Fluorescence Enhancement of Europium Ions in a Scattering Matrix

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Keywords: Fluorescence, Europium, Polyethylene Glycol, Scattering, Droplet Laser.

Abstract: Microlasers are usually composed of organic dyes that emit fluorescence with a high efficiency. Those dyes, however, lose their fluorescence function in a short time because of optically- or thermally-induced bleaching. This degradation is particularly serious with microdevices, since a high-powered beam is focused into a small volume of the device. The problem of the device degradation can be solved, if organic dyes are replaced by fluorescent lanthanide ions (europium, erbium, neodymium, etc.) that have a superior durability against optical and thermal hazards. The lanthanide ions, however, have a smaller absorption cross-section than organic dyes, and hence, a pump light for exciting the ions is absorbed insufficiently inside a microdevice. A long optical path is therefore required to enhance the excitation efficiency. Polyethylene glycol is a useful solvent for dispersing europium ions, since it turns to a translucent matrix by solidification. In this translucent matrix, pump light (396 nm wavelength) is scattered heavily, which leads to extension of the optical path and enhancement of the absorbance. Consequently, fluorescence of the europium ions (613 nm) becomes twofold stronger in the solid phase than the liquid phase.

1 INTRODUCTION

Microfluidic devices are attracting interests in various technical fields including chemical analysis, biological sensing, and material synthesis (Hawkins and Schmidt, 2010). Organic dyes are usually used for yielding a fluorescence function in the liquid. Microdroplet laser is a unique fluidic device in which fluorescence circulates numerous times inducing a stimulated emission. A droplet of dye solution self-forms a perfect sphere with a smooth surface, which facilitates the light circulation. In addition, deformable spheres realize the emission wavelength tuning. Since these unique features are unattainable with solids, droplet lasers have been studied extensively in the last three decades (Tzeng et al, 1984). Disadvantages of the droplet lasers include handling difficulty (fluidity) and instability (volatility), which are essential features of liquids. These problems are avoidable by enclosing a droplet in a silicone rubber (Saito et al, 2008); i.e., whereas an enclosed droplet can be handled like a solid, its fluidity is preserved in a flexible silicone rubber.

In spite of the improvement above, microdroplet lasers still have another problem; i.e., organic dye molecules degrade rapidly because of photochemical or thermochemical reactions during excitation and emission processes. This degradation generally takes place in organic dye lasers (Gersborg-Hansen et al, 2007). Conventional dye lasers, therefore, circulate a dye solution to replace bleached molecules by fresh ones. As regards dye-doped polymer lasers, disk rotation (Kytina et al, 2004) or molecular diffusion (Yoshioka et al, 2012) are achieved to extend the device lifetime. Unfortunately these methods are unadoptable for microdroplet lasers, although the dye bleaching is even more serious in a small droplet that is exposed to a strong laser beam (Barnes et al, 1993).

A possible solution for the degradation problem is replacement of organic dyes by lanthanide elements, e.g., europium (Eu), erbium (Er), neodymium (Nd), thulium (Tm), samarium (Sm), etc. Photoluminescence of these ions are well known (Shionoya and Yen, 1999) and widely used in lasers, amplifiers, and illuminators. Many researchers fabricated microspherical lasers by doping lanthanide ions in crystals and glasses, e.g., Sm-doped fluorite (Garret et al, 1961), Nd-doped glass (Miura et al, 1996), and Er-doped glass (Klitzing et al, 2000). A droplet laser was also fabricated by using a Eu chelate (Lin et al, 1992).

The lanthanide ions, however, have a disadvantage that an absorbance is too low to absorb pump light efficiently in a small droplet. In this respect, organic dyes are superior to the lanthanide ions. It

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has been reported, for example, that the pump-light absorbance of rhodamine is 10,000-fold stronger than that of Er (Tagaya et al, 1997). The optical path has to be extended to absorb pump light efficiently. Dispersion of scattering particles is effective to extend the optical path (Watanabe et al, 2005). Turbid media are also attracting interests for development of random lasers (Wiersma et al, 1995). Polyethylene glycol (PEG) is a useful matrix for dispersing fluorescent materials, since it dissolves various dyes and ions in the liquid phase and becomes translucent in the solid phase (Saito and Nishimura, 2012). Random lasing has been realized by the use of scattering in the solid PEG that contains rhodamine 6G (Saito and Nishimura, 2016). In this study, we prepared a PEG solution of europium chloride ($EuCl_3$) and examined the enhancement of the pump-light absorbance and fluorescence in this scattering solid.

2 SAMPLE PREPARATION

Figure 1(a) shows transmission spectra of aqueous solutions of rhodamine 6G (typical organic dye) in a sample cell of 10 mm thickness. A strong absorption band emerged when the concentration exceeded 10^{-5} mol/l. As the black line in Fig. 1(b) shows, however,

an aqueous solution of $EuCl_3$ in the same sample cell (10 mm) exhibited only a trace of absorption (394 nm) in spite of 1000-fold increase in the concentration (10^{-2} mol/l). The gray line shows the absorption band that became clear by extension of the sample thickness (50 mm). However, both the depth and width of the absorption band were still smaller in a Eu solution than a rhodamine solution. These facts indicate that europium needs a long optical path to absorb pump light. In addition, the pump light wavelength has to be tuned accurately to meet the absorption wavelength.

To extend the optical path, we used PEG as a solvent. As Fig. 2(a) shows, the melting point of PEG changes notably depending on the molecular weight. PEG with a molecular weight of 300 (PEG 300), for example, takes a transparent liquid phase at room temperature, whereas PEG 1000 takes a translucent solid phase. Figure 2(b) shows transmission spectra of PEG 300 and PEG 1000 in a sample cell of 10 mm thickness. PEG 300 is transparent over the visible spectral range, whereas PEG 1000 scatters visible light too strongly to allow transmission. In the sample preparation process, PEG 1000 was heated to ~50 °C for dissolving $EuCl_3$, and then cooled to room temperature. No precipitation took place in the solidification process, and Eu ions were dispersed uniformly in the solid.

Figure 1: Transmission spectra of the aqueous solutions containing (a) rhodamine 6G (10^{-6}–10^{-4} mol/l) or (b) $EuCl_3$ (10^{-2} mol/l). The solutions were put in a sample cell of 10 or 50 mm thickness. Pure water in the same sample cell was used as a blank for the transmittance evaluation.
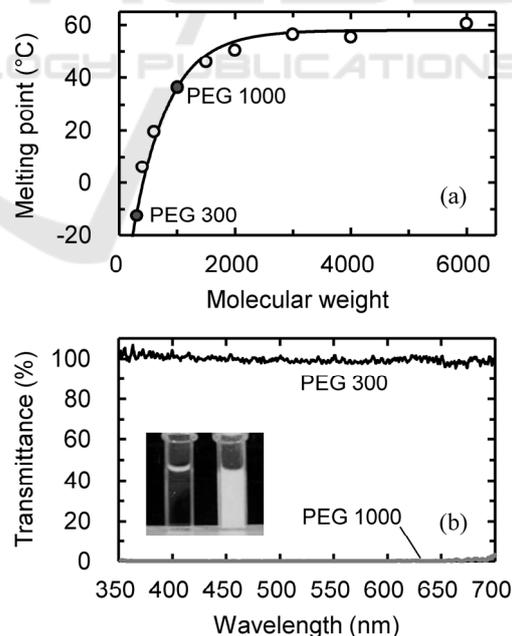
Figure 2: (a) Melting points of PEGs with various molecular weights. (b) Transmission spectra of PEGs at room temperature. The photograph shows the PEGs in the liquid and solid phases.

3 ABSORBANCE

Spectral measurement was conducted for the PEG 300 that contained $EuCl_3$ of 10^{-2} mol/l. The solution was put into a glass cell of 10–50 mm thickness. The PEG containing no salts [the black line in Fig. 2(b)] was used as a blank for evaluation of the transmittance. Figure 3(a) shows the transmission spectra that were measured for the samples of 10 or 50 mm thickness. The absorption band at 394 nm is slightly weaker in the PEG than water [Fig. 1(b)]. In the ultraviolet region (<380 nm), however, the transmittance decreases more notably in the PEG than water. We used the absorption band at 394 nm in the current experiment, since no suitable ultraviolet laser was available in our laboratory.
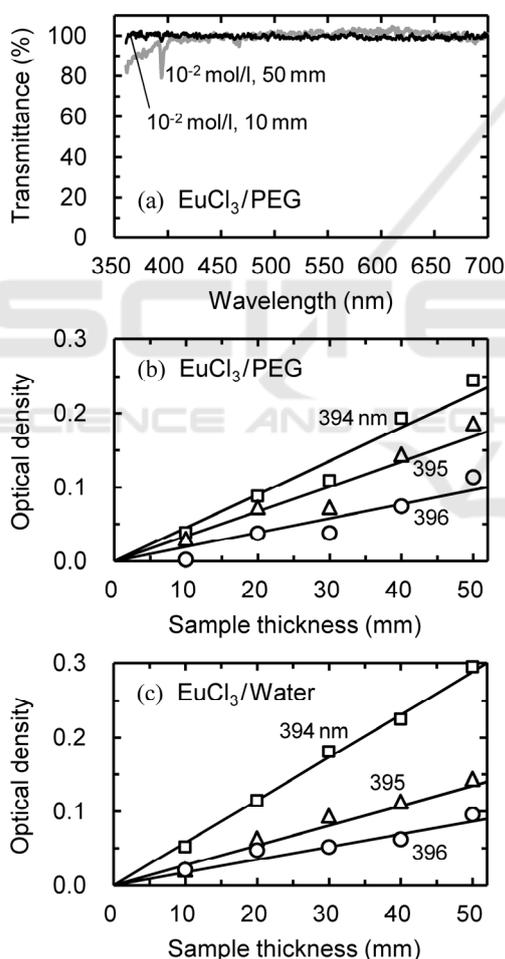
Figure 3(b) shows the absorbance or the optical densities ($-\log T$) that were evaluated from the transmittances (T) at several wavelengths around the absorption band. The optical density increases in proportion to the sample thickness, although some deviation is visible at 30 mm probably due to insufficient optical alignment in the measurement process. The highest absorbance is attainable at 394 nm, and it is halved at 396 nm. Figure 3(c) shows the result for the aqueous solution [Fig. 1(b)]. Although the absorbance at 394 nm is slightly higher in water than PEG 300, these solutions will exhibit similar absorption efficiency for the pump light. As regards the PEG 1000 (solid), the transmission spectrum was not measurable, since no light passed through the sample [the gray line in Fig. 2(b)].

4 FLUORESCENCE

The results in Fig. 3 indicate that efficient excitation is achievable at around 394 nm wavelength. We used a laser diode of 396 nm in the current experiment. The laser power was 100 mW. Figure 4 shows an optical setup for fluorescence measurements. Samples were put into a glass cell of 10 or 50 mm thickness. The laser beam was focused on the input side of the glass cell. Fluorescence was picked up in the direction perpendicular to the laser beam axis, since no strong light emerged from the output side of the glass cell when the sample was translucent (PEG 1000). As the photograph in Fig. 4 shows, the transparent sample (PEG 300) also emitted fluorescence in the perpendicular direction. The collection lens and the probe fiber (core diameter: 400 μm) were moved to change the pickup position, i.e., the distance z from the input side. The fluorescence spectrum was measured by using a multichannel spectrometer (B & W Tek, BTC112E).

Figure 3: (a) Transmission spectra of EuCl3 in PEG 300 (liquid). The concentration was 10–2 mol/l and the sample thickness was 10 or 50 mm. (b, c) The optical densities of EuCl3 in PEG 300 or water. The numerals beside the marks denote wavelengths. The concentration was 10–2 mol/l.
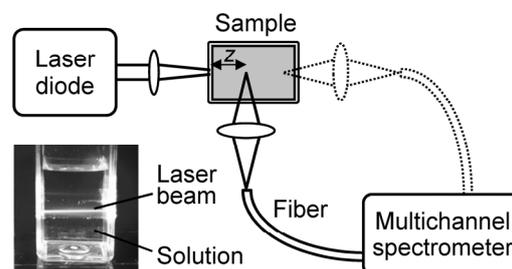
Figure 4: Optical setup for the fluorescence measurement. Fluorescence was picked up from the sample side or the exit end by using a probe fiber of the multichannel spectrometer. The photograph shows fluorescence that is emitted from the laser beam path inside the PEG solution of EuCl3.

Figure 5 shows the fluorescence spectra of the solid sample (PEG 1000, Eu concentration: 10^{-2} mol/l). Measurement position was 0, 1, 3, or 10 mm apart from the input side. Fluorescence peaks are visible at 592, 613, and 698 nm. These peaks correspond to the electronic transitions of $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, and $^5D_0 \rightarrow {}^7F_4$, respectively. The peak at 396 nm is attributed to the scattered pump light. The pump light attenuates gradually as it propagates in the sample because of scattering by the matrix and the absorption by Eu ions. As Fig. 5(d) shows, the pump light penetrates only ~10 mm depth from the input end. According to the pump light attenuation, the fluorescence peaks become lower as the position becomes distant from the input side.

Spectral measurements for the liquid sample (PEG 300, Eu concentration: 10^{-2} mol/l) were conducted in the same manner. Figure 6 shows the spectra that were measured at different positions. The peak at 396 nm is weak and its height changed little with the measurement position. This fact indicates that the pump light propagates with a negligible absorption loss in the transparent solution. Accordingly, fluorescence peaks at 592, 613, and 698 nm exhibit no position dependence. Although the fluorescence in the transparent solution is apparently stronger than that in the translucent solid, the actual fluorescence intensity is thought to be stronger in the solid, since fluorescence also suffers scattering before it is picked up by the probe fiber.

Figure 5: Fluorescence spectra of the solid sample (PEG 1000) that were measured from the sample side. The peak at 396 nm was caused by scattering of the pump laser. Measurement position was (a) 0, (b) 1, (c) 3, or (d) 10 mm from the input side.
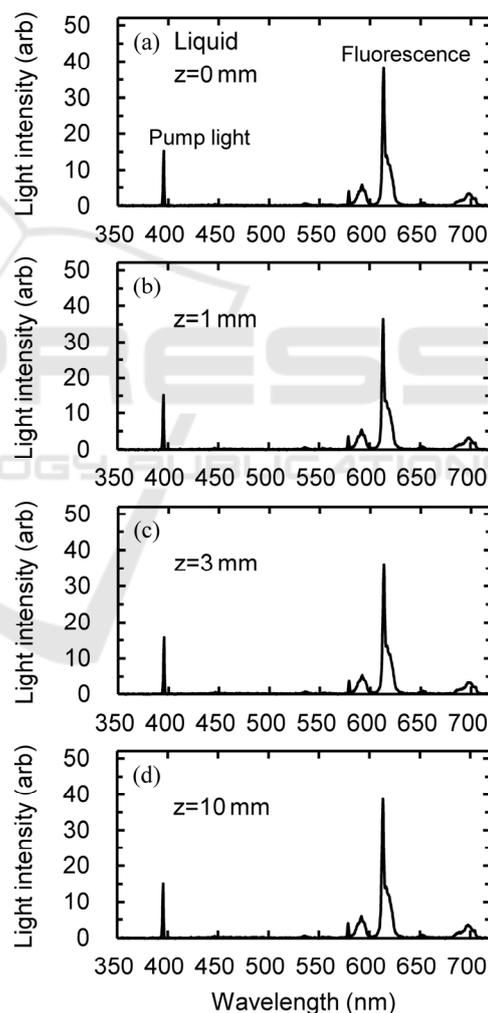
Figure 6: Fluorescence spectra of the liquid sample (PEG 300) that were measured from the sample side. The peak at 396 nm was caused by scattering of the pump laser. Measurement position was (a) 0, (b) 1, (c) 3, or (d) 10 mm from the input side.

Figure 7(a) shows the position dependence of the pump light intensity, i.e., the peak height at 396 nm, in the solid and liquid phases of PEG. The attenuation of the pump light is negligible in the liquid phase. By contrast, the pump light attenuates rapidly in the solid phase. The attenuation length is about 1 mm; i.e., the pump light intensity becomes 1/e of the original value within 1 mm. This fact indicates that the pump light is confined efficiently in a microdroplet if it is composed of the solid PEG.

Figure 7(b) shows the position dependence of the fluorescence intensity in the solid phase. All peaks become lower with the attenuation of the pump power. The attenuation length, however, extends to ∼7 mm, which is longer than that of the pump light. This difference is explained by the scattering of the fluorescence rays. That is, fluorescence rays are emitted in all directions, and some of them emerge form a distant position due to the scattering.

By contrast to the solid phase, the liquid phase yielded no position dependence, as shown in Fig. 7(c). The intensity ratio of the 613-nm peak to the other two peaks is higher in the liquid phase than the solid phase. This fact is related to the width of the 613-nm peak; i.e., as Figs. 5 and 6 show, the peak is narrower in the liquid phase than the solid phase. The ligand field around Eu ions possibly changes through the phase transition process (Wong et al, 2002).

Finally, fluorescence emission was measured in the forward direction to confirm the effectiveness of the scattering. As Fig. 7(a) shows, the pump light excites the solid sample efficiently only within its penetration depth. The samples were therefore put in a thin glass cell in this experiment. As the dotted lines in Fig. 4 illustrate, fluorescence was measured at the exit side of the sample cell. Figures 8(a) and 8(b) show the spectra that were measured for the solid and liquid samples of 1 mm thickness. The fluorescence peak height was twice higher in the solid than the liquid. The effect of the absorption enhancement was notable in these thin samples. As

Figure 7: Position dependence of the measured peak height. (a) shows the pump light intensities in the solid or liquid samples. (b) and (c) shows the fluorescence intensities of the solid and liquid samples, respectively. The numerals beside the lines denote peak wavelengths.
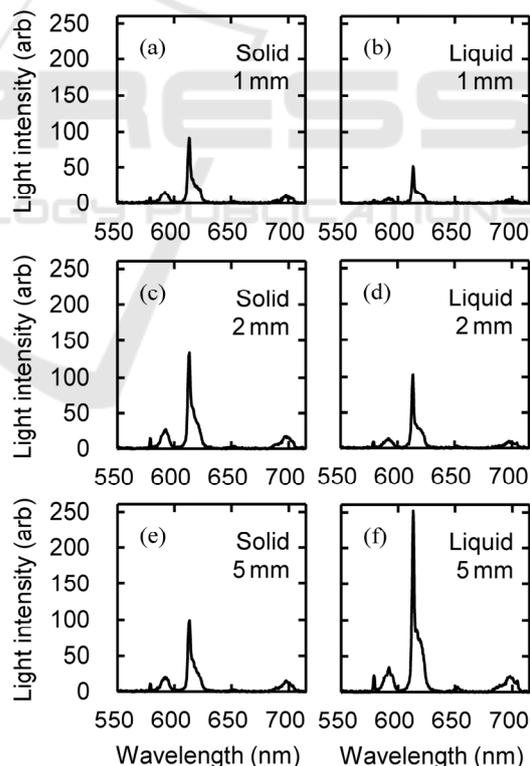
Figure 8: Fluorescence spectra that were measured in the forward direction. The samples were PEG 1000 (solid) or PEG 300 (liquid) that contained EuCl3. The sample thickness was (a, b) 1, (c, d) 2, or (e, f) 5 mm.

Figs. 8(c) and 8(d) show, however, the peak height difference became less notable for the samples of 2 mm thickness. When the thickness extended to 5 mm, the fluorescence peaks shrank in the solid phase, as shown in Fig. 8(e). By contrast, the fluorescence peaks of the liquid grew further with the increase of the sample thickness, as shown in Fig. 8(f).

5 DISCUSSION

In the transparent matrix, e.g., glasses or liquids, fluorescence of lanthanide ions increases in proportion to the sample thickness, since the pump light reaches the exit end with a small optical attenuation. Optical amplifiers or lasers, therefore, use a long fiber to attain a strong fluorescence intensity. If a high-powered laser beam is required, a thick crystal (solution) or a long fiber is a better choice than the scattering PEG. The advantage of the microlaser is an efficient light emission from a small volume. From this viewpoint, PEG is a suitable matrix for creating a fluorescent device whose size is smaller than 1 mm.

As mentioned earlier, the fluorescence peak at 613 nm exhibited different shapes depending on the phase (solid or liquid). We also observed different spectra in the aqueous and PEG solutions. This phenomenon seems to be related to the surrounding ligand field. Further investigation on this phenomenon possibly leads to improvement of the fluorescence efficiency.

In the current experiment, a laser diode of 396 nm was used as a pump light source, since other suitable sources were not available in our laboratory. As Fig. 3(a) shows, the transmittance of the sample solution decreases in the ultraviolet range below 380 nm. If this transmittance decrease originates from the absorption by the Eu ions, ultraviolet pump light will induce more efficient fluorescence emission. Note that this transmittance decrease was certainly induced by addition of $EuCl_3$ since the pure PEG 300 was used as a blank for the transmittance evaluation. It possibly happens, however, that the addition of $EuCl_3$ promotes the ultraviolet absorption of PEG [Fig. 2(b)]. Further experiments are needed to clarify the origin of this transmittance decrease.

As Fig. 2(a) shows, the phase transition of PEGs takes place at around room temperature. In addition, PEGs exhibit a bistable behavior during the phase transition process; i.e., both the solid and liquid phases are stable at a certain temperature. This phenomenon seems useful to create a bistable microlaser. We are currently thinking of creating a random droplet laser on the basis of the current experimental results.

6 CONCLUSIONS

Polyethylene glycol is a suitable matrix for creating a micro optical device that uses lanthanide ions as a fluorescence emitter. It exhibits a strong scattering in the solid phase, and extends an optical path of pump light, leading to efficient excitation of the fluorescent ions. This enhanced fluorescence was demonstrated experimentally by exciting a solution of $EuCl_3$ with a laser diode of 396 nm wavelength. The fluorescence peak at 613 nm became twofold higher in this scattering matrix than the original liquid.

ACKNOWLEDGEMENTS

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