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Solvent-dependent luminescence of eight-coordinated Eu(III) complexes with bidentate phosphine oxide

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ABSTRACT

Solvent-dependent luminescence of Eu(III) complexes composed of oxo-linked bidentate phosphine oxide ligands, 4,5-bis(diphenylphosphoryl)-9,9-dimethylxanthene (xantpo), 4,5-bis(di-*tert*-butylphosphoryl)-9,9-dimethylxanthene (*t*Bu-xantpo) and low-vibrational frequency hexafluoroacetylacetonato (hfa) ligands is reported. The Eu(III) complexes, Eu(hfa)₂(xantpo)₂ and Eu(hfa)₃(*t*Bu-xantpo), exhibit eight-coordinated square antiprism and trigonal dodecahedron structure, respectively. Their emission quantum yield, emission lifetime, and radiative and non-radiative rate constant are characterized using acetone, acetone-*d*₆, toluene, chloroform, and DMF. The relationship between photophysical properties and coordination structures of eight-coordinated Eu(III) complexes is discussed for the first time.

Keywords: Complex, Eu(III), Luminescence, Solvent effect

1. Introduction

Lanthanide complexes with characteristic narrow emission bands and long emission lifetimes have been regarded as attractive luminescent materials for use in electroluminescent (EL) devices [1–4], lasers [3, 5] and luminescent bio-sensing applications [6–8]. In general, the luminescence properties of lanthanide complexes derived from $4f-4f$ transitions are dominated by two factors, radiative (k_r) and non-radiative rate constants (k_{nr}). First, radiative rate constants of the lanthanide complexes depend greatly on the geometrical symmetry of the coordination structure. Richardson has estimated the transition intensity parameters of lanthanide complexes from the ligand field [9]. Binnemans has proposed to evaluate the transition intensity by Judd–Ofelt analysis. [10, 11] Since these studies, it has been widely accepted that the radiative transition probability between $4f$ orbitals is enhanced by reducing the geometrical symmetry of coordination structures [12–14]. Second, the emission properties of lanthanide complexes also depend on the vibronic properties, which dominate the kinetics of the non-radiative transition processes. According to the energy gap theory, the non-radiative transition processes are promoted by the presence of ligands and solvents with high-frequency vibrational modes [15].

In order to prepare an intensely luminescent lanthanide complex, a large radiative rate constant

based on reducing the geometrical symmetry and a small non-radiative rate constant by introducing low-vibrational frequency organic ligands should be required [16–19]. Previously, we have reported on two asymmetric Eu(III) complexes with low-vibrational frequency hexafluoroacetylacetonato (hfa) and bidentate phosphine oxide ligands, 4,5-bis(diphenylphosphoryl)-9,9-dimethylxanthene $\text{Eu}(\text{hfa})_2(\text{xantpo})_2$, and 4,5-bis(di-*tert*-butylphosphoryl)-9,9-dimethylxanthene $\text{Eu}(\text{hfa})_3(\text{tBu-xantpo})$ (Fig. 1) [20]. Their coordination geometries are categorized as eight-coordinated square antiprism (8-SAP) and trigonal dodecahedron (8-TDH) structures, respectively [20–22]. Their coordination structures composed of the low-vibrational frequency phosphine oxide and hfa provide Eu(III) complexes with high emission quantum yields and relatively large radiative rate constants in acetone- d_6 ($\text{Eu}(\text{hfa})_2(\text{xantpo})_2$: $\Phi_{\text{f-f}} = 55\%$, $k_{\text{r}} = 4.4 \times 10^2 \text{ s}^{-1}$; $\text{Eu}(\text{hfa})_3(\text{tBu-xantpo})$: $\Phi_{\text{f-f}} = 67\%$, $k_{\text{r}} = 5.5 \times 10^2 \text{ s}^{-1}$). In the photophysical analyses, we also found that the non-radiative rate constant of $\text{Eu}(\text{hfa})_3(\text{tBu-xantpo})$ ($k_{\text{nr}} = 2.7 \times 10^2 \text{ s}^{-1}$) is smaller than that for $\text{Eu}(\text{hfa})_2(\text{xantpo})_2$ ($k_{\text{nr}} = 3.6 \times 10^2 \text{ s}^{-1}$). We here consider that smaller k_{nr} of $\text{Eu}(\text{hfa})_3(\text{tBu-xantpo})$ might be achieved by specific coordination structure, 8-TDH.

In general, the non-radiative process of Eu(III) complex is also affected by their coordination structures in liquid media [16]. The coordination structure in organic solvent could be directly linked to performance of coordination ability of the solvent molecule, which is related to dielectric constant of solvent [23]. In the present study, we focus on solvent-dependent luminescence of two

types of eight-coordinated Eu(III) complexes, $\text{Eu}(\text{hfa})_2(\text{xantpo})_2$ and $\text{Eu}(\text{hfa})_3(\text{tBu-xantpo})$. Their photophysical properties are estimated using the emission quantum yield, emission lifetime, and radiative and non-radiative rate constant in acetone, acetone- d_6 , toluene, chloroform, and DMF. The relationship between photophysical properties and coordination structures of eight-coordinated Eu(III) complexes is discussed for the first time.

2. Experimental

2.1. Materials

Europium acetate monohydrate (99.9%), acetone- d_6 (D, 99.9%), and chloroform- d (D, 99.8%) were purchased from Wako Pure Chemical Industries Ltd. 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, and 4,5-bis(di-*tert*-butylphosphino)-9,9-dimethylxanthene were obtained from Tokyo Kasei Organic Chemicals and Aldrich Chemical Company Inc. All other chemicals and solvents were reagent grade and were used as received.

2.2. Apparatus

Infrared spectra were recorded on a JASCO FT/IR-420 spectrometer. ^1H (300 MHz) and ^{31}P NMR (200 MHz) spectra were recorded on a JEOL ECP-500. Chemical shifts are reported in δ ppm, referenced to an internal tetramethylsilane standard for ^1H NMR and an external 85% H_3PO_4 standard for ^{31}P NMR. Mass spectra were measured using a JEOL JMS-700M Station. Elemental

analyses were performed using a Perkin Elmer 2400II.

2.3. Preparation of Eu(III) complexes

Eu(hfa)₂(xantpo)₂ and Eu(hfa)₃(*t*Bu-xantpo) were prepared to the procedure described in our previous report [20]. Recrystallization from methanol solution gave colorless block crystals of Eu(hfa)₂(xantpo)₂ and Eu(hfa)₃(*t*Bu-xantpo).

Eu(hfa)₂(xantpo)₂: Yield: 49%. IR (ATR): 1653 (st, C=O), 1137 (st, P=O), 1095–1251 (st, C–O–C and st, C–F) cm⁻¹. ¹H NMR (300 MHz, chloroform-*d*) δ = 6.74–7.65 (m, aryl), 1.88 (s, methyl) ppm. ³¹P NMR (200 MHz, acetone-*d*₆) δ = -92.12 (2P), -98.86 (2P) ppm. ESI–Mass (*m/z*): 1787.3 [M–(hfa)]⁺. Anal. Calcd. for C₉₃H₆₇EuF₁₈O₁₂P₄ ([Eu(hfa)₂(xantpo)₂]⁺[hfa]⁻) · 1.5CHCl₃: C, 52.22; H, 3.18%. Found: C, 52.11; H, 3.25%.

Eu(hfa)₃(*t*Bu-xantpo): Yield: 66%. IR (ATR): 1653 (st, C=O), 1138 (st, P=O), 1098–1249 (st, C–O–C and st, C–F) cm⁻¹. ¹H NMR (300 MHz, chloroform-*d*) δ = 7.41 (m, 2H, aryl), 7.07 (m, 2H, aryl), 6.83 (m, 2H, aryl), 5.92 (s, 3H, hfa-H), 2.97–3.02 (m, 6H, methyl), 1.41–1.68 (m, 36H, *tert*-butyl) ppm. ³¹P NMR (200 MHz, acetone-*d*₆) δ = 68.41 (2P) ppm. ESI–Mass (*m/z*): 1097.2 [M–(hfa)]⁺. Anal. Calcd. for C₄₆H₅₁EuF₁₈O₉P₂: C, 42.38; H 3.94%. Found: C, 42.93; H, 4.00%.

2.4. Optical measurements

UV–Vis absorption spectra were recorded on a JASCO V–550 spectrometer. Emission spectra of the Eu(III) complexes were measured with a JASCO F-6300-H spectrometer and corrected for

the response of the detector system. The intrinsic emission quantum yields of Eu(III) complex solutions (10 mM) degassed with an argon gas were obtained by comparison method with the integrated emission signal (550–750 nm) of Eu(hfa)₃(biphepo) (biphepo: 2,2'-bis(diphenylphosphoryl)biphenyl) as a reference ($\Phi_{f-f} = 0.60$, 50 mM in acetone-*d*₆) [24]. Excitation wavelength was 465 nm (direct excitation of Eu(III) ions). Emission lifetimes of Eu(III) complexes were measured using the third harmonics (355 nm) of a Q-switched Nd:YAG laser (Spectra Physics, INDI-50, fwhm = 5 ns, $\lambda = 1064$ nm) and a photomultiplier (Hamamatsu photonics, R5108, response time ≤ 1.1 ns). The Nd:YAG laser response was monitored with a digital oscilloscope (Sony Tektronix, TDS3052, 500 MHz) synchronized to the single-pulse excitation. Emission lifetimes were determined from the slope of logarithmic plots of the decay profiles.

3. Results and discussion

3.1. Effects of deuterated solvent

The steady-state emission spectra of Eu(hfa)₂(xantpo)₂ and Eu(hfa)₃(*t*Bu-xantpo) in organic solvent are shown in Fig. 2 and Fig. S1 (in Supplementary data). Emission bands are observed at around 578, 591, 613, 650, and 698 nm, and are attributed to the *f-f* transitions of ⁵D₀–⁷F_{*J*} with *J* = 0, 1, 2, 3, and 4, respectively. The spectra are normalized with respect to the magnetic dipole

transition intensity (${}^5D_0-{}^7F_1$) at 591 nm which is known to be insensitive to the surrounding environment of the Eu(III) ion. The emission band at 613 nm (${}^5D_0-{}^7F_2$) is due to electric dipole transition, which is strongly dependent on their coordination geometry. We also estimated the relative emission intensity of ${}^5D_0-{}^7F_2$ transition with respect to that of ${}^5D_0-{}^7F_1$ as $I_{\text{rel}} = I_{613} / I_{591}$ in the normalized emission spectra. The I_{rel} values of $\text{Eu}(\text{hfa})_2(\text{xantpo})_2$ and $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$ are summarized in Table 2. The intrinsic emission quantum yield ($\Phi_{\text{f-f}}$) for $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$ in acetone excited at $4f$ orbitals (excited at 465 nm) was found to be 64% (Table 1). This value is slightly smaller than that for reported $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$ in acetone- d_6 ($\Phi_{\text{f-f}} = 67\%$).

The radiative (k_{r}) and non-radiative (k_{nr}) rate constants estimated using the emission lifetimes (τ_{obs}) and the intrinsic emission quantum yields ($\Phi_{\text{f-f}}$) are summarized in Table 1. The radiative rate constant for $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$ in acetone was estimated to be $5.4 \times 10^2 \text{ s}^{-1}$. This k_{r} value is much similar to that for $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$ in acetone- d_6 ($5.5 \times 10^2 \text{ s}^{-1}$). We also observed that the non-radiative rate constant for $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$ in acetone- d_6 ($2.7 \times 10^2 \text{ s}^{-1}$) is smaller than that for $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$ in acetone ($3.0 \times 10^2 \text{ s}^{-1}$). The relatively smaller k_{nr} for $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$ in acetone- d_6 is attributed to the suppression of vibrational relaxation surroundings of the Eu(III) complex. The non-radiative transitions of lanthanide complexes are affected by the high-vibrational frequency of C–H and O–H bonds of solvent. We consider that

introduction of deuterated solvent is effective for enhancement of emission quantum yield of eight-coordinated Eu(III) complexes.

3.2. Photophysical properties in various organic solvent.

The radiative (k_r) and non-radiative (k_{nr}) rate constants, the emission lifetimes (τ_{obs}), and the intrinsic emission quantum yields (Φ_{f-f}) of $\text{Eu}(\text{hfa})_2(\text{xantpo})_2$ and $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$ are summarized in Table 2. The radiative rate constants of $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$ ($k_r = 3.6\text{--}5.6 \times 10^2 \text{ s}^{-1}$) were larger than that for $\text{Eu}(\text{hfa})_2(\text{xantpo})_2$ ($k_r = 3.0\text{--}4.9 \times 10^2 \text{ s}^{-1}$). Generally, the radiative rate constants of lanthanide complexes are directly linked to their geometrical structures. The symmetrical point groups of $\text{Eu}(\text{hfa})_2(\text{xantpo})_2$ and $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$ are D_{4d} and D_{2d} , respectively. The larger radiative rate constants for $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$ should come from asymmetrical D_{2d} structure related to change of odd parity in organic solvent.

The ability of solvent molecules for the coordination to metal centers can be estimated from the dielectric constant or the donor number [23]. The relationship between rate constants of Eu(III) complexes and dielectric constants of organic solvent are shown in Fig. 3 and Fig. S2. In $\text{Eu}(\text{hfa})_2(\text{xantpo})_2$, k_r and k_{nr} are much dependent of the dielectric constant of organic solvent. These results indicate that coordination geometry and vibrational structure of $\text{Eu}(\text{hfa})_2(\text{xantpo})_2$ (8-SAP) is affected by organic solvent with large dielectric constant, solvation to Eu(III) ion. In contrast, we found that k_r and k_{nr} of $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$ are maintained constant in acetone, toluene, and

chloroform. The structure of 8-TDH in $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$ might not be affected by solvent, although k_r and k_{nr} of 8-SAP are dependent of solvent. We here consider that small non-radiative rate of $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$ is caused by structural stability of 8-TDH in organic media. We also carried out charge density calculations of xantpo and $t\text{Bu-xantpo}$ ligand by DFT calculation (6-31G(d) / B3LYP) based on the X-ray single crystal analyses. According to the calculation, charge densities oxygen atoms in phosphine oxides were found to be -0.51 and -0.48 (xantpo), -0.51 and -0.47 ($t\text{Bu-xantpo}$), respectively (Fig. S3). However, we found that charge densities of phosphorus atoms in $t\text{Bu-xantpo}$ (-0.11 and 0.12) were higher than those in xantpo (0.22 and 0.23), because phosphorus atoms in $t\text{Bu-xantpo}$ were affected by electron donating ability of t -butyl groups. The effective electron donating ability would be also lead to enhancement of coordination and structural stabilities of $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$.

According to the emission process in DMF, k_r of $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$ is similar to that for $\text{Eu}(\text{hfa})_2(\text{xantpo})_2$. $\text{Eu}(\text{hfa})_2(\text{xantpo})_2$ and $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$ might be decomposed in DMF due to coordination to Eu(III) ion of DMF molecules with large dielectric constant. Decomposition of coordination structure by addition of solvent molecule with large dielectric constant has been previously reported [16]. The photosensitized energy transfer efficiency (η_{sens}) based on $\Phi_{\text{f-f}}$ and the total emission quantum yield (Φ_{tot} : ex. 380 nm) of $\text{Eu}(\text{hfa})_2(\text{xantpo})_2$ and $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$ are summarized in Table 2. The photosensitized energy transfer efficiencies in DMF ($\eta_{\text{sens}} = 21\text{--}23\%$)

are smaller than those in toluene, chloroform, and acetone (34–43%). We consider that hfa ligands of the complexes might move away from Eu(III) ion in DMF.

4. Conclusion

We demonstrated solvent-dependent luminescence of $\text{Eu}(\text{hfa})_2(\text{xantpo})_2$ and $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$. We found that non-radiative rate process of Eu(III) complex is directly linked to characteristics of surrounding environment, organic solvent. Smaller k_{nr} of $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$ is achieved by characteristic coordination structure, 8-TDH because of their structural stability in organic media. Solvent-dependent luminescence of lanthanide complex with characteristic eight-coordination structure is expected to provide a novel aspect in the field of lanthanide photochemistry.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi...

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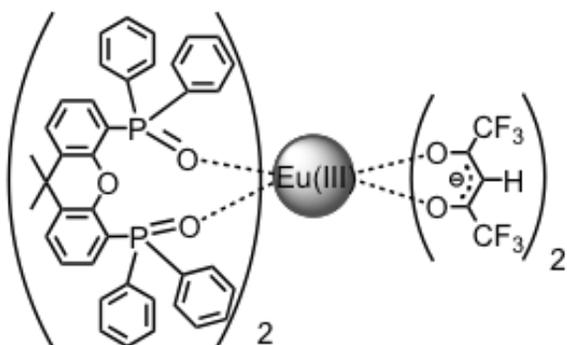
Figure Captions

Fig. 1. Chemical and coordination structures of $\text{Eu}(\text{hfa})_2(\text{xantpo})_2$ and $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$.

Fig. 2. Emission spectra of (a) $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$ and (b) $\text{Eu}(\text{hfa})_2(\text{xantpo})_2$ in acetone at room temperature. Excitation wavelength is 465 nm. The spectra are normalized with respect to the magnetic dipole transition (${}^5\text{D}_0\text{--}{}^7\text{F}_1$).

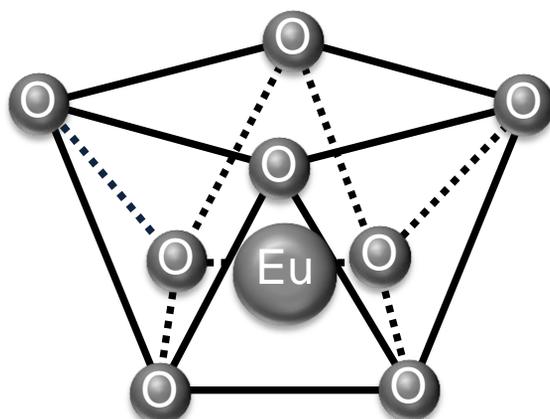
Fig. 3. The relationship between rate constants of Eu(III) complexes and dielectric constants of organic solvent. (a) The radiative (k_r) and (b) non-radiative constant (k_{nr}). (■ : $\text{Eu}(\text{hfa})_3(t\text{Bu-xantpo})$; 8-TDH, ○ : $\text{Eu}(\text{hfa})_2(\text{xantpo})_2$; 8-SAP, 1: toluene, 2: chloroform, 3: acetone, 4: DMF).

Chemical structures

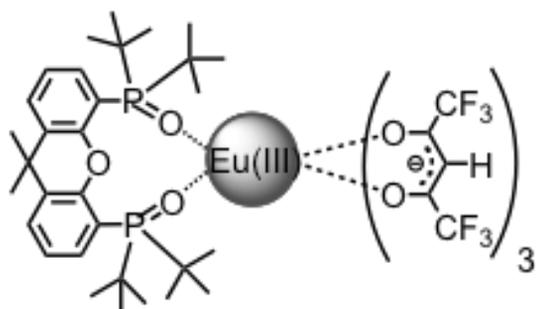


$\text{Eu}(\text{hfa})_2(\text{xantpo})_2$

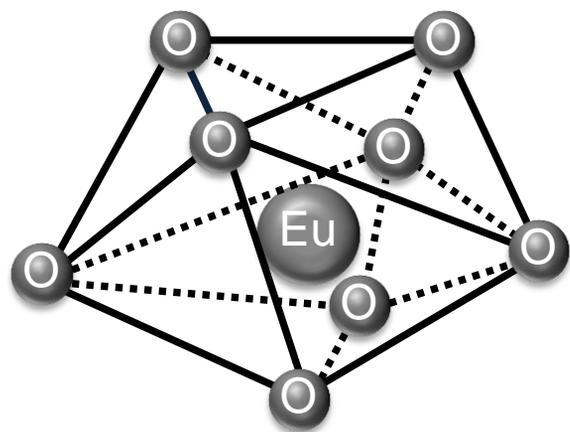
Coordination structures



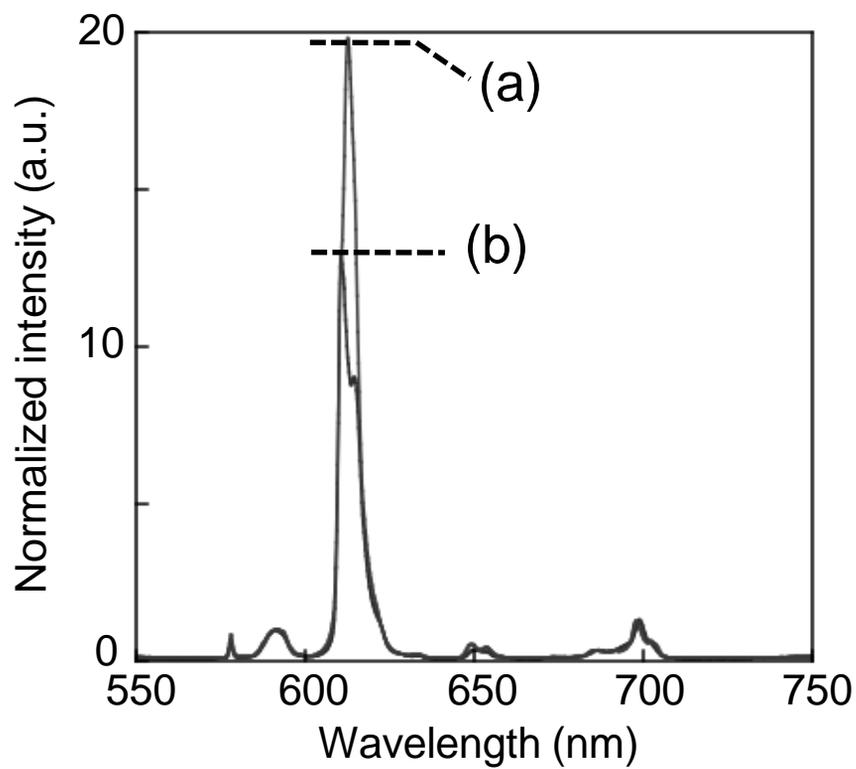
Square antiprism
(8-SAP, D_{4d})



$\text{Eu}(\text{hfa})_3(\text{tBu-xantpo})$



Trigonal dodecahedron
(8-TDH, D_{2d})



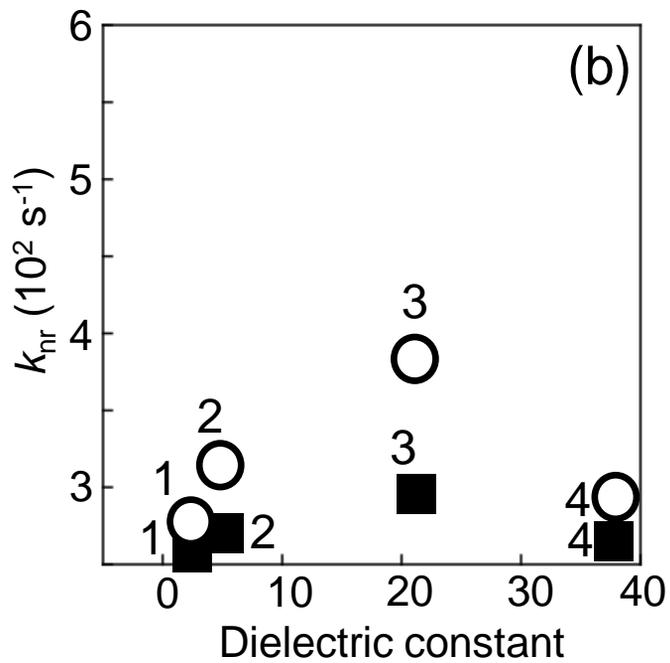
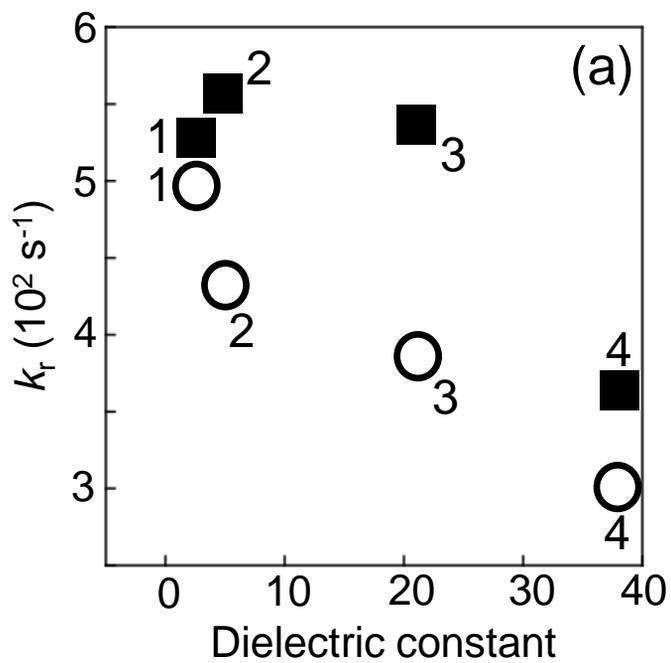


Table 1Photophysical properties of $\text{Eu}(\text{hfa})_3(\text{tBu-xantpo})$ at room temperature.

solvent	τ_{obs} (ms) ^a	$\Phi_{\text{f-f}}$ (%) ^b	k_{r} (s ⁻¹) ^c	k_{nr} (s ⁻¹) ^d
acetone	1.2	64	5.4×10^2	3.0×10^2
acetone- d_6 ^e	1.2	67	5.5×10^2	2.7×10^2

^a Emission lifetime (τ_{obs}) of the Eu(III) complexes were measured by excitation at 355 nm (Nd:YAG 3w).

^b Intrinsic emission quantum yields for Eu(III) complexes were determined by comparing with the integrated emission signal (550–750 nm) of $\text{Eu}(\text{hfa})_3(\text{biphepo})$ as $\Phi_{\text{f-f}} = 0.60$ in acetone- d_6 [23]. Excitation at 465 nm.

^c Radiative rate constants $k_{\text{r}} = \Phi_{\text{f-f}} / \tau_{\text{obs}}$.

^d Non-radiative rate constants $k_{\text{nr}} = 1/\tau_{\text{obs}} - k_{\text{r}}$.

^e Ref. [20].

Table 2

Photophysical properties of Eu(III) complexes in various solvent at room temperature.

complex	solvent	τ_{obs} (ms)	$\Phi_{\text{f-f}}$ (%)	Φ_{tot} (%) ^a	η_{sens} (%) ^b	I_{rel} ^c	k_{r} (s ⁻¹) ^d	k_{nr} (s ⁻¹) ^e
Eu(hfa) ₃ (xantpo) ₂	toluene	1.3	64	24	38	14	4.9×10^2	2.8×10^2
	chloroform	1.3	58	22	38	11	4.3×10^2	3.1×10^2
	acetone	1.3	50	20	40	13	3.9×10^2	3.8×10^2
	DMF	1.7	51	12	23	7.1	3.0×10^2	2.9×10^2
Eu(hfa) ₃ (<i>t</i> Bu-xantpo)	toluene	1.3	67	29	43	16	5.3×10^2	2.6×10^2
	chloroform	1.2	67	24	36	16	5.6×10^2	2.7×10^2
	acetone	1.2	64	22	34	20	5.4×10^2	3.0×10^2
	DMF	1.6	58	12	21	12	3.6×10^2	2.6×10^2

^a Total emission quantum yield (excitation at 380 nm).^b Photosensitized energy transfer efficiency $\eta_{\text{sens}} = \Phi_{\text{tot}} / \Phi_{\text{f-f}}$.Estimated relative errors: $\tau_{\text{obs}}, \pm 4\%$; $\Phi_{\text{f-f}}, \pm 3\%$; $\Phi_{\text{tot}}, \pm 9\%$; $\eta_{\text{sens}}, \pm 12\%$.^c Relative emission intensity of the electric dipole transition (⁵D₀-⁷F₂) to the magnetic dipole transition (⁵D₀-⁷F₁).^d $k_{\text{r}} = \Phi_{\text{f-f}} / \tau_{\text{obs}}$.^e $k_{\text{nr}} = 1/\tau_{\text{obs}} - k_{\text{r}}$.