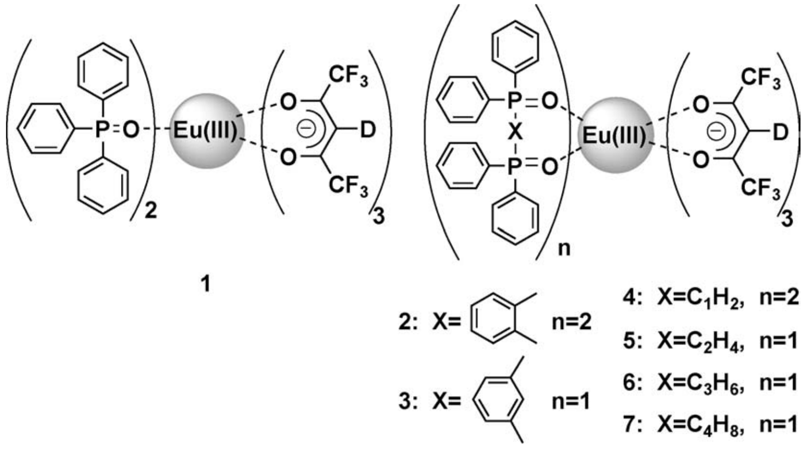

Fig. 1. Chemical structures of **1**–**7**.

determined using hexafluorobenzene as an external standard ($\delta = -162.0$ (s, Ar–F) ppm). Elemental analyses were performed with Perkin-Elmer 240C.

2.2. Materials

Europium acetate tetrahydrate (99.9%), 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfa-H_2) and triphenylphosphine oxide (TPPO) were purchased from Wako Pure Chemical Industries Ltd. 1,1-bis(diphenylphosphino) methane, 1,2-bis(diphenylphosphino) ethane, 1,3-bis(diphenylphosphino) propane and 1,4-bis(diphenylphosphino) butane were purchased from KANTO Chemical Co. Inc. Methanol-d_4 and acetone-d_6 were obtained from Aldrich Chemical Co. Inc. All other chemicals were reagent grade and were used as received.

2.3. Synthesis of novel Eu(III) complexes with bis-phosphine oxide ligands

Tris(hexafluoroacetylacetonato) europium(III) bis(triphenylphospohine oxide) (**1**) was prepared by the reaction of $Eu(hfa)_3(H_2O)_2$ and triphenylphosphine oxide in methanol [9]. Tris(hexafluoroacetylacetonato) europium(III), 1,2-phenylenebis(diphenylphosphine oxide) (**2**) was prepared by reaction between $Eu(hfa)_3(H_2O)_2$ and 1,2-phenylenebis (diphenylphosphine oxide) in methanol under reflux for 8 h. The reaction mixture was concentrated using rotary evaporator. Recrystallization from methanol gave white crystals (**2**). Yield: 56%.

Tris(hexafluoroacetylacetonato) europium(III) 1,3-phenylenebis(diphenylphosphine oxide): **3**, tris(hexafluoroacetylacetonato) europium(III) methylenebis(diphenylphosphine oxide): **4**, tris(hexafluoroacetylacetonato) europium(III) 1,2-ethylenebis(diphenylphosphine oxide): **5**, tris(hexafluoroacetylacetonato) europium(III) 1,3-propylenebis(diphenylphosphine oxide): **6**, tris(hexafluoroacetylacetonato) europium (III) 1,4-butylenebis(diphenylphosphine oxide): **7** were also prepared by the same method as for **1** and **2**. These compounds were identified by ^{1}H NMR, ^{19}F NMR and elemental analysis.

For **2**: ^{1}H NMR (acetone-d_6, 270 MHz, 298 K), δ (ppm) 9.7–9.4 (8H, br), 8.2–8.0 (32H, br), 6.200 (8H, s). ^{19}F NMR (acetone-d_6, 270 MHz, 298 K) δ (ppm) -75.3 (CF_3, s). Anal. found: C, 51.20; H, 3.11; calc. for $C_{75}H_{57}EuF_{18}O_{10}P_4 + 0.80MeOH$: C, 51.89; H, 3.31%. For **3**: ^{1}H NMR (acetone-d_6, 270 MHz, 298 K) δ (ppm) 8.2–7.5 (20H, br), 7.262–7.154 (4H, m). ^{19}F NMR (acetone-d_6, 270 MHz, 298 K) δ (ppm) -77.29 (CF_3, s). Anal. found: C, 43.10; H, 2.21; calc. for $C_{45}H_{33}EuF_{18}O_8P_2$: C, 42.98; H, 2.64%. For **4**: ^{1}H NMR (acetone-d_6, 270 MHz, 298 K) δ (ppm) 8.22 (8H, br), 7.58–7.55 (4H, t), 7.38 (8H, s). ^{19}F NMR (acetone-d_6, 270 MHz, 298 K) δ (ppm) -76.07 (CF_3, s). Anal. found: C, 48.83; H, 3.12; calc. for $C_{65}H_{53}EuF_{18}O_{10}P_4$: C, 48.43; H, 3.31%. For **5**: ^{1}H NMR (acetone-d_6, 270 MHz, 298 K) δ (ppm) 8.99–8.91 (8H, br), 7.78–7.69 (12H, m), 5.38 (2H, s), 0.78 (2H, br). ^{19}F NMR (acetone-d_6, 270 MHz, 298 K) δ (ppm) -76.94 (CF_3, s). Anal. found: C, 40.46; H, 2.37; calc. for $C_{41}H_{33}EuF_{18}O_8P_2$: C, 40.75; H, 2.75%. For **6**: ^{1}H NMR (acetone-d_6, 270 MHz, 298 K) δ (ppm) 9.31 (8H, br), 7.81 (12H, br), 5.35 (2H, br), 0.248 (4H, br). ^{19}F NMR (acetone-d_6, 270 MHz, 298 K) δ (ppm) -76.98 (CF_3, s). Anal. found: C, 41.05; H, 2.39; calc. for $C_{42}H_{35}EuF_{18}O_8P_2$: C, 41.23; H, 2.88%. For **7**: ^{1}H NMR (acetone-d_6, 270 MHz, 298 K) δ (ppm) 9.20 (8H, br), 7.65 (12H, br), 5.55 (2H, br), 0.25 (4H, br), 0.18 (2H, br). ^{19}F NMR (acetone-d_6, 270 MHz, 298 K) δ (ppm) -76.75 (CF_3, s). Anal. found: C, 41.9; H, 2.71; calc. for $C_{43}H_{37}EuF_{18}O_8P_2$: C, 41.73; H, 3.01%.

2.4. Preparation of deuterated Eu(III) complexes in deuterated solvent

Deuterated Eu(III) complexes were obtained by the exchange reaction via keto–enol tautomerism of **1**–**7** with CD_3OD for 6 h under vacuum [9]. Samples for measurements of the luminescence of Eu(III) complexes in organic media were prepared under deoxygenated conditions. Solutions (0.05 M) of the Eu(III) complexes were prepared in 2.0 mL of acetone-d_6 under 10^{-3} torr and then transferred to a quartz cell for optical measurements (optical path length, 5 mm) [9,10].

2.5. Optical measurements

Emission spectra were measured at room temperature using a Spex Fluorolog system. The samples were excited at 465 nm ($^7F_0 \rightarrow {}^5D_2$). The emission lifetimes were determined by using Q-switched Nd:YAG laser (Spectra Physics INDI-50, fwhm = 5 ns, $\lambda = 1064$ nm) and photomultiplier (Hamamatsu Photonics R7400U-03, response time ≤ 0.78 ns). Samples were excited by the third harmonic (355 nm) of the fundamental nanosecond pulse. Nd:YAG response was monitored with a digital oscilloscope (Sony Tektronix, TDS3052, 500 MHz) synchronized to the single-pulse excitation. The emission quantum yields were determined by the standard procedures with an integrating sphere (diameter 6 cm) [9,10].

2.6. Judd–Ofelt analysis

Absorption spectra of Eu(III) complexes were measured at room temperature using a HITACHI U-3300 system. Judd–Ofelt analysis of Eu(III) complexes was carried out using the $^7F_0 \rightarrow {}^5D_2$ transition (465 nm). Concentrations of the Eu(III) complexes in solvent were 0.05 M. Tensor parameters U^λ of Eu(III) are referred in the following literatures [11–13].

2.7. Crystallography

Colorless single-crystals of complexes **2**–**4** were mounted on a glass fiber using epoxy resin. X-ray diffraction intensities were collected with a Rigaku RAPID imaging plate diffractometer at 223 K (for **2** and **4**) and a Rigaku AFC-5R four circle diffractometer (for **3**) at 293 K using Mo Kα radiation in w–2θ scan mode. Corrections for decay and Lorentz-polarization effects were made, with empirical absorption corrections solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotoropically. Hydrogen atoms were placed in calculated positions (C–H, 0.95 Å) but not refined. All calculations were performed using the TEXSAN crystallographic software package.

3. Results and discussion

3.1. Geometrical structures

The crystal structures of Eu(III) complexes **2**–**4** were determined by single-crystal X-ray diffraction. The ORTEP diagrams of complexes **1**–**4** and crystallographic data are shown in Fig. 2 and Table 1 [9], respectively. The com-

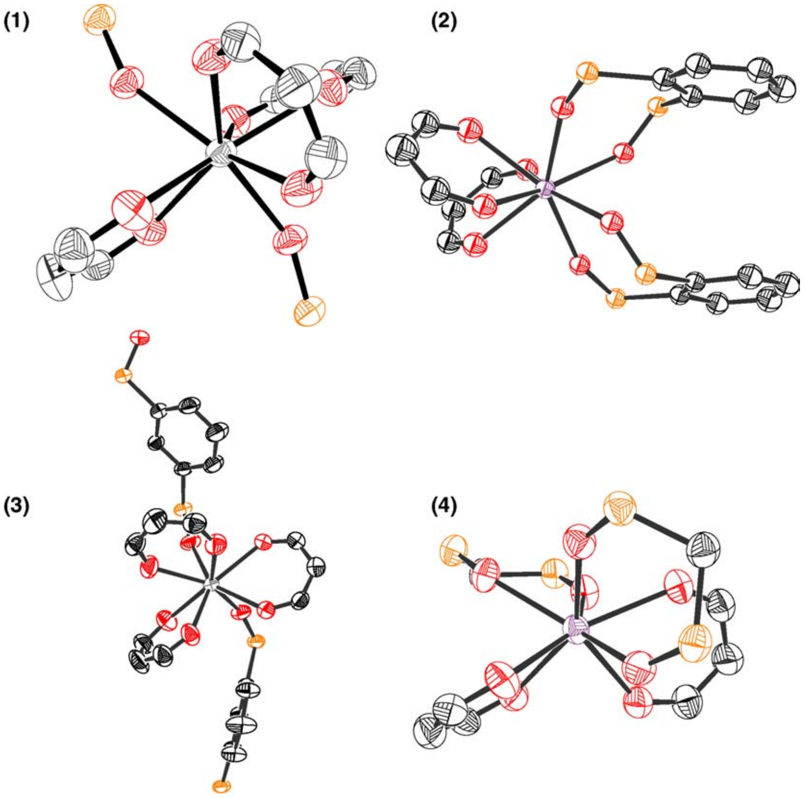

Fig. 2. ORTEP drawing of the complexes **1**–**4**.

Table 1
Summary of crystal data of **2**–**4**, data collection and refinement details

	2	**3**	**4**
Empirical formula	$C_{51}H_{37}EuF_{18}O_8P_2$	$C_{51}H_{37}EuF_{18}O_8P_2$	$C_{65}H_{47}F_{18}EuO_{10}P_4$
Formula weight		1251.58	1605.91
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a (Å)	13.2759(6)	13.913(3)	14.9145(4)
b (Å)	22.4970(8)	22.288(2)	31.8787(9)
c (Å)	24.894(1)	16.510(2)	15.8722(4)
α (°)	90	90	90
β (°)	102.653(2)	92.60(1)	116.0074(6)
χ (°)	90	90	90
V (Å^3)	7254.5(6)	5114(1)	6782.3(3)
Z	4	4	4
Reflections collected	37269	14899	14784
Independent reflections	25028	8535	10712
T (K)	213	296	296
R_{int}	0.111	0.090	0.054
Final R_1, wR_2	0.1628, 0.3681	0.0476, 0.2358	0.0723, 0.1887

plex **3** formed a column structure because the neighboring Eu(III) ions were connected by bis-phosphine ligands. From the coordination site angles, the geometrical structure of complexes **1**–**4** were determined to be an anti-symmetrical square-antiprism. This result indicates that those Eu(III) complexes have no inverted center in crystal field, resulting in an increase in electron transitions in the 4f orbitals due to odd parity. The two P=O groups in the complex **3** occupied the upper square and lower square, respectively. The coordination structure of **3** was similar to that of **1** [9]. The coordination structures of **5**–**7** would be similar coordination structures to those of **1** and **3**. On the other hand, the coordination structures of **2** and **4** were different from those of corresponding **1** and **3**. The central Eu(III) ions in the complexes **2** and **4** were coordinated by two bis-phosphine oxide ligands. One of the two bis-phosphine oxide ligands of the complex **4** bridged the two squares. In contrast, the two bis-phosphine oxide ligands of the complex **2** did not bridge the two squares but simply occupied the two coordination sites of the upper and lower square. The geometrical structure of Eu(III) complex should affect the emission spectrum based on the changes of Stark splitting on the radiative transition of Eu(III) ions.

3.2. Emission properties in liquid media

The emission spectra of **1**–**7** in acetone-d_6, which were synthesized in this study were shown in Fig. 3. The emission spectral shape of the $^5D_0 \rightarrow {}^7F_2$ (electric dipole) transition of **2** and **4** was quite different from those of corresponding **1**, **3**–**7**. The FWHM of the $^5D_0 \rightarrow {}^7F_2$ transition band of **2** was found to be 2.1 nm, and was much smaller than those of **1**, **3**–**7** (FWHM were shown in Table 2). The narrowing of the emission band of the Eu(III) complex was achieved in **2**. Stark splitting and transition probability in the f-orbitals of Eu(III) ion was dependent on symmetry of Eu(III) complexes [14]. Generally, degenerated ^7F_J states of Eu(III) complexes split into some Stark levels (maximum: $2J+1$) according to decreasing of symmetry

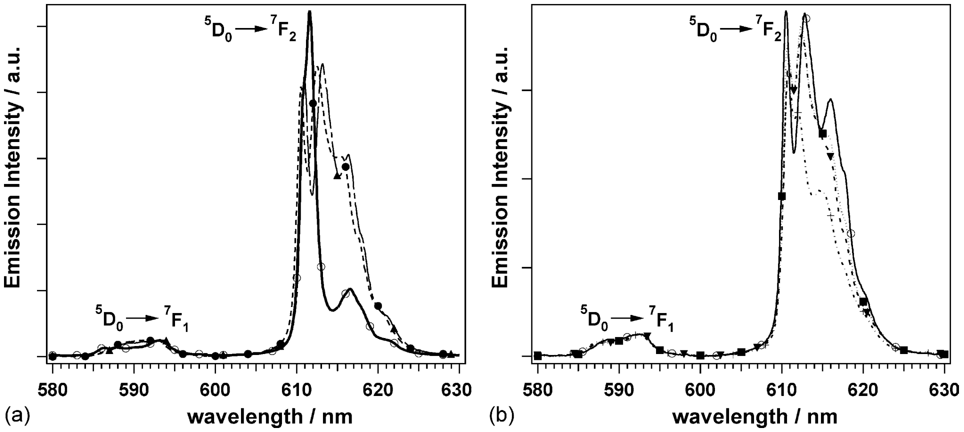

Fig. 3. Emission spectra of Eu(III) complexes in acetone-d_6 (excitation at 465 nm). All spectra were normalized with respect to the $^5D_0 \rightarrow {}^7F_1$ (magnetic dipole) transition. (a) **1** (●), **2** (○) and **3** (▲); (b) **4** (+), **5** (■), 6 (▼) and 7 (○).

Table 2
Photophysical properties of **1**–**7** (emission lifetimes, τ_{obs}, emission quantum yields[a], Φ, Judd–Ofelt parameters[b], Ω_2, Einstein coefficients[c], A and emission cross-sections[d], σ_p, in acetone-d_6)

	τ_{obs}(ms)	Φ	$\Omega_2 \times 10^{-20}$(cm^2)	$A(\times 10^2 s^{-1})$	$\Delta\lambda_{eff}$(nm)	σ_p ($\times 10^{-20}$ cm^2)
1	0.93	0.90	26.2	9.68	7.0	1.42
2	1.28	0.48	14.2	3.75	2.1	1.80
3	0.96	0.91	–[e]	9.47	7.1	1.39
4	0.95	0.55	17.8	5.79	6.0	0.97
5	0.89	0.82	23.6	9.21	6.6	1.41
6	0.98	>0.95	35.6	9.69	6.9	1.42
7	0.93	0.40	31.8	4.30	7.1	0.55

[a] Emission lifetimes of the Eu(III) complexes were measured by the excitation at 355 nm (Nd:YAG 3ω). Emission quantum yields of the Eu(III) complexes were measured by the excitation at 465 nm ($^7F_0 \rightarrow {}^5D_2$) in acetone-$d_6$. Concentrations of Eu(III) complexes were 0.05 M.

[b] Judd–Ofelt parameter Ω_2 is sensitive to the symmetry and sequence of ligand field of lanthanide(III) complexes.

[c] Einstein coefficient was determined using $A = 1/\tau_R = \Phi/\tau_{obs}$.

[d] Emission cross-sections were determined by Eq. (1).

[e] The Ω_2 parameter of **3** was not estimated because of their low solubility. The low solubility of the complex **3** is considered to come from the columnar structure of the complex **3**.

of Eu(III) complexes. The transition from $^5D_0$ state to degenerated $^7F_2$ state leads to narrower emission band than those of the normal transition. The coordination structure of the complex **2** would be much different from those of corresponding **1**, **3**–**7**. From X-ray crystallography and the low Ω_2 value of the Judd–Ofelt analysis (Table 2), we concluded that the symmetry of the complex **2** was higher than those of corresponding **1**, **3**–**7**. The symmetrical structures of **2** induce the degeneration of the Stark levels of the $^7F_2$ state in Eu(III) ion. Degeneration of the Stark levels of the complex **2** would give the unique sharp emission (Fig. 3). The high symmetry in the structure of Eu(III) complex decreases transition probability of the f–f transitions, leading to the longer emission lifetime for complex **2** (Table 2).

In order to construct a high power laser system, a lanthanide(III) complex should show the emission property with large stimulated emission cross-section, which is one of the most important factors for laser amplification. The stimulated emission cross-section can be expressed by:

$$\sigma_p(\lambda_p) = \frac{{\lambda_p}^4}{8\pi c n^2 \Delta\lambda_{eff}} A(bJ' : aJ) \qquad (1)$$

where c, λ_p, $\Delta\lambda_{eff}$, n and A are speed of light, wavelength of oscillation peak, FWHM of oscillation peak, refractive index of the matrix and Einstein coefficient A, respectively [15]. Einstein coefficients A were determined by using the emission quantum yields and the lifetimes ($A = k_r = \Phi/\tau_{obs}$).

According to the Eq. (1), the emission cross-section values of **2** was found to be 1.80×10^{-20} cm^2 (Table 2), which was much larger than those of other corresponding Eu(III) complexes although Einstein coefficient A of **2** was smaller than those of others. We would emphasize that the smaller $\Delta\lambda_{eff}$ (FWHM) value induces the increase of the emission cross-section.

4. Conclusion

In conclusion, we had successfully synthesized the series of Eu(III) complexes with bis-phosphine oxide ligands, and observed that the novel Eu(III) complex **2** achieved remarkably sharp emission and larger stimulated emission cross-section than those of corresponding other Eu(III) complexes with bis-phosphine oxide. We are now examining lasing properties of those series of Eu(III) complexes in relation with stimulated emission cross-section [16]. Since the stimulated emission cross-section of **2** is the same order as the values of Nd–glass laser for practical use ((1.6–4.5) $\times 10^{-20}$ cm^2) [8], the luminescent materials using **2** are promising for application such as the high-power laser medium.

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