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Molecular design of luminescent Eu(III) complexes as lanthanide lasing material and their optical properties

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Abstract

Luminescent polymer (PMMA) containing a Eu(III) complex with a fast radiation rate and a high luminescence quantum efficiency ($75 \pm 5\%$), (bis-triphenylphosphineoxide)(tris-hexafluoroacetylacetonato)europium(III) (Eu(hfa)$_3$(TPPO)$_2$), was fabricated. The quantum yield and the radiation rate of the luminescent polymer were found to be $75 \pm 5\%$ and $1.1 \times 10^3\,\mathrm{s}^{-1}$, respectively. An Eu(III) complex-doped polymer thin-film was also prepared by use of polyphenylsilsesquioxane (PPSQ) to construct a waveguide lanthanide laser. We propose a strategy for the molecular design of luminescent Eu(III) complexes aiming at lanthanide lasing.

Keywords: Polymer; Thin-film; Luminescence

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1. Introduction

An organic medium incorporating lanthanide(III) complex is promising for constructing functional devices such as the polymer fiber laser, and the plastic thin-film laser. Especially, europium(III) complexes have been regarded to be attractive for use as luminescent materials because of their red emissions (around 615 nm) [1]. Characteristic emissions of Eu(III) complexes mainly come from electric dipole transitions [2–13]. The red emissions from Eu(III) complexes are attributed to four-levels transitions, therefore population inversion in 4f orbitals is deadly available, which is a great advantage in the development of plastic laser applications [14–17].

A key goal in laser transmission and photo-induced amplification using Eu(III) complex is to achieve low transmission threshold levels for practical uses. Transmission threshold, ΔN_{th}, can be expressed as,

$$\Delta N_{\mathrm{th}} = \frac{\Delta N_0}{1 + 2B\rho_{\mathrm{s}}T} \qquad (1)$$

where ΔN_0, B, ρ_{s} and T are the number of excited Eu(III) complexes (excitation energy), Einstein coefficient, energy density and relaxation time in cavity, respectively [2]. In order to obtain low ΔN_{th} values, Eu(III) complexes that exhibit both high emission quantum yields and fast radiation rates are desirable luminescent materials. Thus, Eu(III) complexes should be designed to meet two criteria: (1) higher emission quantum yields to increase ρ_{s}, (energy density) values and (2) faster radiation rates to produce large B (Einstein coefficient: (Einstein A coefficient $= 8\pi h\nu^3/c^3 \times B$, $h\nu =$ photon energy, $c =$ light velocity) Einstein A coefficient is transition rate of spontaneous emission) values.

Here, we report a luminescent Eu(III) complex with fast radiation rates and high luminescence quantum efficiencies, (bis-triphenylphosphineoxide)(tris-hexafluoroacetyl

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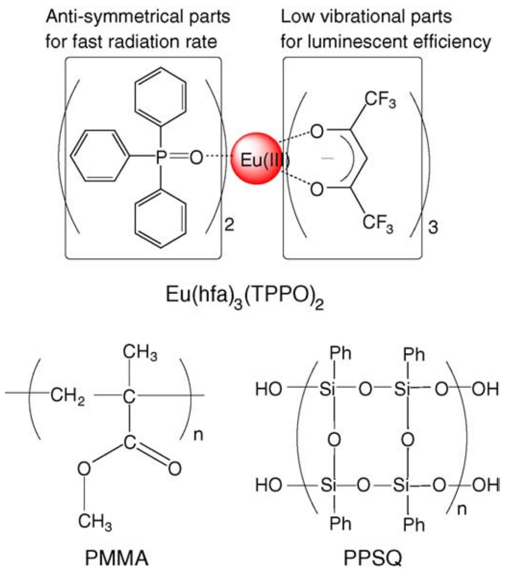

Fig. 1. Chemical structures of (a) $Eu(hfa)_3(TPPO)_2$, (b) PMMA and (c) PPSQ.

acetonato)europium(III) ($Eu(hfa)_3(TPPO)_2$: Fig. 1a). The high emission quantum yield of the Eu(III) can be achieved by low-vibrational hexafluoroacetylacetonato ligands. In addition, the phosphine oxide ligands provide anti-symmetrical structures promoting a faster radiation rate. We discuss characteristics of the Eu(III) complex and luminescent polymers in terms of emission properties. We have successfully developed luminescent polymethylmethacrylate (PMMA: Fig. 1b) containing the Eu(III) complex, which exhibited the highest quantum yield and fastest radiation rate (quantum yield = 75 ± 5%, radiation rate = $1.1 \times 10^3\ s^{-1}$) among even observed. The radiation rate of the Eu(III) complex in PMMA is of the same order as those of Nd:YAG, etc. (radiation rate ≈ $1.5 \times 10^3\ s^{-1}$).

Furthermore, we improved the Eu(III) thin-film using polyphenylsilsesquioxane (PPSQ: Fig. 1c) polymer. A Eu(III) thin-film patterning using a photoresist mask enables construction of a waveguide laser. In addition, the waveguide lanthanide(III) laser on the Si-wafer leads to potential applications for an optical computing device [18]. Here, we fabricated PPSQ thin-film containing the Eu(III) complexes. The thin-film consists of a PPSQ containing the Eu(III) complexes. PPSQ is an inorganic polymer with a ladder type structure of siloxane bonds as a main chain and phenyl groups as side chain. As PPSQ has also high optical transparency, PPSQ has been suggested as a promising material for wafer-scale optical waveguide interconnects [19]. The micro-cavity was constructed by high refractive film of PPSQ (refractive index: 1.558) on the glass and Si-wafer substrate. The novel Eu(III) thin-film laser will likely generate new applications in compact lasers.

2. Experiment

2.1. Apparatus

Infrared spectra used to identify the synthesized materials were obtained with a Perkin-Elmer FT-IR 2000 spectrometer. Elemental analyses were performed with a Perkin-Elmer 240C. ^{13}C and ^{19}F NMR data were obtained with a JEOL EX-270 spectrometer. ^{13}C NMR chemical shifts were determined using tetramethylsilane (TMS) as an internal standard, while ^{19}F NMR chemical shifts were determined using hexafluorobenzene as an external standard ($\delta = -162.0$ (s, Ar–F) ppm).

2.2. Materials

Europium acetate monohydrate (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 (CD_3OD, 99.8%) and DMSO-d_6 (CD_3SOCD_3, 99.8%) were obtained from Aldrich Chemical Company Inc. PPSQ ($M_w = 5.2 \times 10^4$) was obtained from MITSUBISHI Electric Corporation [19]. All other chemicals were reagent grade and were used as received.

2.3. Preparation of tris-(hexafluoroacetylacetonato) europium(III) dehydrates ($Eu(hfa\text{-}H)_3(H_2O)_2$)

Europium acetate monohydrate (5.0 g, 12.5 mmol) was dissolved in 20 ml of distilled water by stirring at 0 °C. A solution of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (7 g, 33.6 mmol) in methanol (5 ml) was added dropwise to the above solution. The mixture produced a precipitate of white yellow powder after stirring for 3 h. The reaction mixture was filtered. The resulting white yellow needle crystals were recrystallized in methanol/water. Yield: 95%, IR(KBr): 1650 (st, C=O), 1258–1145 (st, C–F) cm^{-1}. ^{19}F NMR (CD_3COCD_3) $\delta = -72.80$ (s, CF_3) ppm. Anal. Calcd. for $C_{15}H_7O_8F_{18}Eu$: C, 22.48; H, 0.88%. Found: C, 22.12; H, 1.01%. Decomposition point: 220 °C.

2.4. Preparation of tris-(hexafluoroacetylacetonato) europium(III) bis(triphenylphospine oxide) ($Eu(hfa\text{-}H)_3(TPPO)_2$)

The Eu(III) complex was characterized by ^1H and ^{19}F NMR spectroscopy, IR spectroscopy, elemental analysis and single-crystal X-ray diffraction. Methanol (100 ml) containing $Eu(hfa\text{-}H)_3(H_2O)_2$ (4.28 g, 6 mmol) and triphenylphospine oxide (TPPO) (2.78 g, 10 mmol) were refluxed under stirring for 12 h. The reaction mixture was concentrated using 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

([Eu(hfa-H)$_3$]·2(TPPO)). Yield: 74%, IR(KBr): 1650 (st, C=O), 1250–1150 (st, C–F), 1125 (st, P=O) cm^{-1}. ^{1}H NMR (CD_3COCD_3) $\delta = 7.6$ (m, aromatic C–H), 5.4 (s, c-H) ppm. ^{19}F NMR (CD_3COCD_3) $\delta = -76.7$ (s, C–F) ppm. Anal. Calcd. for $EuC_{51}H_{33}O_8F_{18}P_2$: C, 45.96; H, 2.50%. Found: C, 45.94; H, 2.57%. Decomposition point: 250 °C.

2.5. Preparation of polymethylmethacrylate (PMMA) containing Eu(III) complex

Eu(III) complexes (0.1 mmol) were dissolved in 2 ml of CD_3OD. After degassing the solution, deuteration of the ligands was carried out by exchange reactions via keto–enol tautomerism in CD_3OD for 6 h under vacuum. After evaporation under vacuum (~10^{-3} Torr), deuterated Eu(III) complex, Eu(hfa-D)$_3$(TPPO)$_2$ was obtained as white yellow powders. Deuterated Eu(III) complex (0.05 M) was dissolved in a 1 ml mixture of purified anhydrous methylmethacrylate (MMA) and AIBN in a Pyrex tube (Eu(III) ion 0.7 wt%, AIBN 0.05 wt% and DMSO-d_6 6.6 wt%). The Pyrex tube was sealed off under 10^{-3} Torr, and thermostated at 60 °C for polymerization of MMA (samples 1, 2 and 4). After polymerization, optical samples were ground using Al_2O_3 nanoparticles.

2.6. Preparation of PPSQ thin-films containing Eu(III) complex

Polymer matrix, PPSQ beads were dissolved in 5 ml of anisole. The Eu(III) complex was 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 [20]. The film thickness was found to be 1.71 μm using surface profiler (Veeco Instruments Inc. DEK-TAK3).

2.7. Optical measurements

Emission spectra were measured at room temperature using a HITACHI F-4500 system. The spectra were corrected for detector sensitivity and lamp intensity variations. Emission lifetimes were measured with a 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). Nanosecond light pulses used to excite the samples ($\lambda = 465$ nm, power = 0.1 mJ) were generated by a dye laser (USHO optical systems DL-50, dye = coumarin 120). Emissions from the samples were filtered using a monochromator (Shimazu SPG-100ST) placed in front of the detector. Nd:YAG response was monitored with a digital oscilloscope (Sony Tektronix, TDS3052, 500 MHz) synchronized to the single pulse excitation.

The Quantum yields were determined using a standard integrating sphere (diameter 6 cm) [21,22]. Optical path length of the cell was 5 mm. The emission quantum yields of OPP-3 (Ex at 285 nm, 300–450 nm, emission quantum yield = 95 ± 5%) and rhodamine 6G in PMMA (Ex at 488 nm, 510–760 nm, emission quantum yield = 93 ± 3%) determined by the present procedure agreed well with the reported values [23].

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) (Fig. 3). Emission from the edge of 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 using a digital oscilloscope (SONY Tektronics TDS540) synchronized to the excitation pulse. Energy of the beam spot (excitation energies of the samples) was measured by thermo-power meter.

3. Results and discussion

3.1. Molecular design of luminescent Eu(III) complex

Creation of lanthanide(III) complexes with higher emission quantum yields is directly linked to suppression of radiationless transitions caused by vibrational excitations in surrounding media [24–27]. According to energy gap theory [28], such radiationless transitions are promoted by ligands and solvents with high frequency vibrational modes. In earlier studies, we reported the suppression of radiationless quenching of Nd(III) systems by complexing Nd(III) with β-diketonato ligands composed only of low vibrational C–D and C–F bonds [26,27]. Suppression of such vibrational excitations in Eu(III) complexes requires deuteration of C–H and O–H bonds or replacement of C–H bonds with C–F bonds in ligating molecules.

In contrast, radiation rates of Eu(III) complexes are linked to geometric structure. If there is no inversion symmetry at lanthanide ion sites, odd ligand field components can mix with opposite-parity states in 4f^n-configuration levels. Electric-dipole transitions are then no longer strictly forbidden in the ligand fields, resulting in faster electron transition radiation rates [2]. Eu(III) complexes with odd-parity can be created using certain geometrical and coordination structures. Coordination numbers of lanthanide ions in solution are known to vary between 8 and 10 depending on the nature of the ligating molecules [29–31]. Generally, Ln(hfa-D)$_3$ complex has two coordinating water or solvent molecules in solution [32]. Eight-coordinate Eu(III) complex was synthesized using [Eu(hfa-D)$_3$] and two phosphine oxide molecules. From coordination X-ray analysis, the geometrical structure was determined to be an asymmetrical square-anti prism [33]. Phosphine oxide ligands can produce anti-symmetrical structures that promote faster radiation rates. This result indicates that Eu(hfa)$_3$(TPPO)$_2$ has no inversion center in the crystal

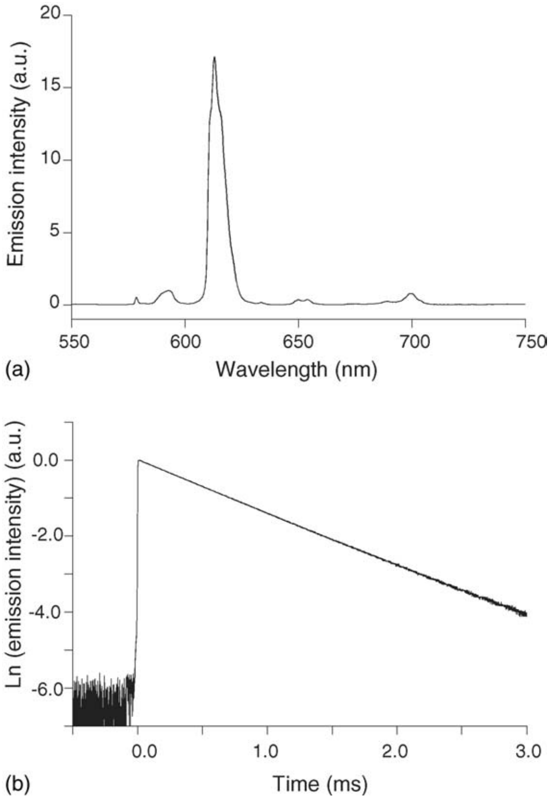

Fig. 2. (a) Emission spectrum of Eu(hfa)$_3$(TPPO)$_2$ in PMMA (Eu: 0.7 wt%). The excitation at 465 nm is due to the $^7F_0 \rightarrow {}^5D_2$ transition. Spectra in (a) were normalized with respect to the $^5D_0 \rightarrow {}^7F_1$ (magnetic dipole) transition. (b) Emission decays profile of Eu(hfa)$_3$(TPPO)$_2$ in PMMA (Eu: 0.7 wt%) shown on a logarithmic scale. Excitation at 465 nm ($^7F_0 \rightarrow {}^5D_2$) was caused by a dye laser (coumarin 120).

field, resulting in an increase in electron transitions in the 4f orbitals due to odd parity.

3.2. Emission properties in polymer

In order to examine photophysical properties of Eu(hfa)$_3$(TPPO)$_2$ in PMMA, emission spectrum and emission lifetime were measured under the excitation at 465 nm ($^7F_0 \rightarrow {}^5D_2$: f–f transition). Emission spectrum of Eu(III) complex in PMMA is shown in Fig. 2a. Emission bands were observed at 578, 590, 613, 651 and 698 nm and were attributed to f–f transitions $^5D_0 \rightarrow {}^7F_0$ (zero–zero band: forbidden transition), $^5D_0 \rightarrow {}^7F_1$ (magnetic dipole transition), $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ (electric dipole transitions), respectively. The spectrum shown in Fig. 2a was normalized with respect to the $^5D_0 \rightarrow {}^7F_1$ (magnetic dipole) transition. Emission decay of Eu(III) complex in PMMA was also measured (Fig. 2b). Single exponential decay emission suggests the presence of a single luminescent site in PMMA and homogeneity of the sample. Emission lifetime was determined from the slopes of logarithmic plots of the decay profiles. Luminescent polymer with Eu(hfa)$_3$(TPPO)$_2$ exhibited the higher quantum yield (75 ± 5%) and faster emission rate ($1.1 \times 10^3\ \mathrm{s}^{-1}$) than those of corresponding with other Eu(III) complexes [33]. The emission quantum yield of the Eu(III) complex in acetone-d_6 was found to be >95%.

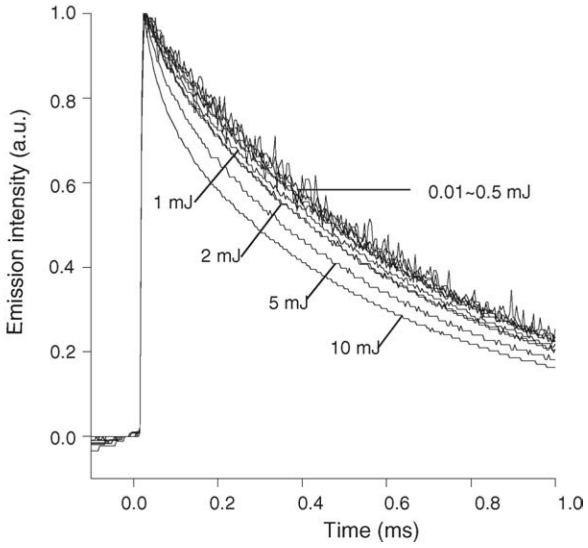

Fig. 4. Normalized time dependence of the emission from the Eu(III) thin-film at edge of PPSQ thin-films including Eu(hfa)$_3$(TPPO)$_2$.

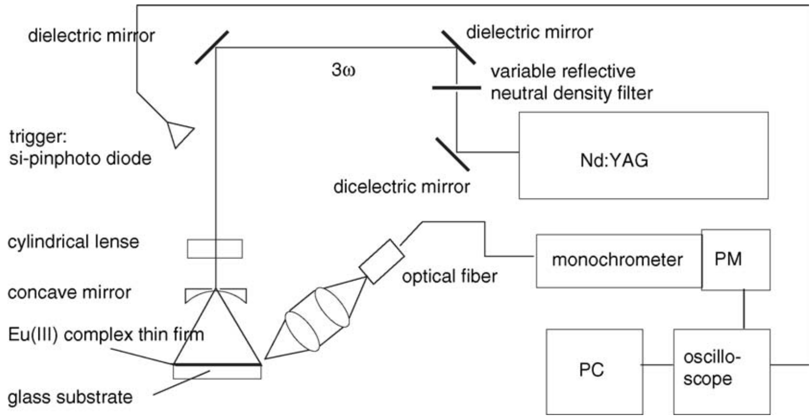

Fig. 3. Experimental set-up for ASE measurements of PPSQ thin-films including Eu(hfa)$_3$(TPPO)$_2$.

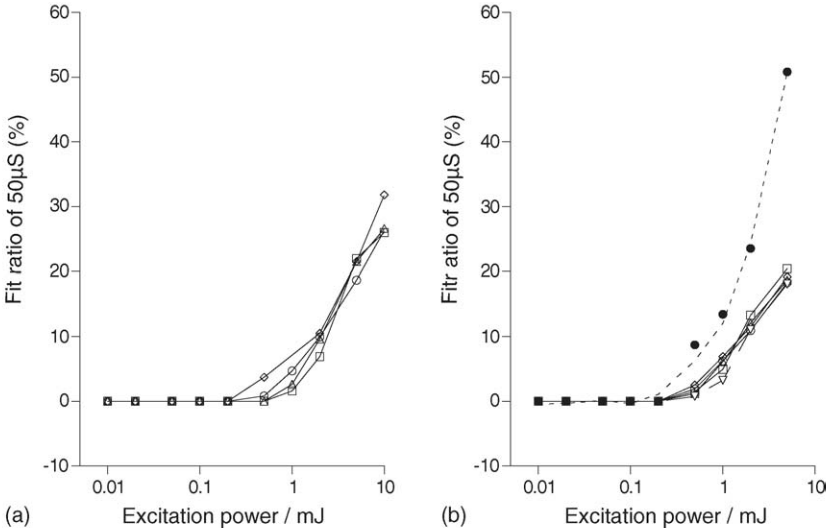

Fig. 5. Relation between excitation energy and the fraction of the faster component. (a) Concentrations of $Eu(hfa)_3(TPPO)_2$ in PPSQ were 13 wt% (○), 23 wt% (□), 37 wt% (◊) and 54 wt% (△). (b) Thickness of the films on the glass substrate were 0.47 μm (○), 0.61 μm (□), 0.76 μm (◊), 1.05 μm (△), 1.48 μm (△) and 2.03 μm (▽). Thickness of the Si-wafer was 2.03 μm (●).

3.3. ASE properties

We carried out the amplified spontaneous emission (ASE) measurements of PPSQ thin-films including $Eu(hfa)_3(TPPO)_2$ by use of Nd:YAG laser system (Fig. 3). Fig. 4 shows the emission decay profiles observed at the edge of the Eu(III) thin-film ($Eu(hfa)_3(TPPO)_2$: 37 wt%, film thickness: 2 μm). The emission lifetime measured at the weakest excitation power (0.01 mJ) was found to be 0.650 ms, which agreed well with the lifetime observed a top surface of the Eu(III) complex in PPSQ (0.660 ms). The emission decays at a strong excitation energy (given $\geq$1 mJ) consisted of a normal component (0.650 ms) and a fast component (0.050 ms). The shape of the decay for the film top surface excited at 10 mJ agreed well with that from the film edge excited at 0.1 mJ. These observations suggest that the faster component was due to ASE from the Eu(III) complexes in the micro-cavity. The emission lifetimes were analyzed by a least-squares fitting of the double exponential function. The emission intensity is given by,

$$I = a\mathrm{e}^{-bt} + c\mathrm{e}^{-dt} \tag{2}$$

where the fast lifetime and the slow lifetime are fixed at 0.050 ms ($=-1/b$) and 0.650 ms ($=-1/d$), respectively. The fraction of the faster component is expressed by,

$$\text{ratio} = \frac{a}{a+c} \tag{3}$$

The relation between the fraction of the faster component and the excitation energy is shown in Fig. 5. In Fig. 5a and b, we measured the ASE dependencies on the concentration of Eu(III) complex (13, 23, 37 and 54 wt%) and film thickness (0.47, 0.61, 0.76, 1.05, 1.48 and 2.03 μm). The ASE properties of the samples were independent of the concentration and film thickness on the glass substrate.

In order to make an effective photon confinement in the polymer thin-films, we fabricated PPSQ thin-film with Eu(III) complex on a Si wafer substrate. The ASE property on the Si wafer was shown in Fig. 5b. We observed enhancement of the ASE property of Eu(III) complex thin-film on the Si wafer (Fig. 5b). The enhancement of ASE might be due to mirror effect of the Si wafer. We propose that effective micro-cavity is formed on the Si wafer surface. We are now trying to fabricate the applied wave-guide cavity using photo-resist pattern and Al evaporation technique.

In the lasing of lanthanide(III) ions, the narrowing of the emission spectra and the changing of the branching ratio between emission bands were not observed, because electrically forbidden transition in f orbitals was not perturbed by laser transmission [28]. In the future, the emission lines at 590, 615, 650 and 700 nm will be used for tuning the high-power laser.

4. Conclusion

We report molecular design of luminescent Eu(III) complexes for lanthanide lasing medium. Luminescent polymer including $Eu(hfa)_3(TPPO)_2$ exhibited the highest quantum yield (75 ± 5%) and fastest emission rate ($1.1 \times 10^3\ \mathrm{s}^{-1}$) in PMMA matrix. Enhancement of the ASE properties of Eu(III) complex in PPSQ thin-films was obtained on a Si-wafer surface. The waveguide lanthanide(III) laser on the Si wafer leads to potential applications for an optical computing device. The Eu(III) thin-film laser is expected to generate new applications for high-power and compact lasers.

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