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Enhanced Lasing Properties of Dissymmetric Eu(III) Complex with Bidentate Phosphine Ligands

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The luminescent and lasing properties of Eu(III) complexes were enhanced by using an dissymmetric Eu(III) complex. The photophysical properties (the emission spectral shapes, the emission lifetimes, the emission quantum yields, and the stimulated emission cross section (SEC)) were found to be dependent on the geometrical structures of Eu(III) complexes. The geometrical structures of Eu(III) complexes were determined by X-ray single crystal analyses. The symmetrical group of Eu(hfa)$_3$(BIPHEPO) (tris(hexafluoroacetylacetonato)-europium(III) 1,1′-biphenyl-2,2′-diylbis(diphenylphosphine oxide)) was found to be C_1, which was more dissymmetric than Eu(hfa)$_3$(TPPO)$_2$ (tris(hexafluoroacetylacetonato)europium(III) 1,2-phenylenebis(diphenylphosphine oxide): C_2 symmetry) and Eu(hfa)$_3$(OPPO)$_2$ (tris(hexafluoroacetylacetonato)europium(III) 1,2-phenylenebis(diphenylphosphine oxide): C_2 symmetry). The analytical data were supported by Judd−Ofelt analysis. The most dissymmetrical Eu(III) complex, Eu(hfa)$_3$(BIPHEPO), showed large electron transition probability and large SEC (4.64×10^{-20} cm^2). The SEC of Eu(hfa)$_3$(BIPHEPO) was superior to even the values of Nd-glass laser for practical use ($1.6-4.5 \times 10^{-20}$ cm^2). The lasing properties of Eu(III) complexes in polymer thin film were measured by photopumping of a Nd:YAG laser (355 nm). The threshold energy of lasing oscillation was found to be 0.05 mJ. The increasing rate of the lasing intensity of Eu(hfa)$_3$(BIPHEPO) as a function of the excitation energy was much larger than that of Eu(hfa)$_3$(TPPO)$_2$ and Eu(hfa)$_3$(OPPO)$_2$. The dissymmetrical structure of Eu(hfa)$_3$(BIPHEPO) promoted the enhancement of the lasing property.

Introduction

The development of strong luminescent molecules is an active area of photofunctional chemistry.[1] Strong luminescent molecules are required to possess the remarkable high emission quantum yields, characteristic emission wavelength, and shapes. Their emission properties can be controlled by adding characteristic chemical species.[2] In particular, James and Shinkai have reported the luminescent molecular sensor by addition of sugar derivatives.[3] de Silva also described a concept of luminescent molecular logic gates.[4] Furthermore, Fabbrizzi and Walkup have reported fluorescence switching by using particular cations or anions.[5] The addition of chemical species is regarded as a significant factor to change the emission properties.

We focus here on the manipulation of characteristic luminescence phenomena, lasing properties, by addition of chemical species. Concerning the manipulation of the lasing properties, some studies have achieved the changes of the laser emission by addition or connecting of particular chemical species.[6] Chemical species play an important role as the manipulator of light amplification. Those manipulations of lasing properties have been reported about organic dye molecules.[7,8] The organic laser dye molecule with chemical species is the best suitable to construct a wavelength-tunable laser;[8,9] however, because of the organic dye's three-level electric transitions, there is difficulty in the amplification of lasing intensities.[10,11] To improve the amplification of the lasing intensities, we consider using lanthanide(III) complexes, strong luminescent molecules, with chemical species. The lanthanide(III) complexes are ideal molecules as a lasing medium, because they have 4-level electric transitions for effective formation of population inversion.[11−14] A large number of studies about luminescent molecules using the lanthanide(III) complexes were reported.[15−17] Parker and Gunnlaugsson have reported the control of luminescent properties using addition of chemical species, cation, and proton sources.[18] Ziessel also studied anion sensing using luminescent lanthanide(III) complexes.[19] According to the laser action for

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CHART 1: Schematic Diagrams of Supposable SAP Structures and Chemical Species

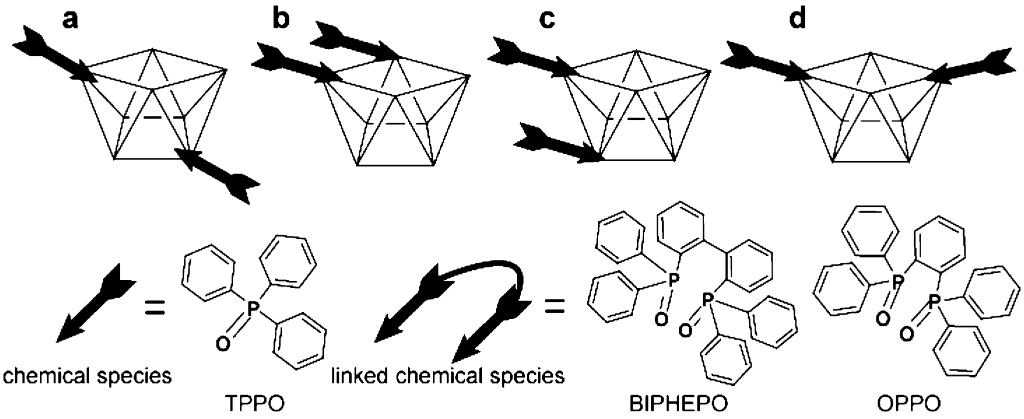
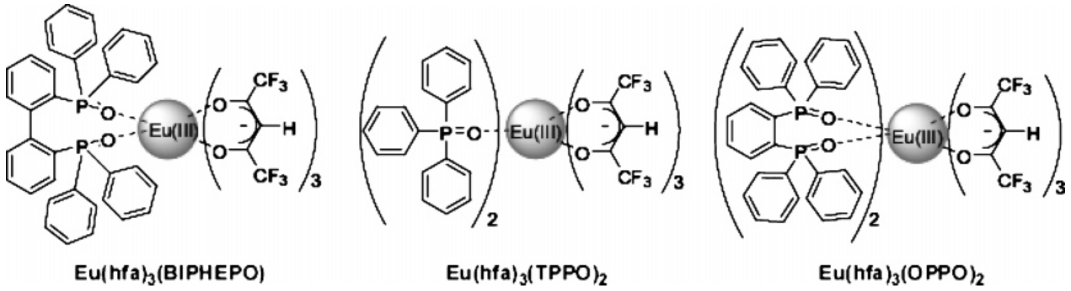


CHART 2: Chemical Structures of Eu(III) Complexes



the lanthanide(III) complex, Samelson et al. reported a europium chelate liquid laser.[20] However, studies on the laser action of lanthanide(III) complexes necessarily involved high-power excitation energy for lasing.

We recently observed effective lasing phenomena by using strong luminescent lanthanide(III) complexes.[21] An important purpose of the study described here is to control lasing properties from f−f electric transitions of lanthanide(III) ions by the addition of chemical species. We treated the chemical species as powerful tools for control of the electric transitions in f-orbitals, which are parity forbidden. It is well-known that reducing the symmetry of the lanthanide complex enhances its photophysical properties.[15−19] The electric transition in f-orbitals related to the emission and lasing properties can be enhanced by control of the coordination symmetry of lanthanide(III) complexes.[16,22] The chemical species can act as a key species which control the symmetry of the coordination sphere around lanthanide(III) ions. The coordination sphere of the lanthanide(III) complex forms an 8-coordinated square-antiprism (SAP) structure, generally.[17,23] The possible combinations of the SAP structure and two chemical species are shown in Chart 1. The coordination structures of the lanthanide(III) complexes are transformed by addition of chemical species into those coordination sites. Structures **a** and **d** contain the symmetry axis and mirror plane, respectively. Structures **b** and **c** have no symmetry axis, mirror plane, or inversion center. To enhance the lasing properties, the lanthanide(III) complex should form a low symmetrical structure for increase of f−f transition probability.[12] Therefore, structures **b** and **c** would have a great advantage for enhancement of the emission intensities relating to lasing properties. The large transition probability leads to enlargement of the stimulated emission cross-section (SEC) value, which is one of the most important factors for lasing amplification.[24]

Phosphine oxides as a chemical species are known to interact with lanthanides and have been used to enhance the emission of lanthanide complexes.[25] To achieve effective lasing amplification, we used Eu(III) complexes with chemical species which were linked to each other (BIPHEPO and OPPO) for construction of either structure **b** or **c**. Coordination sites of the chemical species consist of low vibrational phosphine oxide groups. The low vibrational phosphine oxide molecules (P═O: $1125\ \mathrm{cm^{-1}}$) provide Eu(III) complexes with high emission quantum yields because of suppression of radiationless transitions caused by vibrational excitations.[20,25] The Eu(III) complexes, Eu(hfa)$_3$(BIPHEPO) and Eu(hfa)$_3$(OPPO)$_2$, having bidentate phosphine oxides and another low vibrational ligand (hfa), were synthesized (Chart 2). The Eu(III) complex constructing structure **a**, which has two isolated phosphine oxides (Eu(hfa)$_3$(TPPO)$_2$), was also prepared for comparison of the correlation between the geometrical structures and the lasing properties.[25] We found that the Eu(III) complex with BIPHEPO (structure **b**) showed the best lasing property in lanthanide(III) complexes. The enhancement of lasing behavior of lanthanide(III) complexes by using chemical species is reported for the first time. This study is a significant report that directly connects with photophysical chemistry and photofunctional molecular science.

Experimental Section

Apparatus. ^{1}H NMR and ^{19}F NMR data were obtained with a JEOL EX-270 spectrometer. ^{19}F NMR chemical shifts were determined with hexafluorobenzene as an external standard (δ −162.0 (s, Ar−F) ppm). Elemental analyses were performed with a Perkin-Elmer 240 C.

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. Methanol-d_4 and acetone-d_6 were obtained from Aldrich Chemical Co. Inc. Polyphenylsilsesqioxane (PPSQ) ($M_w = 5.2 \times 10^4$) was obtained from MITSUBISHI Electric Corporation.[26] All other chemicals were reagent grade and were used as received.

Synthesis of 1,1′-Biphenyl-2,2′-diylbis(diphenylphosphine oxide): BIPHEPO. 1,1′-Biphenyl-2,2′-diylbis(diphenylphosphine oxide) (BIPHEPO) was obtained by the same method as previously reported by Schlosser et al.[27] (2-Iodophenyl)-diphenylphosphine oxide was prepared by *ortho-lithiation* of triphenylphosphine oxide followed by iodolysis of the organometallic intermediate. In succession, the copper promoted reductive coupling (Ullman coupling) of (2-iodophenyl)diphenylphosphine oxide gave BIPHEPO in 78% yield.

Synthesis of Tris(hexafluoroacetylacetonato)europium(III) 1,1′-Biphenyl-2,2′-diylbis(diphenylphosphine oxide): Eu(hfa)$_3$(BIPHEPO). Methanol (100 mL) containing tris(hexafluoroacetylacetonato)europium (III) dehydrates (4.05 g, 5 mmol) and BIPHEPO (2.50 g, 4.5 mmol) was refluxed under stirring for 12 h. The reaction mixture was concentrated with a rotary evaporator. Recrystallization from methanol gave white crystal in 35% yield. ^{1}H NMR (270 MHz, [D$_6$]acetone, 20 °C, TMS) δ (ppm) 8.67−8.58 (m, 4H), 8.05−7.91 (m, 4H), 7.84 (br, 6H), 7.31−7.27 (m, 4H), 7.01−6.94 (m, 4H), 6.53 (dd, J = 13.8 Hz, 4H), 6.44 (dd, J = 7.5 Hz, 2H) 6.26 (s, 3H; C−H). ^{19}F NMR (270 MHz, [D$_6$]acetone, 20 °C, hexafluorobenzen) δ (ppm) −76.16 (s; CF$_3$). Elemental analysis calcd for $C_{51}H_{31}EuF_{18}O_8P_2$: C 46.14, H 2.35. Found: C 45.91, H 2.42. MALDI-TOF-MS *m/z* 1367.3 ([M + K]$^+$).

Synthesis of Tris(hexafluoroacetylacetonato)europium(III) Bis(triphenylphosphine oxide): Eu(hfa)$_3$(TPPO)$_2$. Eu(hfa)$_3$(TPPO)$_2$ was prepared with the previously reported method.[25] Methanol (100 mL) containing tris(hexafluoroacetylacetonato)europium(III) dehydrates (4.28 g, 5.3 mmol) and triphenylphospine oxide (TPPO) (2.78 g, 10 mmol) was refluxed under stirring for 12 h. The reaction mixture was concentrated with a rotary evaporator. Reprecipitation by addition of excess hexane solution produced crude crystals, which were washed in toluene several times. Recrystallization from hot toluene/cyclohexane gave white needle crystals in 74% yield. ^{1}H NMR (270 MHz, [D$_6$]acetone, 20 °C, TMS), δ (ppm) 7.6 (m, aromatic C−H), 5.4 (s, c-H). ^{19}F NMR (270 MHz, [D$_6$]acetone, 20 °C, hexafluorobenzen) δ (ppm) −76.7 (s, C−F). Elemental analysis calcd for $EuC_{51}H_{33}O_8F_{18}P_2$: C, 45.96; H, 2.50. Found: C, 45.94; H, 2.57.

Synthesis of Tris(hexafluoroacetylacetonato)europium(III) 1,2-Phenylenebis(diphenylphosphine oxide): Eu(hfa)$_3$(OPPO)$_2$. Eu(hfa)$_3$(OPPO)$_2$ was prepared by the reaction of tris(hexafluoroacetylacetonato)europium(III) dehydrates (3.80 g, 4.7 mmol) and 1,2-phenylenebis(diphenylphosphine oxide) (2.15 g, 4.5 mmol) in methanol (100 mL) under reflux for 12 h.[28] Recrystallization from methanol gave white crystals in 28% yield. ^{1}H NMR (acetone-d_6, 270 MHz, 298K) 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). Elemental analysis calcd for $C_{75}H_{57}EuF_{18}O_{10}P_4 + 0.80MeOH$: C, 51.89; H, 3.31. Found: C, 51.40; H, 3.11.

Preparation of Deuterated Eu(III) Complexes in Deuterated Solvent. Deuterated Eu(III) complexes were obtained by the proton−deuterium ion exchange reaction via keto−enol tautomerism of hexafluoroacetylacetonato ligands in Eu(III) complexes with CD$_3$OD for 6 h under vacuum.[24,25,29] Samples for measurements of the luminescence of deuterated 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).[25]

Crystallography. A colorless single crystal of Eu(hfa)$_3$(BIPHEPO) was mounted on a glass fiber with epoxy resin. X-ray diffraction intensities were collected with a Rigaku RAPID imaging plate diffractometer with Mo Kα radiation in $\omega-2\theta$ scan mode at 223 K. 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 with the TEXSAN crystallographic software package. Crystallographic data (excluding structure factors) for the Eu(hfa)$_3$(BIPHEPO) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers. Copies of the data can be obtained free of charge on application to CCDC 292377, 12 Union Road, Cambridge CB21EZ, UK (fax (+44)1223−336-033; e-mail deposit@ccdc.cam.ac.uk).

Judd−Ofelt Analysis. Absorption spectra of the Eu(III) complexes were measured at room temperature with a HITACHI U-3300 system. Broad absorption bands due to $\pi-\pi^*$ transitions in the ligands of the Eu(III) complexes overlapped with $f-f$ transitions in Eu(III) ion below 400 nm. Therefore, Judd−Ofelt analysis of the Eu(III) complexes were carried out with use of the $^7F_0 \rightarrow {}^5D_2$ transition (465 nm) to determine Ω_2 parameters. Concentration of the Eu(III) complexes in solvent was 0.05 M. In Judd−Ofelt treatment, the oscillator strength between the two states i and j in 4f orbitals is given by

$$f(i \rightarrow j)\frac{2J+1}{e^2 \upsilon} = \sum_{\lambda=2,4,6} \Omega_\lambda |\langle i|U^\lambda|\, j\rangle|^2 \tag{1}$$

The left-hand side of the equation can then be expanded to

$$\frac{3h}{8\pi cN}\frac{(n^2+2)^2}{9n}\int A\, d\lambda\, \frac{2J+1}{e^2\lambda_{\max} \times 10^{-7}} = S_M \tag{2}$$

where Ω_λ, U^λ, e, J, c, h, $\lambda_{\max}$, N, η, and $\int A\, d\lambda$ are Judd−Ofelt parameters (constants), tensor parameters, elementary charge (1.6022×10^{20} ems), angular momentum (Eu(III): 0), the speed of light (2.998×10^{-10} cm s^{-1}), Plank's constant (6.626×10^{-27} erg s), center wavelength at the absorption band (nm), density of ions in the matrix, refractive index of the solution, and absorption integral, respectively.[30,31] Tensor parameters U^λ of Eu(III) are given below:[32]

$$U = \begin{bmatrix} ^7F_0 \rightarrow {}^5L_6 \\ ^7F_0 \rightarrow {}^5D_3 \\ ^7F_0 \rightarrow {}^5D_2 \\ ^7F_0 \rightarrow {}^5D_1 \end{bmatrix};\ U_2 = \begin{bmatrix} 0 \\ 0.0004 \\ 0.0008 \\ 0 \end{bmatrix};\ U_4 = \begin{bmatrix} 0 \\ 0.0012 \\ 0 \\ 0 \end{bmatrix};\ U_6 = \begin{bmatrix} 0.0155 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

The Ω_2 parameters were calculated by a least-squares fitting of the calculated oscillator strengths to the absorption line strength of $^7F_0 \rightarrow {}^5D_2$ transition (465 nm).

Optical Measurements. Emission spectra were measured at room temperature with a Spex Fluorolog-τ3 (JOBIN YVON) system. The samples were excited at 465 nm ($^7F_0 \rightarrow {}^5D_2$). The emission lifetimes were determined by using a Q-switched Nd:YAG laser (Spectra Physics INDI-50, fwhm = 5 ns, λ = 1064 nm) and a photomultiplier (Hamamatsu Photonics R7400U-03, response time ≤0.78 ns). Samples were excited by the third harmonic (355 nm) of the fundamental nanosecond pulse.

Emission from the sample was guided to the photomultiplier through a monochromator (JOBIN YVON, Triax320). Emission decays were monitored with a digital oscilloscope (Sony Tektronix, TDS3052, 500 MHz) synchronized to single-pulse excitation. The quantum yields were determined by standard procedures with an integral sphere (diameter 6 cm) mounted on a spectrofluorometer (HITACHI F-4500).[25,33] The optical path length of the cell was 5 mm. Quantum yield, Φ, was calculated by the equation

$$\Phi = \frac{N_{\text{emission}}}{N_{\text{absorption}}} = \frac{\int \frac{\lambda}{hc} I_{\text{em}}(\lambda)\, \mathrm{d}\lambda}{\int \frac{\lambda}{hc}\{I_{\text{ex}}(\lambda_{\text{ref}}) - I_{\text{ex}}(\lambda_{\text{sam}})\}\, \mathrm{d}\lambda} \qquad (3)$$

The corrected intensity functions of the light absorption (from eq 3 above) ($I_{\text{ex}}(\lambda_{\text{ref}})$: without sample (acetone-d_6); $I_{\text{ex}}(\lambda_{\text{sam}})$: with sample (solution of Eu(III) complexes in acetone-d_6: 0.05 M)) were determined by the excitation spectra of the system (450−480 nm, scan rate = 60 nm/min), whereas the corrected intensity function of the emission, $I_{\text{em}}(\lambda)$, was determined by the emission spectra (550−800 nm, scan rate = 60 nm/min). The quantum yield Rodamine 6G in ethanol determined by the procedure agreed well with the reported value (0.94 ± 0.05). The errors of the emission quantum yields were determined by the difference between the average and maximum values in measurements for ten times.

Preparation of Polyphenylsilsesquioxane (PPSQ) Thin Films Containing Eu(III) Complexes. Polymer matrix, PPSQ beads were dissolved in 5 mL of anisole. The Eu(III) complexes were then added to the solution. An Eu(III) thin film was prepared on a glass substrate from the anisole solution via the spin-coating method. The film thickness was found to be 2.0 μm, using surface profiler (Veeco Instruments Inc.DEKTAK3). PPSQ is a ladder-type polymer having siloxane bonds as a main chain, and has high transparency in the visible and ultraviolet region.[26] The optical microcavity was constructed by forming a high refractive film of PPSQ (refractive index: 1.558) on the glass substrate.

ASE Measurements. Eu(III) thin film was excited by the third harmonic (355 nm) of a nanosecond Nd:YAG laser (B. M. industries 502DNS, 10 Hz, fwhm = 9 ns, beam spot = 5 mm). The optical waveguide on the film was excited with a combination of a cylindrical lens (f = 200 mm) and a concave lens (f = 100 mm). Emission from the edge of the thin film was filtered by a low-cut optical filter (Toshiba Glass L-39, $\lambda > 365$ nm) and a monochromator (Jobin Yvon H-20 Vis) placed in front of the detector (Photomultiplier: Hamamatsu Photonics R928). The response of the photomultiplier was monitored by using a digital oscilloscope (SONY Tektronics TDS540) synchronized to the excitation pulse. The emission spectra from the edge were measured with a photonic multichannel analyzer system (Ocean Optics USB2000) under different excitation energy. the energy of the beam spot (excitation energies of the samples) was measured by a thermopower meter.

Results and Discussion

Geometrical Structures of the Eu(III) Complexes. The ORTEP diagrams and schematic illustrations of the coordination sites around the Eu(III) ions of Eu(hfa)$_3$(BIPHEPO), Eu(hfa)$_3$(TPPO)$_2$, and Eu(hfa)$_3$(OPPO)$_2$ are shown in Figure 1. The coordination spheres of Eu(hfa)$_3$(BIPHEPO) and Eu(hfa)$_3$(TPPO)$_2$ consisted of three hexafluoroacetylacetonato (hfa) ligands and two phosphine oxide groups. In contrast, the coordination sphere of Eu(hfa)$_3$(OPPO)$_2$ was formed by two hfa ligands and four phosphine oxide groups. The positions of the coordination sites occupied by the phosphine oxide groups depended on the geometrical structures (distances and angles) of the linker moieties. The geometrical structures of Eu(hfa)$_3$(BIPHEPO), Eu(hfa)$_3$(TPPO)$_2$, and Eu(hfa)$_3$(OPPO)$_2$ were determined to be an antisymmetrical square-antiprism (SAP). The symmetrical group of the Eu(hfa)$_3$(BIPHEPO) was found to be C_1, which was more dissymmetric than both Eu(hfa)$_3$(TPPO)$_2$ and Eu(hfa)$_3$(OPPO)$_2$ (C_2 symmetry). These results indicate that Eu(hfa)$_3$(BIPHEPO), Eu(hfa)$_3$(TPPO)$_2$, and Eu(hfa)$_3$(OPPO)$_2$ had no inverted center in the crystal field, causing an increase in the electron transition probability ($^5D_0 \rightarrow {}^7F_2$ transition) in the 4f orbitals due to odd parity. The SAP structure of Eu(hfa)$_3$(BIPHEPO) formed the **b**-form, which is the most dissymmetric structure in Chart 1. In contrast, linked wedge OPPO did not give the **b**-form in Chart 1. According to the results, the geometrical structure and free rotation of biphenylene-linker moiety in a BIPHEPO is necessary to keep the BIPHEPO in a desirable position for construction of the **b**-form. On the other hand, the SAP structure of Eu(hfa)$_3$(TPPO)$_2$ shows the **a**-form in Chart 1. This demonstrated that the bis-phosphine oxide ligand with the biphenylene group (BIPHEPO) gives the most dissymmetric environment to the Eu(III) ion (C_1 symmetry).

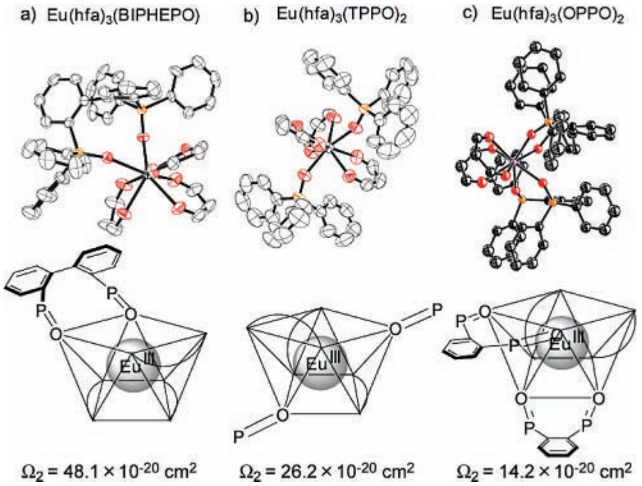


Figure 1. ORTEP diagrams and schematic diagrams of coordination structures and Judd−Ofelt parameter Ω_2 of the Eu(III) complexes. ORTEP diagrams of Eu(hfa)$_3$(TPPO)$_2$ and Eu(hfa)$_3$(OPPO)$_2$ were cited from the literature.[25,28]

To discuss the geometrical structures of the Eu(III) complexes in solution, Judd−Ofelt analyses were carried out with ues of the absorption spectra of the Eu(III) complexes. The Judd−Ofelt analysis is a useful tool for estimating the population of odd parity electron transition.[34] It is well-known that the value of Ω_2 is more sensitive to the symmetry of ligand fields than those of Ω_4 and Ω_6.[30,35] Therefore, the relationship between electron transition probability and symmetry of the Eu(III) complexes in the solution was estimated by using the Judd−Ofelt parameter Ω_2.[30] The Ω_2 parameter of Eu(hfa)$_3$(BIPHEPO) was calculated to be 48.1×10^{-20} cm^2 (Figure 1). This Ω_2 parameter was much larger than those of the corresponding Eu(hfa)$_3$(TPPO)$_2$ and Eu(hfa)$_3$(OPPO)$_2$ (26.2×10^{-20} and 14.2×10^{-20} cm^2, respectively), suggesting that Eu(hfa)$_3$(BIPHEPO) has the most dissymmetric structure in organic media among the three complexes, in agreement with the data of the crystal structures noted above. The dissymmetric structure of Eu(hfa)$_3$(BIPHEPO) should lead to the largest electron transition probability among the three complexes. Because of the large

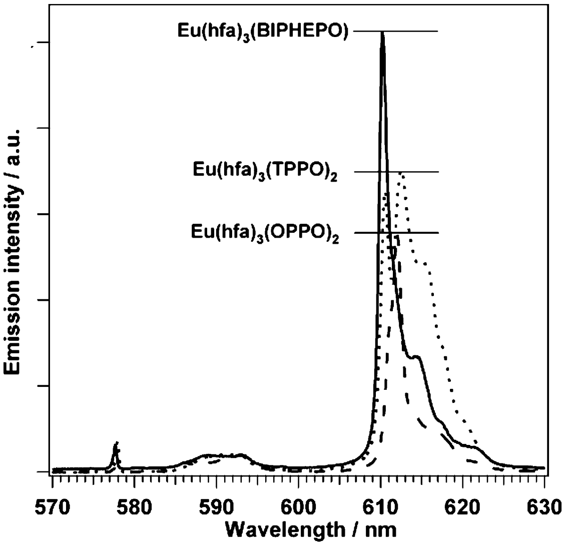


Figure 2. Emission spectra of Eu(hfa)$_3$(BIPHEPO) (solid line), Eu(hfa)$_3$(TPPO)$_2$ (dotted line), and Eu(hfa)$_3$(OPPO)$_2$ (dashed line) in acetone-d_6 excited at 465 nm.

electron transition probability caused by dissymmetric structure, addition of the BIPHEPO in the SAP structure was expected to enhance the emission and lasing properties.

Phorophysical Properties of the Eu(III) Complexes. The emission spectra of deuterated Eu(III) complexes in acetone-d_6 are shown in Figure 2. All the spectra were normalized with respect to the $^5D_0 \rightarrow {}^7F_1$ (magnetic dipole) transition. Emission bands were observed at around 580, 590, 615, 650, and 700 nm, and are attributed to the $f-f$ transitions $^5D_0 \rightarrow {}^7F_J$ ($J = 0$, 1, 2, 3, and 4, respectively). The strongest emission band at around 615 nm ($^5D_0 \rightarrow {}^7F_2$) was due to the electronic dipole transition. The emission spectral shape of the $^5D_0 \rightarrow {}^7F_2$ (electric dipole) transition of Eu(hfa)$_3$(BIPHEPO) was remarkably narrow (fwhm = 1.6 nm) and quite different from those of the corresponding Eu(hfa)$_3$(TPPO)$_2$ (fwhm = 7.1 nm) and Eu(hfa)$_3$(OPPO)$_2$ (fwhm = 2.1 nm). The characteristic coordination structure (**b**-form) of Eu(hfa)$_3$(BIPHEPO) led to a remarkably narrow emission shape.

The relative emission intensities of $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ transition (I_{rel}) and the fwhm of the $^5D_0 \rightarrow {}^7F_2$ transition ($\Delta\lambda_{eff}$), emission lifetimes (τ_{obs}), emission quantum yields (Φ_{ln}), radiative rates (k_r), and stimulated emission cross-section (SEC) (σ_r) of the Eu(III) complexes in acetone-d_6 are summarized in Table 1. Eu(hfa)$_3$(BIPHEPO) and Eu(hfa)$_3$(TPPO)$_2$ showed high emission quantum yields. Those high emission quantum yields were achieved by prevention of radiationless transition via vibrational excitation. The prevention of radiationless transition is due to three deuterated hfa ligands which have only low-vibrational C−F or C−D bonds. On the other hand, Eu(hfa)$_3$(OPPO)$_2$ had only two hfa ligands in the vicinity of the Eu(III) ion. Because the excited state of the Eu(III) ion of Eu(hfa)$_3$(OPPO)$_2$ was quenched by vibrational excitation of the C−H bonds of two OPPO ligands, the emission quantum yield of Eu(hfa)$_3$(OPPO)$_2$ was lower than those of Eu(hfa)$_3$(BIPHEPO) and Eu(hfa)$_3$(TPPO)$_2$.

The radiative rate of Eu(hfa)$_3$(BIPHEPO) was the same order as that of Eu(hfa)$_3$(TPPO)$_2$ when considering errors for measurements, although addition of the BIPHEPO to SAP structure was expected to enhance the radiative rate by Judd−Ofelt analyses (ground state analyses). These results might come from the difference between the structures in the ground state and the excited state. The distorted structures of metal complexes in the excited state have been discussed.[36] Furthermore, Riehl has reported the discrepancy between dissymmetry factors of the Eu(III) complex from the ground state (g_{abs}: CD measurements) and those from the excited state (g_{lum}: CPL measurements).[37] The dissymmetry factors express the structural information on each state. The data indicate structural changes of the lanthanide(III) complex in the excited state. In the present experiments, we propose that the geometrical structures of Eu(hfa)$_3$(BIPHEPO) in the excited state might be different from that in the corresponding ground state by changing the dihedral angle of the biphenyl moiety on ligand excitation (355 nm), although structural changes of the lanthanide(III) complex with the biphenyl ligand in the excited state have never been reported. The relative emission intensity of the $^5D_0 \rightarrow {}^7F_2$ transitions (electric dipole) of Eu(hfa)$_3$(BIPHEPO) (I_{rel} =25.6) (**b**-form in Chart 1) was much larger than those of Eu(hfa)$_3$(TPPO)$_2$ (**a**-form in Chart 1) (I_{rel} =17.6) and Eu(hfa)$_3$(OPPO)$_2$ (I_{rel} =13.4). The relative emission area of the $^5D_0 \rightarrow {}^7F_2$ transitions was found to be 1010 (Eu(hfa)$_3$(BIPHEPO)), 1120 (Eu(hfa)$_3$(TPPO)$_2$), and 518 (Eu(hfa)$_3$(OPPO)$_2$). The characteristic spectral shapes of the $^5D_0 \rightarrow {}^7F_2$ might be related to the symmetry of the excited geometrical structures after optical absorption. To estimate the capability of those Eu(III) complexes for being a lasing medium, the SEC values were determined. The SEC value is one of the most important factors for laser amplification. The SEC can be expressed by

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

where c, λ_p, $\Delta\lambda_{eff}$, n, and A are the speed of light, the wavelength of the oscillation peak, fwhm (full width at half maximum) of the oscillation peak, refractive index of the matrix, and Einstein coefficient A, respectively.[23] The SEC of Eu(hfa)$_3$(BIPHEPO) was found to be 4.64×10^{-20} cm^2, being much larger than that of both Eu(hfa)$_3$(TPPO)$_2$ ($\sigma_r = 1.42 \times 10^{-20}$ cm^2) and Eu(hfa)$_3$(OPPO)$_2$ ($\sigma_r = 1.80 \times 10^{-20}$ cm^2). The smaller $\Delta\lambda_{eff}$ value (fwhm) and high emission quantum yield of Eu(hfa)$_3$(BIPHEPO) led to an increase of the SEC value. The SEC of Eu(hfa)$_3$(BIPHEPO) was superior to even the values of Nd-glass laser

TABLE 1: Photophysical Properties of Eu(III) Complexes: Relative Intensities of the $^5D_0 \rightarrow {}^7F_2$ Transition[a] (I_{rel}), Fwhm of the $^5D_0 \rightarrow {}^7F_2$ (615 nm) Transition ($\Delta\lambda_{eff}$), Emission Lifetimes[b] (τ_{obs}), Emission Quantum Yields[c] (Φ_{ln}), Radiative Rates[d] (k_r), and Stimulated Emission Cross Sections[e] (σ_r) in Acetone-d_6

	I_{rel}	$\Delta\lambda_{eff}$/nm	τ_{obs}/ms	Φ_{ln}	$k_r/\times 10^2$ s^{-1}	$\sigma_p/\times 10^{-20}$ cm^2
Eu(hfa)$_3$(BIPHEPO)	25.6	1.6	1.1	0.87 ± 0.03	7.37	4.64
Eu(hfa)$_3$(TPPO)$_2$	17.6	7.0	0.93	0.90 ± 0.05	9.68	1.42
Eu(hfa)$_3$(OPPO)$_2$	13.4	2.1	1.2	0.48 ± 0.04	3.75	1.80

[a] Relative intensity of the $^5D_0 \rightarrow {}^7F_2$ transition (electron dipole) to the $^5D_0 \rightarrow {}^7F_1$ (magnetic dipole) transition. [b] Emission lifetimes of the Eu(III) complexes were measured by the excitation at 355 nm (Nd:YAG 3ω). [c] Emission quantum yields of the Eu(III) complexes were measured by using standard procedures with an integrating sphere (diameter 6 cm) by the excitation at 465 nm ($^7F_0 \rightarrow {}^5D_2$) in acetone-$d_6$.[25,33] Concentrations of the Eu(III) complexes were 0.05 M. [d] Radiative rates were determined by using $k_r = 1/\tau_R = \Phi_{ln}/\tau_{obs}$. [e] Stimulated emission cross sections were determined according to the reported method.[24]

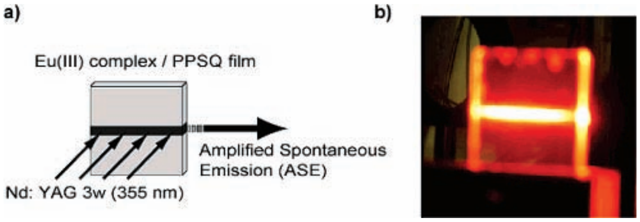


Figure 3. (a) Schematic diagram of photopumped PPSQ film containing Eu(III) complex. The pump beam focused onto the surface of the PPSQ film, and the ASE output beam emitted from the edge of the film. (b) Photograph of the oscillation of ASE of the Eu(III) complex from PPSQ film.

for practical use (1.6−4.5 × 10^{-20} cm^2).[14] These results have led us to the conclusion that the luminescent materials with Eu$(hfa)_3$(BIPHEPO) having the **b**-form structure are promising for applications such as a high-power laser medium.

Amplified Spontaneous Emission (ASE) Properties of the Eu(III) Complexes. The ASE properties of the Eu(III) complexes were measured by incorporating them into polymer thin films of PPSQ.[26] The PPSQ thin films containing the Eu(III) complexes were excited by the third harmonic generation of a nanosecond Nd:YAG laser (355 nm), and the emission decays of the $^5D_0 \rightarrow {}^7F_2$ transition (615 nm) from the edges of the thin films were monitored (Figure 3). Parts a, b, and c of Figure 4 show the emission decay profiles observed at the edge of the PPSQ thin films containing the Eu(III) complexes (Eu(III) complexes: 37 wt %; film thickness: 2 μm). Each emission lifetime measured at the weakest excitation power (0.01 mJ) consisted of a single component (Eu$(hfa)_3$(BIPHEPO): 0.68 ms; Eu$(hfa)_3(TPPO)_2$: 0.65 ms; and Eu$(hfa)_3(OPPO)_2$: 0.70 ms). The emission lifetimes of Eu(III) complexes in polymer thin films (PPSQ) are shorter than those in acetone-d_6 (Table 1). The shorter spontaneous emission lifetimes in polymer are due to the radiationless transition via vibrational relaxation of the C−H bond in PPSQ. The emission decays observed for the stronger excitation energy (>1 mJ) consisted of the normal components (lifetimes of the spontaneous emission) and the fast components (Eu$(hfa)_3$(BIPHEPO): 0.085 ms; Eu$(hfa)_3(TPPO)_2$: 0.088 ms; and Eu$(hfa)_3(OPPO)_2$: 0.10 ms). These observations suggest that the faster components were attributed to the ASE from the Eu(III) complexes in the microcavity.[20,38]

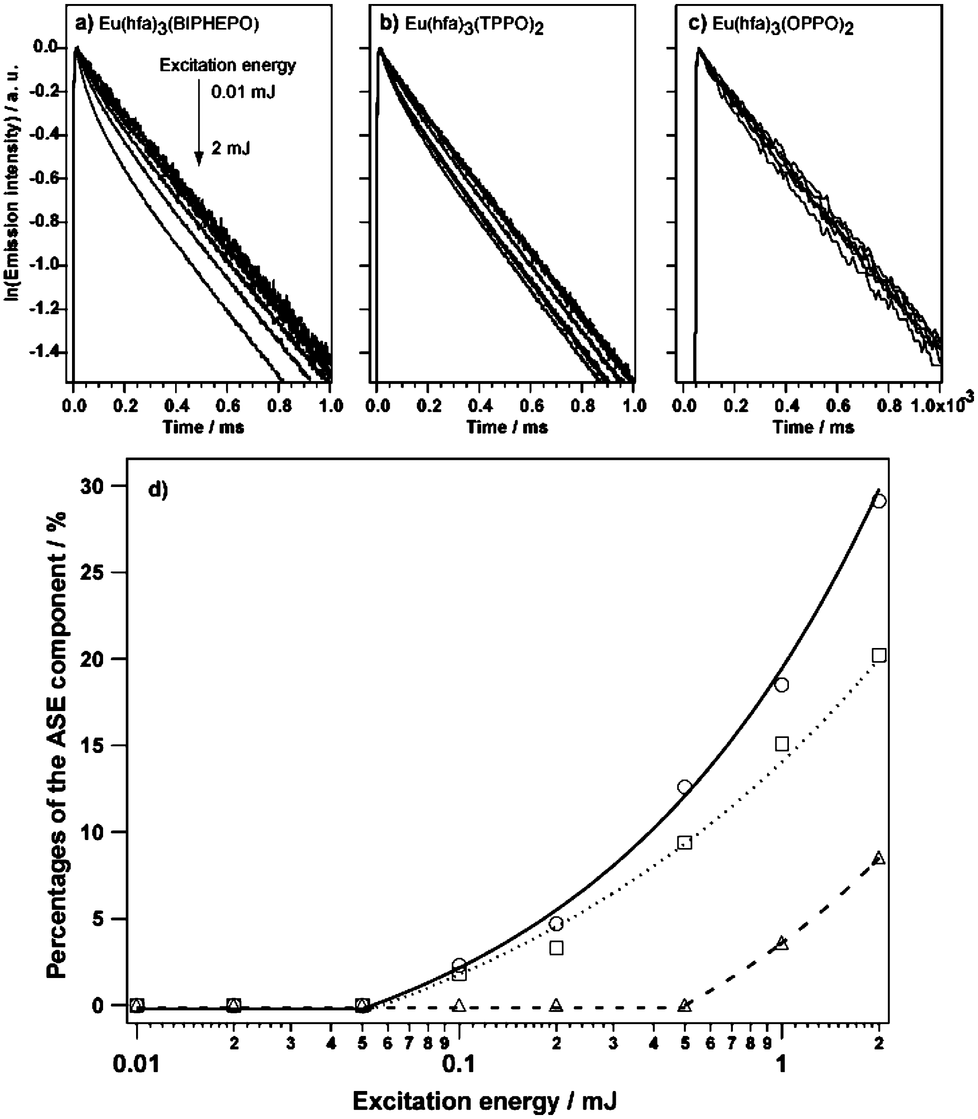


Figure 4. Normalized time dependence of the emission from the edge of the thin-film containing Eu(III) complexes shown on logarithmic scale under different excitation energy: (a) Eu$(hfa)_3$(BIPHEPO), (b) Eu$(hfa)_3(TPPO)_2$, and (c) Eu$(hfa)_3(OPPO)_2$. (d) The relationship between the excitation energy and percentages of the ASE component of Eu$(hfa)_3$(BIPHEPO) (solid line), Eu$(hfa)_3(TPPO)_2$ (dotted line), and Eu$(hfa)_3(OPPO)_2$ (dashed line).

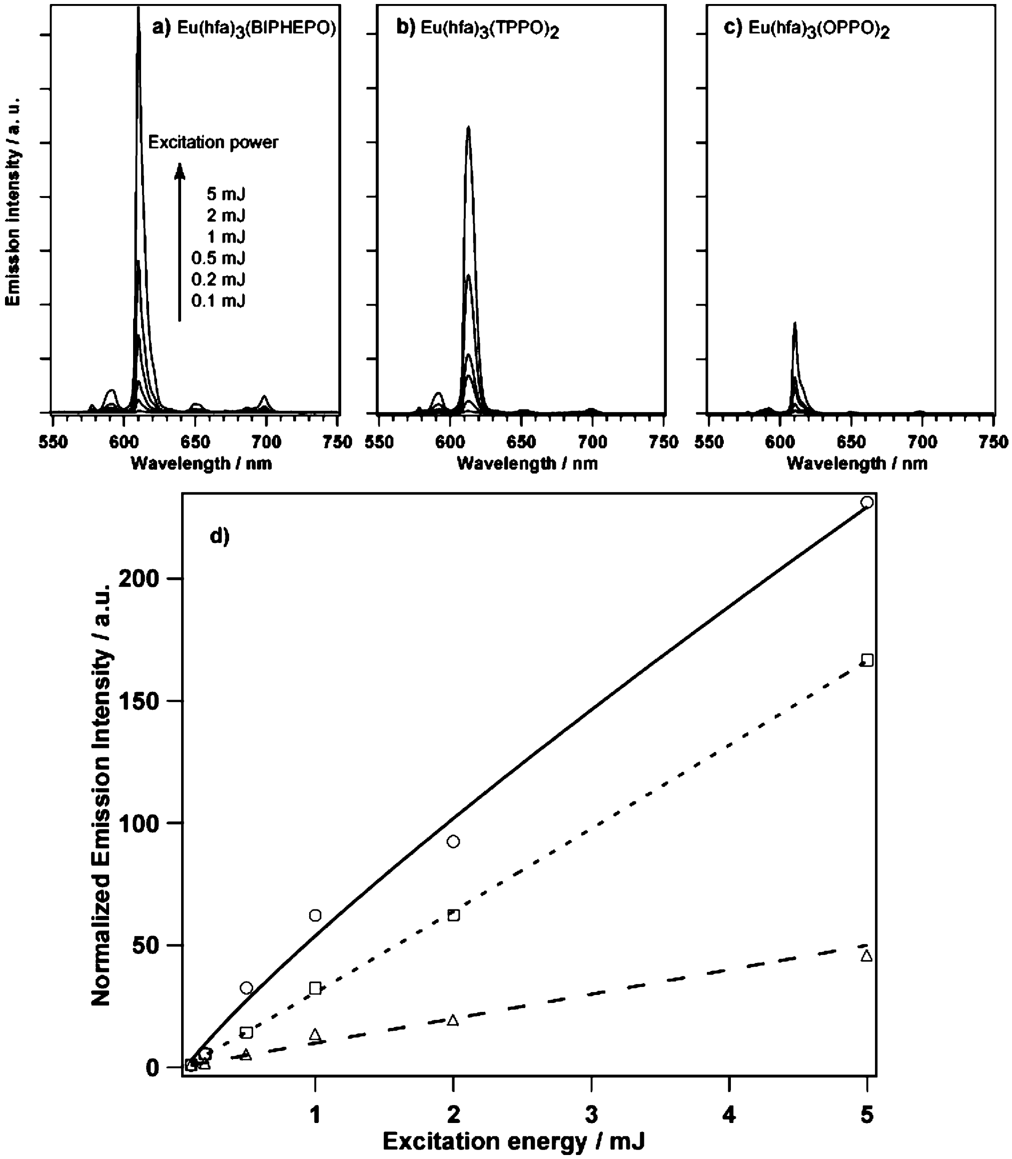


Figure 5. Edge emission spectra of the Eu(III) complexes in the PPSQ film under different excitation energy: (a) Eu(hfa)$_3$(BIPHEPO), (b) Eu(hfa)$_3$(TPPO)$_2$, and (c) Eu(hfa)$_3$(OPPO)$_2$. (d) The dependence of integrated emission intensities of the Eu(III) complexes on excitation power: Eu(hfa)$_3$(BIPHEPO) (solid line), Eu(hfa)$_3$(TPPO)$_2$ (dotted line), and Eu(hfa)$_3$(OPPO)$_2$ (dashed line).

The emission lifetimes were analyzed by a least-squares fitting of the double exponential function. The emission intensity is given by

$$I = a \exp(-bt) + c \exp(-dt) \qquad (5)$$

where a and c are branching ratio functions. The slower lifetime ($-1/d$) was fixed at 0.68 ms for Eu(hfa)$_3$(BIPHEPO), 0.65 ms for Eu(hfa)$_3$(TPPO)$_2$, and 0.70 ms for Eu(hfa)$_3$(OPPO)$_2$. The data measured at stronger excitation power (1.0 and 2.0 mJ) gave good fits of decays; faster lifetimes ($-1/b$) were found to be 0.08$-$0.10 ms. The percentages of the ASE components were determined by

$$ASE\ (\%) = \frac{a}{a + c} \times 100 \qquad (6)$$

However, the faster component of lifetimes measured at weaker excitation power (0.1, 0.2, and 0.5 mJ) could not be analyzed without fixing shorter lifetime components because of their small ASE percentages. To determine the percentages of ASE (a and c parameters) at weaker excitation power, we executed an analysis with fixed faster lifetimes ($-1/b$) between 0.08 and 0.10 ms.

The percentages of the ASE of the Eu(III) complexes in the whole emission are shown in Figure 4d. The percentages increased with an increase of the excitation energy, and the threshold energies of Eu(hfa)$_3$(BIPHEPO) and Eu(hfa)$_3$(TPPO)$_2$ were found to be 0.05 mJ. In contrast, the threshold energy of Eu(hfa)$_3$(OPPO)$_2$ was much larger (0.5 mJ) than those of Eu(hfa)$_3$(BIPHEPO) and Eu(hfa)$_3$(TPPO)$_2$. The high emission-quantum yields and fast radiative rates of the Eu(III) complexes Eu(hfa)$_3$(BIPHEPO) and Eu(hfa)$_3$(TPPO)$_2$ have led to low threshold energy for the ASE oscillation. On the other hand, the amplification of the ASE components (inclination of the curves) of Eu(hfa)$_3$(BIPHEPO) was much greater than those of the corresponding Eu(hfa)$_3$(TPPO)$_2$ and Eu(hfa)$_3$(OPPO)$_2$. This great amplification of the ASE of Eu(hfa)$_3$(BIPHEPO) should be ascribed to the large SEC values of the Eu(hfa)$_3$(BIPHEPO) achieved by structural optimization.

The emission spectra from the edge of the thin films containing the Eu(III) complexes were also measured under different excitation energy. The emission intensities of the

Eu(III) complexes increased with an increase of the excitation energy as shown in Figure 5a−c. However, the emission shapes of the Eu(III) complexes did not change under different levels of excitation energy. Generally, the emission line width (fwhm) of the organic laser dye molecules gradually decreases as the pumping energy increases because of progression of ASE between excited and ground states. In contrast, the emission line width of the corresponding Eu(III) complexes depends on the stark splitting of the crystal fields and is characterized by the geometrical structure of the Eu(III) complex.[22,39] For this reason, the emission shape of the ASE would not change as the pumping energy increases.[39,40] These results indicate that the geometrical structures of the Eu(III) complexes underwent no significant change even during the stronger excitation. Figure 5d shows the dependence of integrated emission intensities (output power) of the Eu(III) complexes on excitation energy. The integrated emission intensities were normalized with those of 0.1 mJ excitation. When the excitation energy was increased by 20 times (2 mJ), the emission intensities of Eu(hfa)$_3$(BIPHEPO), Eu(hfa)$_3$(TPPO)$_2$, and Eu(hfa)$_3$(OPPO)$_2$ were amplified by 92.2, 64.9, and 19.2 times, respectively. The amplifications of the emission intensities of Eu(hfa)$_3$(BIPHEPO) and Eu(hfa)$_3$(TPPO)$_2$ exceeded the degree of the increase of the excitation energy. Those amplifications clearly give proof of the existence of ASE components. The increasing rate of the emission intensity of Eu(hfa)$_3$(BIPHEPO) as a function of excitation energy was much larger than those of Eu(hfa)$_3$(TPPO)$_2$ and Eu(hfa)$_3$(OPPO)$_2$. These results were in agreement with the amplification of the ASE components indicated by lifetime measurements. The large ASE components of the Eu(hfa)$_3$(BIPHEPO) having **b**-form structure would promote the relative increasing rate of their emission intensity, compared with the other Eu(III) complexes.

Conclusion

We have demonstrated the enhancement of the lasing properties of Eu(III) complexes by the use of chemical species for the first time. The emission and lasing properties of luminescent molecules can be controlled by the addition of chemical species. This work deals with the importance of molecular design for the creation of optical devices. Furthermore, a luminescent molecule having (1) high emission quantum efficiency, (2) fast radiative rate, and (3) large SEC is also essential for the construction of a high-power, compact laser system. We are now examining the lasing properties of PPSQ films having a waveguide structure constructed by the photolithography method. The molecular design of luminescent lanthanide complexes is expected to open up new fields in photonic molecular science.

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Supporting Information Available: X-ray crystallographic data for Eu(hfa)$_3$(BIPHEPO), in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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