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Absorption cross-section control of Eu(III) complexes for increase of amplified spontaneous emission excited by third harmonic of nanosecond Nd:YAG laser

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ABSTRACT

The amplified spontaneous emission (ASE) properties of polymer thin-films containing Eu(III) complexes were demonstrated by observing emissions from the edge of excited polymer thin-films. The amplification of the ASE components of Eu(III) complexes was increased in proportion to the absorption cross-sections. In particular, the amplitude percentages of the ASE component of Eu(III) complexes having naphthyl groups (absorption cross-section at 355 nm: 850×10^{-19} cm^2) were estimated to be over 60% under 10 mJ excitation.

1. Introduction

Lanthanide(III)-doped luminescent materials are expected to open up the development of some optical devices such as laser and photo-amplifier systems because of their f–f electric transition which is ideal for the formation of population inversion [1–3]. In particular, luminescent polymer incorporating europium(III) complexes have been regarded as attractive for use as luminescent materials. Koike has introduced the possibility of organic fiber laser systems using Eu(III) complexes incorporated organic optical fibers of polymethylmethacrylate (PMMA) [4]. We have also reported that strong luminescent Eu(III) complexes showed amplified spontaneous emission (ASE) from Eu(III) complexes in polymer thin-film micro-cavities by using a polyphenylsilsesqioxane (PPSQ) [5,6]. Furthermore, Kido has studied that dielectric sphere systems containing Eu(III) complexes performed efficient ASE by using smaller excitation energy for laser oscillation [7]. Luminescent polymer systems containing Eu(III) complexes are promising materials for novel polymer-based optical devices.

We have reported on the molecular design of luminescent Eu(III) complexes for the enhancement of ASE properties. The enhancement of ASE properties from luminescent polymer systems containing Eu(III) complexes is realized by increasing the stimulated emission cross-section (SEC) and the absorption cross-section [8]. The stimulated emission cross-sections of the luminescent Eu(III) complexes are closely related to full width at half maxims (FWHMs) of the emission spectra, which is dominated by the geometrical structure of the Eu(III) complexes. Previously, we have observed that the narrow FWHMs of anti-symmetrical Eu(III) complexes lead to the increase of stimulated emission cross-sections and enhanced ASE properties [9,10]. The control of the geometrical structures in Eu(III) complexes is a key contributing factor in the increase of stimulated emission cross-sections.

Here, we focus on the effect of the absorption cross-section on the ASE properties of luminescent polymers including Eu(III) complexes. In order to control the absorption cross-section, luminescent Eu(III) complexes with various absorption coefficients at the excitation wavelength (excitation wavelength: 355 nm, third harmonic of nanosecond Nd:YAG laser) were prepared. The absorption coefficients of the Eu(III) complexes were manipulated by organic β-diketonato ligands having methyl, trifluoromethyl, phenyl and naphthyl groups (Fig. 1). According to the polymer matrix for the preparation of polymer thin-films, we selected polyphenylsilsesquioxane. PPSQ is a ladder-type polymer with siloxane bonds as a main chain, and has high transparency in the

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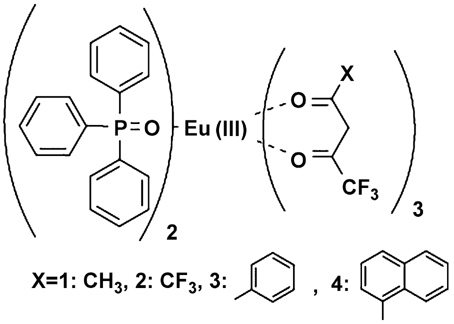

Fig. 1. Chemical structures of Eu(III) complexes.

visible and ultraviolet region [11]. The optical micro-cavity was constructed by forming a high refractive film of PPSQ (refractive index: 1.558) on the glass substrate. Polymer thin-films containing Eu(III) complexes were excited by the third harmonic (355 nm) of nanosecond Nd:YAG laser. The ASE properties of the polymer thin-films containing Eu(III) complexes were demonstrated by observating the emissions from the edge of excited polymer thin-films as we reported previously. In this present work, we report that the increased absorption cross-section of Eu(III) complexes at 355 nm is directly linked to the enhancement of ASE properties by using a Nd:YAG laser.

2. Experimental

2.1. Apparatus

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

2.2. Materials

Europium acetate tetrahydrate (99.9%), 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfa-H_2), 4,4,4-trifluoro-butane-1,3-dione, 4,4,4-trifluoro-1-(phenyl)butane-1,3-dione, 4,4,4-trifluoro-1-(1-naphthyl)butane-1,3-dione, and triphenylphosphine oxide (TPPO) were purchased from Wako Pure Chemical Industries Ltd. and ACT-Chem Ltd. Methanol-d_4 and acetone-d_6 were obtained from Aldrich Chemical Co. Inc. PPSQ was obtained by MITSUBISHI Electric Corporation. Tris(hexafluoroacetylacetonato)europium(III)bis(triphenylphosphine oxide): **2** was prepared by the reaction of tris(hexafluoroacetylacetonato)europium(III)dihydrate and triphenylphoshine oxide in methanol following a procedure described in the previous literature [6]. The Eu(III) complexes **1**, **3** and **4** were also prepared by the same method as for **2**. Those compounds were identified by ^1H NMR, ^{19}F NMR and elemental analyses. All other chemicals were of reagent grade and were used as received.

Deuterated Eu(III) complexes were obtained by the exchange reaction via keto–enol tautomerism **1**–**4** CD_3OD for 6 h under vacuum. Obtained Eu(III) complexes were then added to anisole solution containing PPSQ. An Eu(III) thin-film was prepared on a glass substrate from the anisole solution via spin-coating method. The film thickness was found to be 2.0 mm, using a surface profiler (Veeco Instruments Inc., DEK-TAK3).

2.3. Optical measurements

Emission spectra were measured at room temperature using 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, $l = 1064$ 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 emission quantum yields were determined by standard procedures with an integrating sphere (diameter 6 cm) mounted on a spectrofluorometer (HITACHI F-4500) [12].

2.4. 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 using 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, $l > 365$ 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 using a digital oscilloscope (SONY Tektronics TDS540) synchronized to the excitation pulse. The emission decays containing two components (normal spontaneous emission lifetimes; and faster emission lifetimes) were analyzed by a least-square fitting of the double exponential function. The emission intensity is given by

$$I = a\exp(-bt) + c\exp(-dt) \qquad (1)$$

where a and c are branching ratio functions. The faster components and normal components of the emission lifetimes were $-1/b$ and $-1/d$, respectively. The percentages of the ASE components were determined by

$$\mathrm{ASE}\ (\%) = \frac{a}{a+c} \times 100 \qquad (2)$$

The emission spectra from the edge were measured by 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 thermo-power meter.

3. Results and discussion

3.1. Absorption and emission properties of Eu(III) complexes

The absorption spectra of the Eu(III) complexes **1**–**4** in methanol are shown in Fig. 2. The broad absorption band in the Eu(III) complexes were assigned to π–π* transitions of the β-diketonato ligands. The wavelengths of absorption maxima ($\lambda_{\mathrm{abs.\ max}}$) were shifted from 298 to 337 nm. The red shift of the absorption maxima of Eu(III) complexes was owing to the expansion of delocalized π-conjugation systems of the ligands. The molecular absorption coefficients and absorption cross-sections at 355 nm (optically pumping wavelength) of the Eu(III) complexes are summarized in Table 1. The absorption cross-sections at 355 nm of complexes **1** and **2** were found to be 2.0 and 6.0×10^{-19} cm^2, respectively. In contrast, those of complexes **3** and **4** were much larger than those of complexes **1** and **2** (330 and 850×10^{-19} cm^2).

The emission spectra of the deuterated Eu(III) complexes in acetone-d_6 are shown in Fig. 3. We observed five emission peaks, 580, 590, 615, 650, and 700 nm, which were attributed to the f–f transitions $^5D_0$–^7F_J ($J = 0$–4, respectively). The strongest emission at 615 nm ($^5D_0$–$^7F_2$) is due to the electronic dipole transition. The

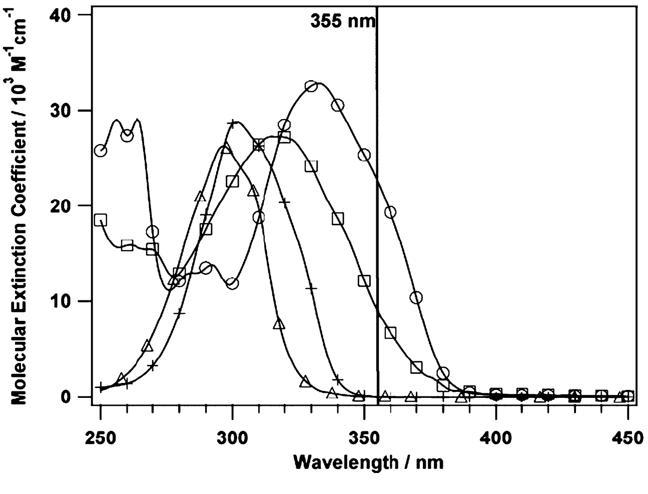

Fig. 2. UV–vis absorption spectra of the Eu(III) complexes (triangle: complex **1**; cross: complex **2**; square: complex **3**; circle: complex **4**).

Table 1
Absorption properties and photophysical properties of Eu(III) complexes. Wavelength of the absorption maxima ($\lambda_{\text{abs. max}}$) and absorption cross-sections[a] (σ_{abs}) at 355 nm of the Eu(III) complexes in acetone. Emission lifetimes[b] (τ_{obs}), emission quantum yields[c] (Φ_{ln}), radiative rates[d] (k_r), and stimulated emission cross-sections[e] (σ_ρ) in acetone-d_6.

Complex	$\lambda_{\text{abs. max}}$ (nm)	σ_{abs} ($\times 10^{-19}$ cm^2) (355 nm)	τ_{obs} (ms)	Φ_{ln}	k_r ($\times 10^2$ s^{-1})	σ_ρ ($\times 10^{-20}$ cm^2)
1	298	2.0	0.72	0.70	9.7	1.41
2	303	6.0	0.93	0.90	9.7	1.42
3	320	330	0.77	0.72	9.4	1.37
4	337	850	0.75	0.80	10.7	1.56

[a] Absorption cross-sections were determined using $\sigma_{\text{abs}} = \varepsilon/(2.6 \times 10^{20})$.

[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 using standard procedures with an integrating sphere (diameter 6 cm) by the excitation at 465 nm ($^7F_0$–$^5D_2$) in acetone-d_6. Concentrations of the Eu(III) complexes were 0.05 M.

[d] Radiative rates were determined using $k_r = 1/\tau_R = \Phi_{\text{ln}}/\tau_{\text{obs}}$.

[e] Stimulated emission cross-sections were determined according to the reported method.

emission peaks of $^5D_0$–$^7F_2$ transitions of the Eu(III) complexes were split into five Stark levels (610, 612, 616, 618 and 620 nm). The shapes of emission spectra of Eu(III) complexes **1**, **3** and **4** were similar to that of previously reported Eu(III) complex **2**. The spectral shapes of Eu(III) complexes are dependent on symmetricity of the geometrical structures in Eu(III) complexes [13,14]. These results suggest that geometrical structures of Eu(III) complexes **1**, **3** and **4** are similar to that of Eu(III) complex **2**. The emission lifetimes (τ_{obs}), emission quantum yields (Φ_{ln}), radiative rates (k_r) and stimulated emission cross-section (σ_ρ) of the Eu(III) complexes in acetone-d_6 are also summarized in Table 1. The complexes **1**–**4** showed long emission lifetimes and high emission quantum yields. Those high emission quantum yields were achieved by the prevention of radiationless transition via vibrational excitation. The prevention of radiationless transition is due to three deuterated hexafluoroacetylacetonato ligands which have only low-vibrational C–F or C–D bonds [6]. On the other hand, radiative rates and stimulated emission cross-sections of the Eu(III) complex **2** were similar to those of corresponding Eu(III) complexes **1**, **3** and **4**. Generally, the radiative rates (transition probabilities) of the f–f transitions depend on the geometrical structures of Eu(III) complexes [15]. We conclude that the geometrical structures of Eu(III) complexes **1**, **3** and **4** are similar to that of Eu(III) complex **2** in acetone-d_6.

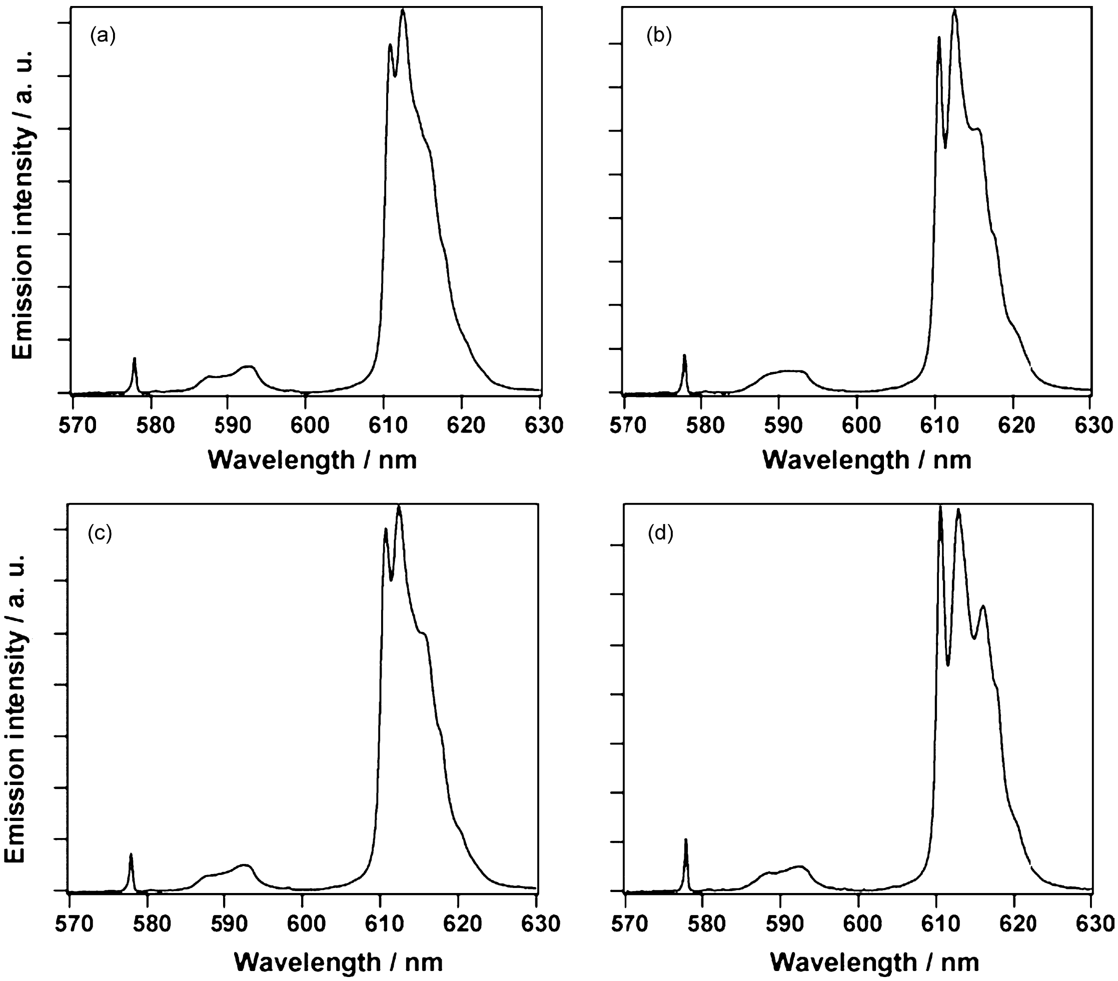

Fig. 3. Emission spectra of (a) Eu(III) complexes **1**; (b) complex **2**; (c) complex **3**; and (d) complex **4**.

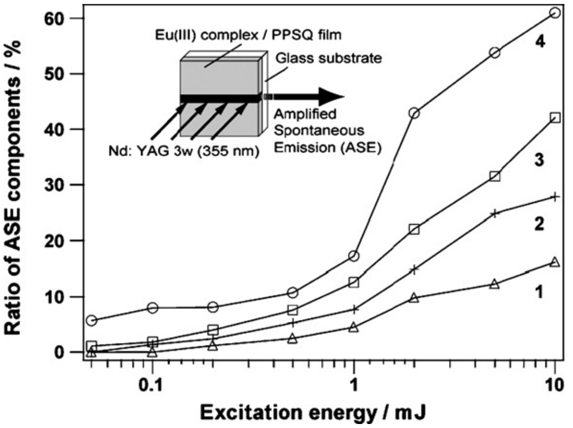

Fig. 4. The relation between the excitation energy and percentages of the ASE components of the Eu(III) complexes (triangle: complex **1**; cross: complex **2**; square: complex **3**; circle: complex **4**). The percentages of the ASE components were determined by lifetime analysis.

3.2. ASE properties of Eu(III) complexes

The emission lifetimes were measured at the weakest excitation power (0.01 mJ) consisting of single components, (**1**: 0.59 ms, **2**: 0.65 ms, **3**: 0.61 ms, and **4**: 0.60 ms), which agreed well with the spontaneous emission lifetimes of Eu(III) complexes in PPSQ films. The emission decays under the stronger excitation energy (>1 mJ) consisted of normal components (lifetimes of the spontaneous emission) and fast components (**1**: 0.075 ms, **2**: 0.088 ms, **3**: 0.080 ms, and **4**: 0.078 ms). These observations suggest that the faster components are attributable to the ASE from the Eu(III) complexes in the polymer thin-films micro-cavity [5]. The ASE components in the whole emission were determined by a least-squares fitting of the double exponential function. The percentages of the ASE component of the Eu(III) complexes as a function of excitation energy are shown in Fig. 4. They increased along with the increase of excitation energy, and the threshold energies of **1** and **2** were found to be 0.1 mJ. In contrast, the threshold energy of the **3** and **4** was 0.05 mJ and less than 0.05 mJ, respectively. We also found that the amplification of the ASE components of the Eu(III) complexes were increased in proportion to the absorption cross-sections at 355 nm. In particular, the amplitude percentage of the ASE component of complex **4** was estimated to be over 60% under 10 mJ excitation. This large amplification of the ASE of **4** should be ascribed to the large absorption cross-section value of **4**. The large absorption cross-section of complex **4** would promote the formation of population inversion leading to effective stimulated emission under optical pumping.

4. Conclusion

We have demonstrated that the ASE properties of Eu(III) complexes excited by the third harmonic of Nd:YAG laser depend on not only the emission cross-sections, but also the absorption cross-sections at 355 nm. The optimum manipulation of the photophysical properties of luminescent Eu(III) complexes by molecular design is an essential factor in creating superlative optical materials. Eu(III) complex **4** would be desirable for developing application in novel polymer materials such as plastic optical fibers [4]. Conceptual molecular design of Eu(III) complexes and fabrication of luminescent polymer are expected to open up pioneering fields in opto-material science.

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